Replacement of Hexavalent Chrome Passivations on Galvanized Steel

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End of Life Vehicles

Future of Hexavalent Chromium

- duty to avoid, recycle or re-use of rubbish
- who causes has to care
- instructions for the dismantling, re-use and recycling of car parts
- vehicles for the European market must be free of lead, mercury, cadmium and must contain less than 2 g/vehicle of hexavalent chromium after 6. 2003
- last user should be able to dispose his vehicle correctly and free of charge
- destruction certificate as a proof

Metallic chromium and chromium (III) are NOT banned.

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The barrier effect of a passivation layer leads to an increasing corrosion protection
As thicker the layer as better the corrosion protection

Cr(VI) in the passivation layer in mg/m^2	layer thickness in nm	corrosion protection neutral spray test in hrs to first attack
0 *1	25-80	20-40
80-220	250-500	200-300
300-400	1000-1500	400-500

*1 conventional “thin layer” Cr(III) passivation

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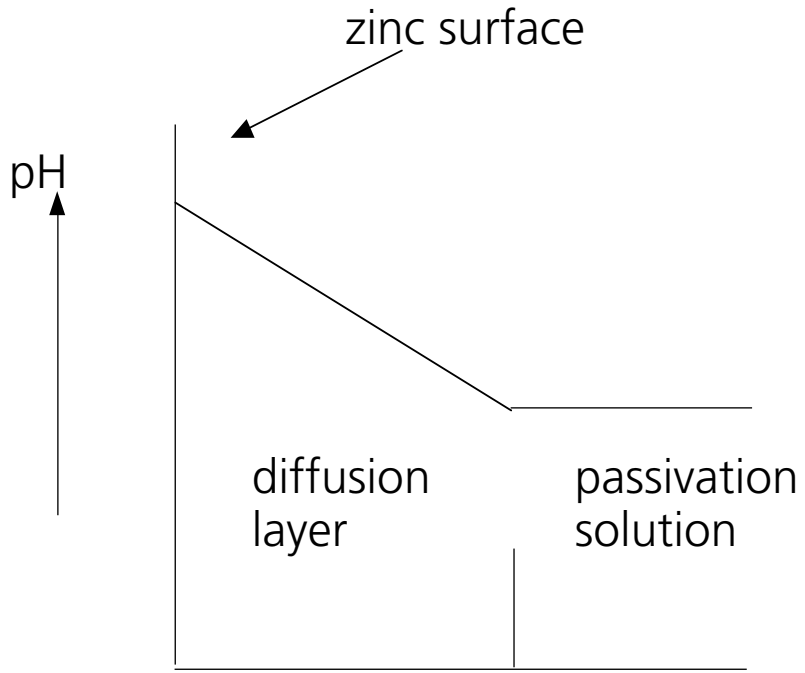
$$Zn + 2\,H^{+} \xrightarrow{k_1} Zn^{2+} + H_2$$



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for Cr(VI), yellow passivation:

$$x\,Cr^{6+} + y\,Zn + z\,H_2 \xrightarrow{k_2} x\,Cr^{3+} + y\,Zn^{2+} + 2z\,H^+$$

The Cr^{3+} intermediate has two reaction paths, building a complex and moving into the solution or precipitates as chrome hydroxide; $k_1, k_3 > k_2$

$$Cr^{3+} + 3\,(OH)^- \xrightarrow{k_3} Cr(OH)_3 \downarrow$$

$$Cr(OH)_3 + Zn^{2+} + A^- + Cr^{6+} \longrightarrow (Cr^{3+}, Cr^{6+}, Zn^{2+}, OH^-, A^-) \downarrow$$

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for Cr(VI)-free processes, Cr(III) is almost complexed in water:

$$Cr(NO_3)_3 + 6\ H_2O \longrightarrow Cr(H_2O)_6(NO_3)_3$$

the Cr(III)-complex precipitates at the zinc surface:

$$Cr^{3+}(complex) + 3\ OH^- \underset{k_5}{\overset{k_4}{\rightleftharpoons}} Cr(OH)_3 \downarrow + complex$$

$$Cr(OH)_3 + complex + Zn^{2+} + A^- \longrightarrow (Cr^{3+}, complex, OH^-, Zn^{2+}, A^-) \downarrow$$

In opposite to the Cr(VI)process where k_2 is the speed limiting factor for Cr(III) it is k_4.
k_4 depends on the ligand. A higher temperature leads to a higher k_4.

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Ligand = water, complex is weak this leads to a high k_4 thick powdery deposition with no adhesion

Ligand = fluoride, complex is strong leading to a low k_4 thin coating because k_5 becomes important, good adhesion

A ligand who is not too weak or not too strong is prefered for a thick homogeneous passivation with a good adhesion.

k_4, water > k_4, thick layer passivation > k_4, fluoride

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Experimental:

Test pieces: 21 cm x 15 cm, 10 µm zinc

Passivation parameters:
Solution: 12.5 Vol% SurTec 680 (thick layer passivation)
Temperature: 40, 55 and 70 °C
Contact time: 2, 4, 6, 8 and 10 s
pH-value: 1.6-1.9

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Process steps

-degreasing of the zinc plated steel samples
-rinsing with DI-water
-spray (0.5 bar) or dip (stirring) application
-rinsing with DI-water (optional)
-organic top coat (optional)
-squeeze
-drying

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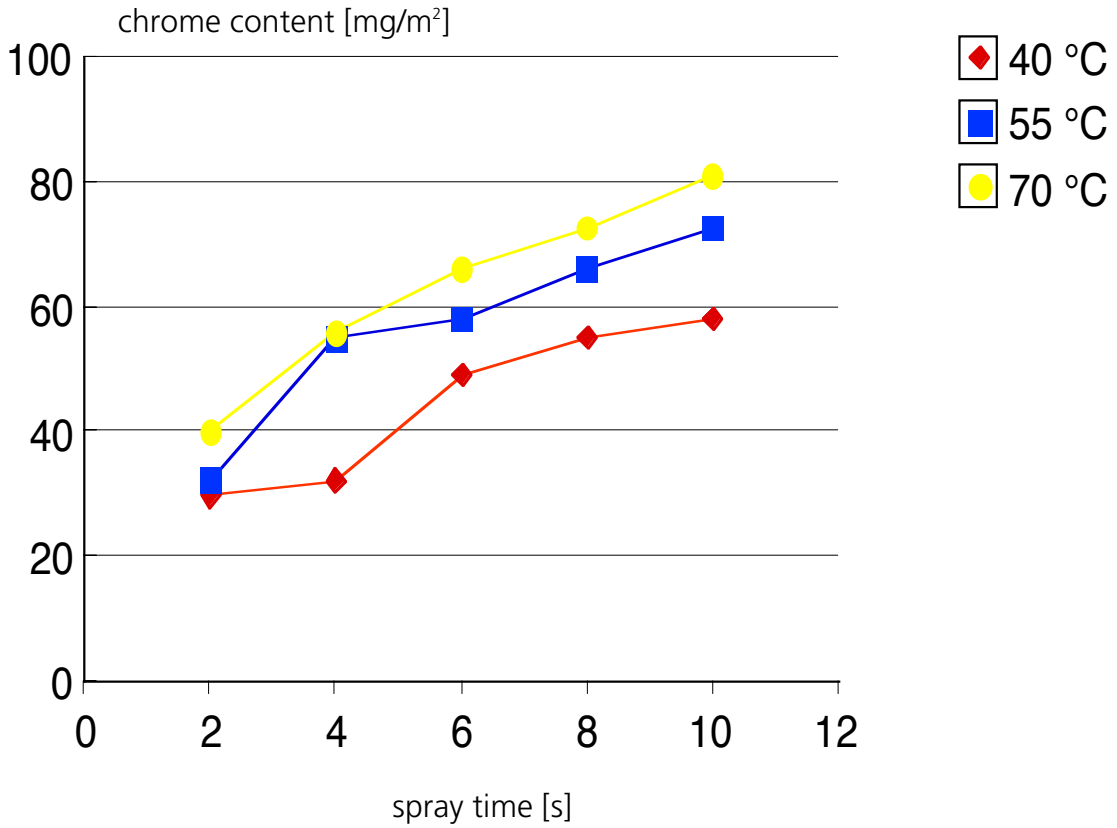

Coating weight vs. coating time and temperature for spray application.
No activation before passivation, rinsing after passivation.

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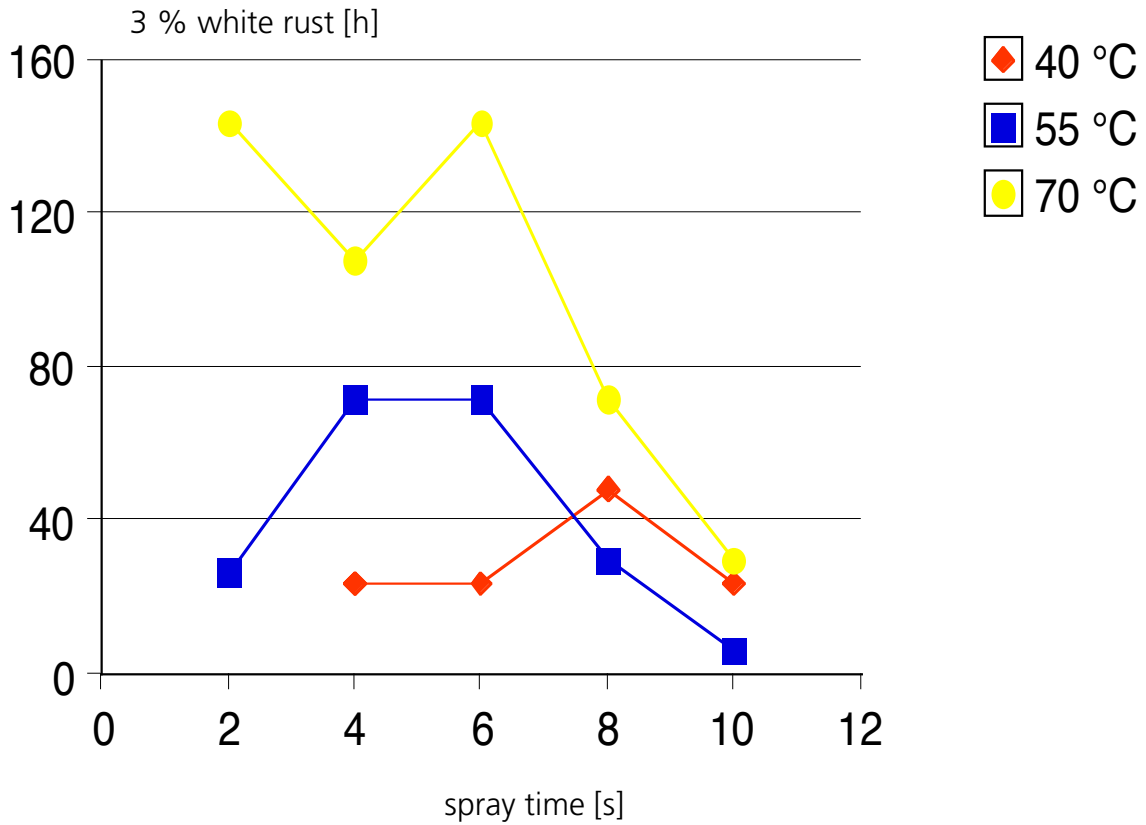

Corrosion protection vs. coating time and temperature for spray application.
No activation before passivation, rinsing after passivation.

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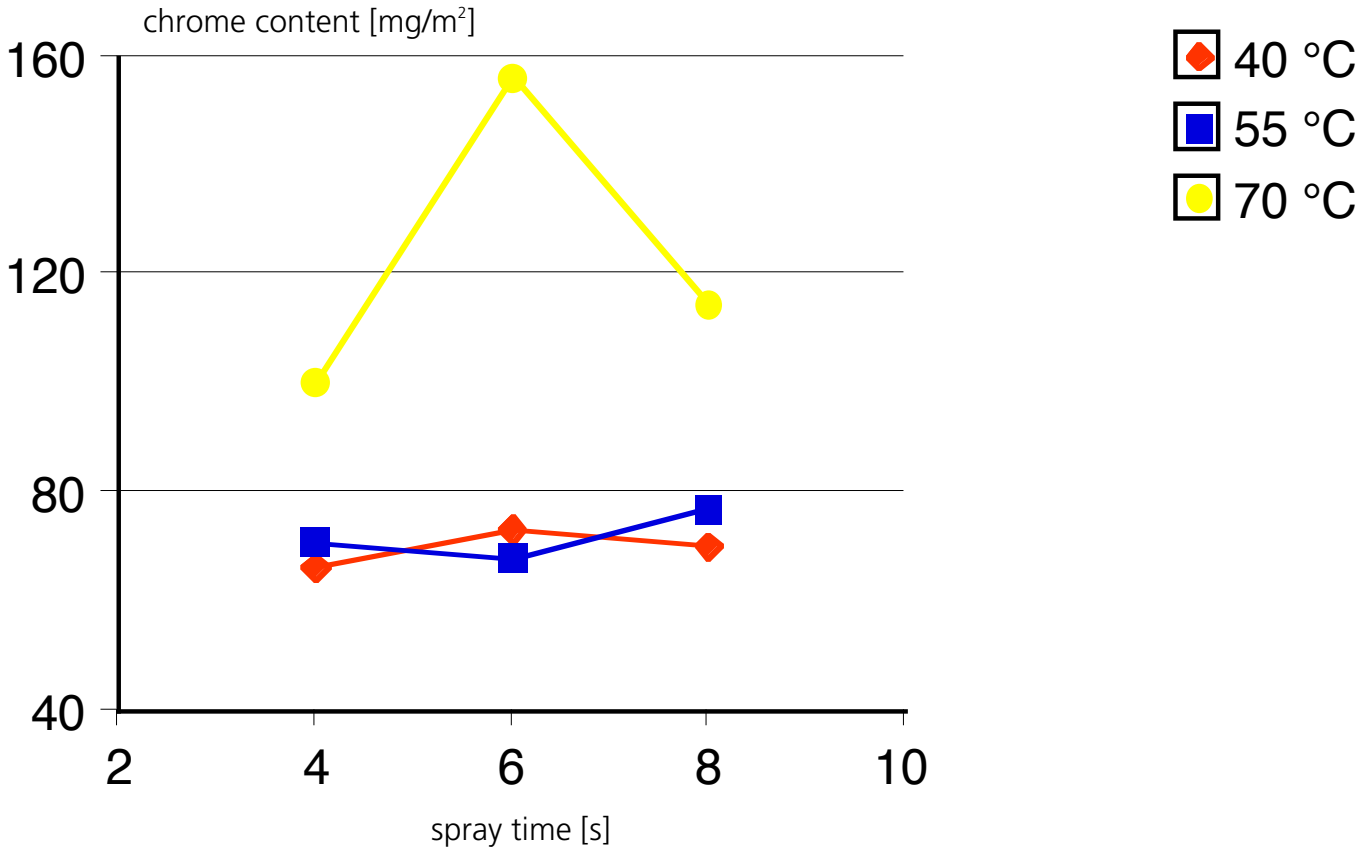

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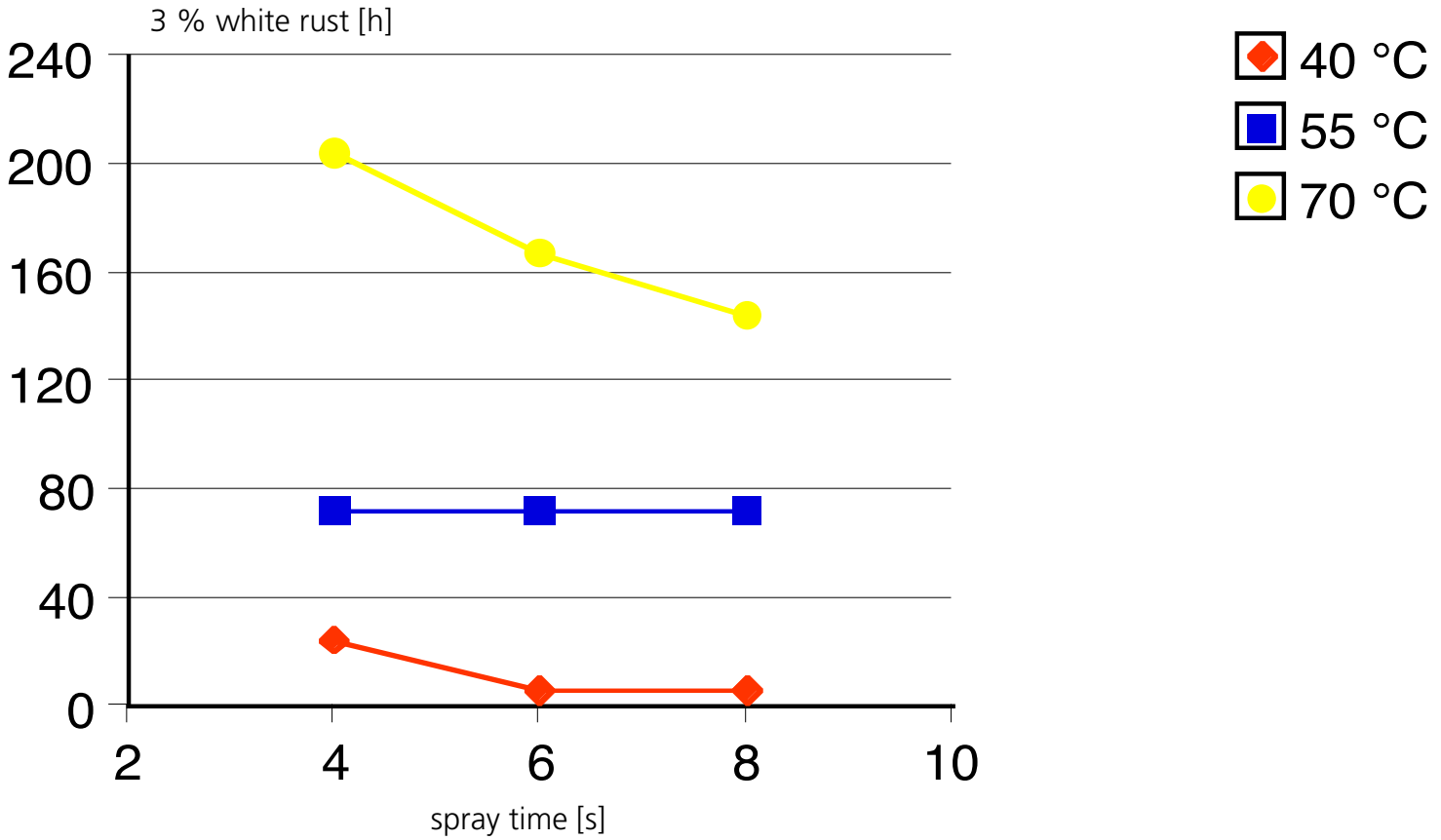

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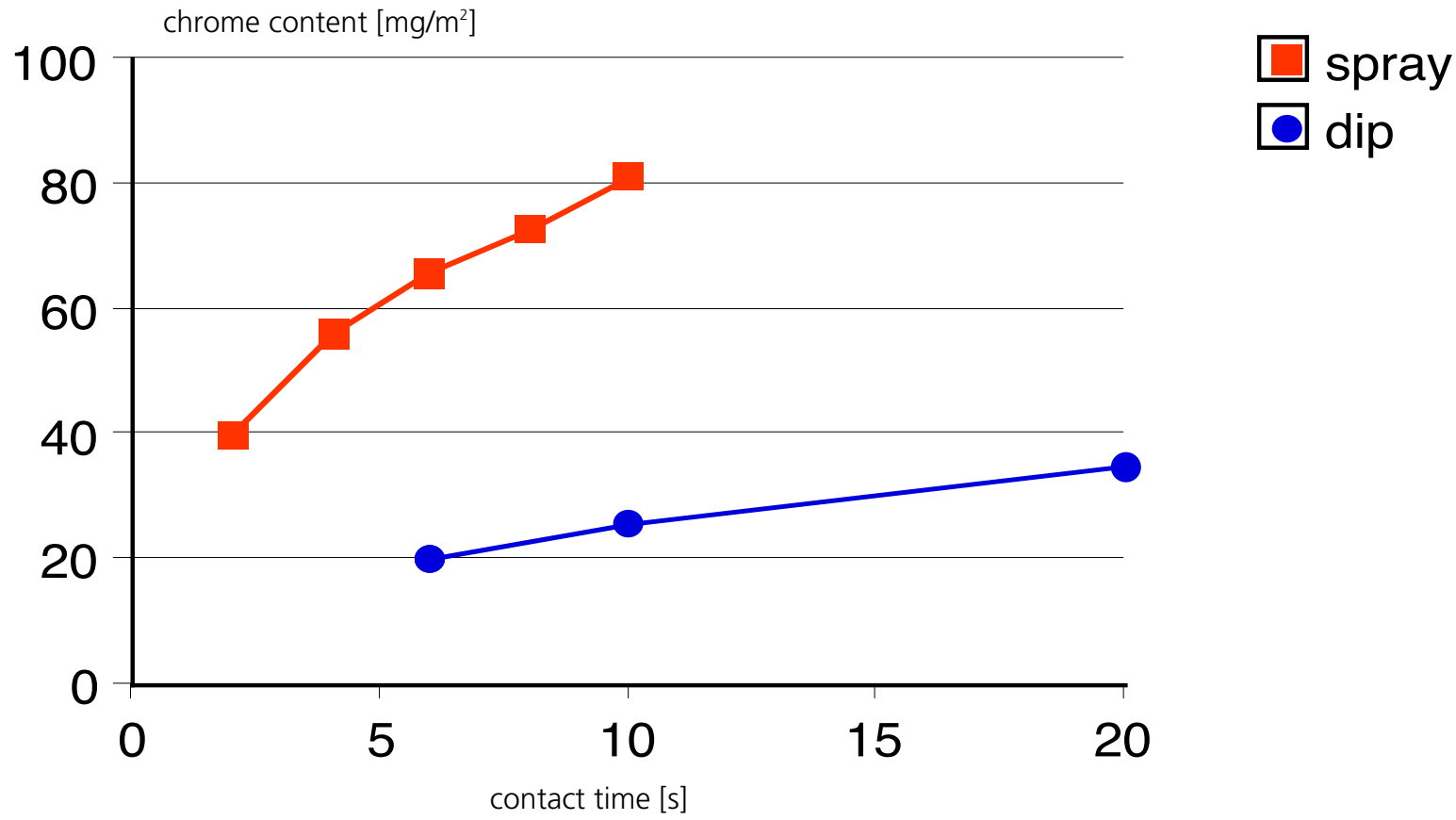

Coating weight of spray and dip application vs. contact time.
Temperature 70 °C, no activation, rinse after passivation

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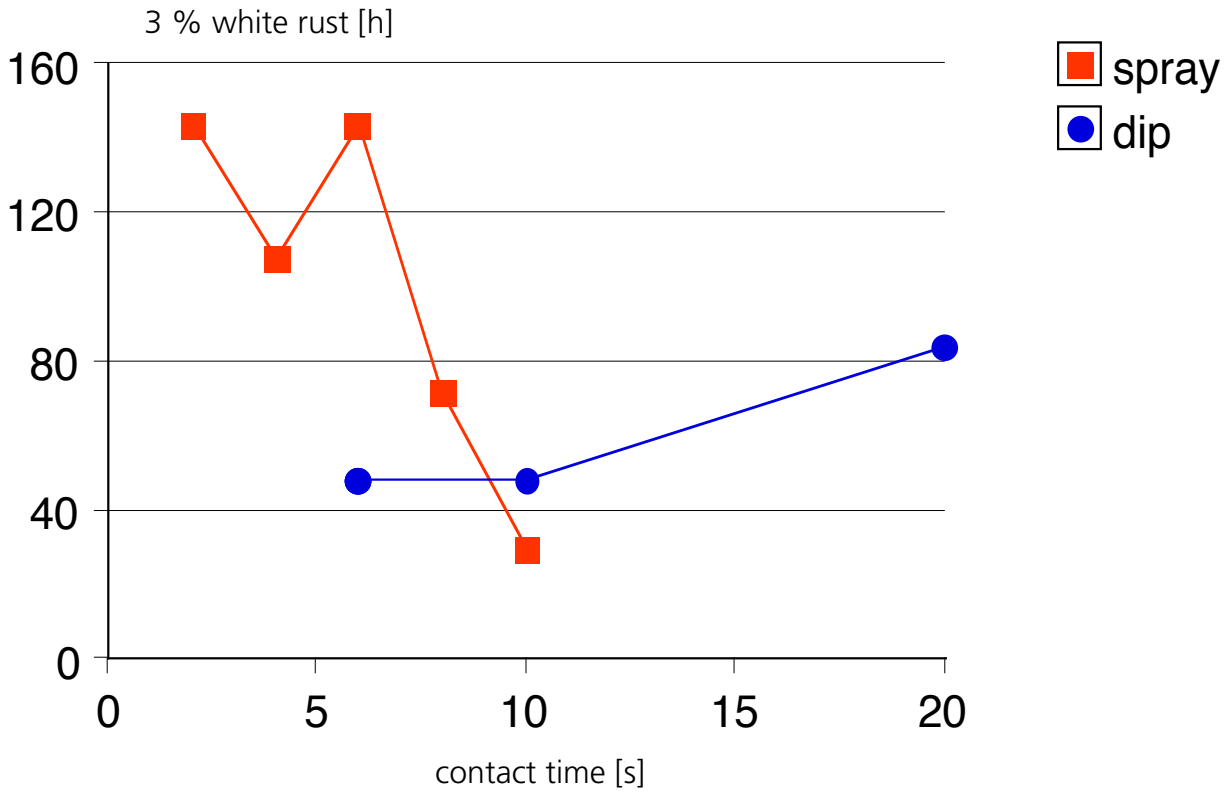

Begin of white rust for spray and dip application vs. contact time.

Temperature 70 °C, no activation, rinse after passivation

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Post treatment

Process	Temp/ °C	Time/s	post treatment	white rust 3 %/h
Dip	70	6	-	48
"	70	6	X	144
"	70	10	-	48
"	70	10	X	168
Spray	70	6	-	144
"	70	6	X	484

Variation of passivation parameter, 12.5 Vol% SurTec 680, pH 1.8
post treatment: Anti finger print, 1 g/m^2, different supplier

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Stack test

Process parameter for the stack test, one cycle:

- 6 h 20 °C, 90 % rel. humidity
- 6 h 35 °C, 90 % rel. humidity
- 6 h 35 °C, 40 % rel. humidity
- 6 h 20 °C, 40 % rel. humidity

Result:

with rinse >>> no rinse

70 °C > 55 °C > 40 °C

with corrosion protecting oil >> no corrosion protecting oil

With rinse and T = 70-55 °C no blackening was observed.

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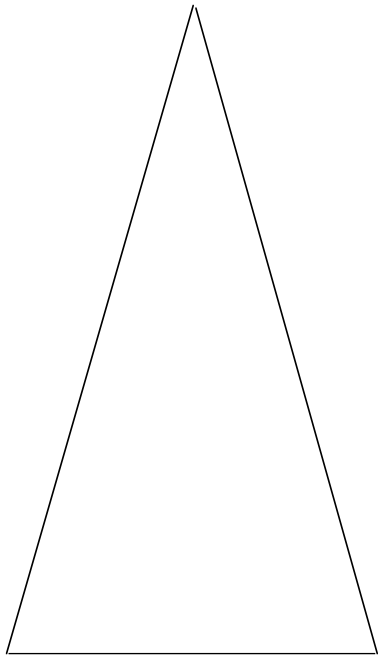
Appearance:

Influence of the layer thickness on the appearance



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Practical Test

Process steps

- zinc plating (vertical cells)
- rinsing
- surface conditioning
- zinc phosphating
- rinsing
- trivalent chrome passivation, SurTec 680, spray application
- squeeze
- rinsing
- drying
- anti finger print
- drying

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Result

- Compared to the old hexavalent chromate better corrosion protection 76 h instead of 30 h for beginning white rust is observed
- slightly bluish-yellowish appearance
- brighter surface than before
- adhesive power for the anti finger print is the same
- because of the lower pH-value of the trivalent chrome passivation (pH 1.8) compared to the hexavalent chromate (pH 4) in use an efficient rinsing is important to prevent the drag in of passivation solution into the anti finger print because of coagulation at a low pH.

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Conclusion

- The corrosion protection of a “thick layer Cr(VI)-free passivation is similar or even better compared to a Cr(VI)-passivation, depending on the process parameter
- Application of organic top coats are possible leading to an significant increase of corrosion protection
- Short reaction times for spray application (2 s) are possible
- A rinse after passivation is necessary

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