

TRIVALENT PRE-TREATMENT – THE SAFE ALTERNATIVE FOR CHROMATE CONVERSION

The forthcoming restriction of Cr(VI) through REACH does not inevitably mean that the surface treatment technology must completely dispense with chrome. Cr(III)-containing conversion layers represent an efficient and safe alternative which also fulfils the highest quality requirements and durability. The comparative study of a Cr(III)-containing and a chrome-free system may show differences in performance.

In the course of the conversion of Cr(VI)- containing pre-treatments to alternative systems, the question arises for many coaters: Which pre-treatment is extremely robust and offers the best possible protection against corrosion?

The great many alternatives that are offered by different suppliers are barely manageable. They range from chrome-free systems based on zirconium and/or titanium, silan solutions right through to chrome(III) containing products, each for the so-called “Rinse” or “No-Rinse” application.

A detailed discussion by the technical staff of the chemical suppliers is a prerequisite for an optimal choice of alternative systems. Whether the work is to be based on Immersion or spraying, or whether a Rinse or No-Rinse process will be used, in most cases, will be decided by the existing plant lay-out.

What is more important, is to take into account client and end-customer specific wishes. Technical performance like corrosion protection and adhesion are vital factors for the painting process. Furthermore, the process performance such as the robustness

of the chemistry, process reliability and the type of quality control are significant. **CHROMATE-FREE OR CHROME-FREE?** Replacing the chromating, coaters are often wrongly advised to decide on Chromium-free systems. It is argued that the use of chrome (VI) compounds was prohibited by REACH and therefore Chrome had to be set aside. However, it is not explained to the coaters that chrome(VI)-free does not automatically mean chrome-free.

Through REACH, only Cr(VI) compounds are restricted. Cr(III) compounds, corresponding process solutions and also surfaces treated with chrome(III) are not affected. Cr(III) is chrome in its most stable oxidation state. Its oxide is non-toxic and not subject to specific labelling requirements. From earlier studies it is known that the application of Cr(III) is crucial for the best possible protection from corrosion [1-7]. Why, therefore, should the positive characteristics of chrome in corrosion protection be voluntarily abandoned when it is really not necessary.

As shown in Figure 1, applying Cr(III) enables a bigger buffer to achieve the desired minimum requirements in corrosion protection. Upon reversion, this means greater reliability for the coater to achieve the desired quality requirements.

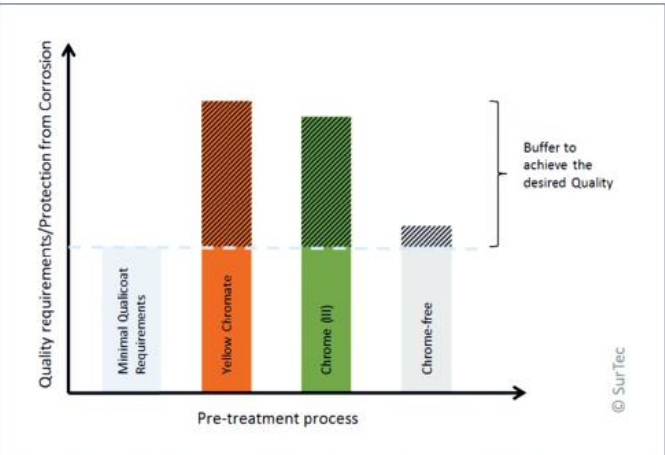


Figure 1: Overview of the different quality processes in relation to protection from corrosion

GENERAL PROCESS DIFFERENCES BETWEEN CR(VI)-CONTAINING AND ALTERNATIVE SYSTEMS

Switching the conversion to alternative Systems, besides the actual conversion treatment, the process water balance is the most important. In contrast with chromate passivation the chrome-free processes as well as those based on Cr(III) must be run with deionised water. The water quality of the subsequent rinse, if one is used, must also be very good, to guarantee best corrosion protection as well as optimal paint adhesion.

The waste water treatment is, however, much simpler than with chromate processes. During the chromate processes, Chrome(VI) must be reduced to Cr(III) before treating with lime, while in Cr(III)-containing solutions this first reduction step is omitted. The same is valid for Zirconium and/or titanium based chrome-free systems, which can also be treated directly with the lime process step and the precipitate subsequently is filtered and disposed of.

CHROME(III) VERSUS CHROME-FREE

To compare the capabilities of Cr(III)- containing against chromium-free systems, two analogous procedures treating EN-AW 6060 alloy were investigated with respect to paint adhesion and protection from corrosion. SurTec 653, a Cr(III)-containing no-rinse pre-treatment was compared with a chrome-free no-rinse process, both applied in spray application. For all parts the preparation prior to the conversion was an acidic pickle degreaser followed by two rinses with DI-Water (Figure 3). In both cases, a colourless coating was formed and dried at 100 °C in a hot air oven. After cooling down, a polyester powder paint was applied and subsequently cured at 200 °C. The samples coated in this way were then tested and assessed in accordance with the prevailing Qualicoat standards.

THE RESULTS

Paint adhesion

The results obtained with regard to paint adhesion were comparable for the chromefree and Cr(III)-containing system (see Figure 5). Figure 4 shows examples of the results of the specimens treated with SurTec 653. Very good results were obtained with both systems.

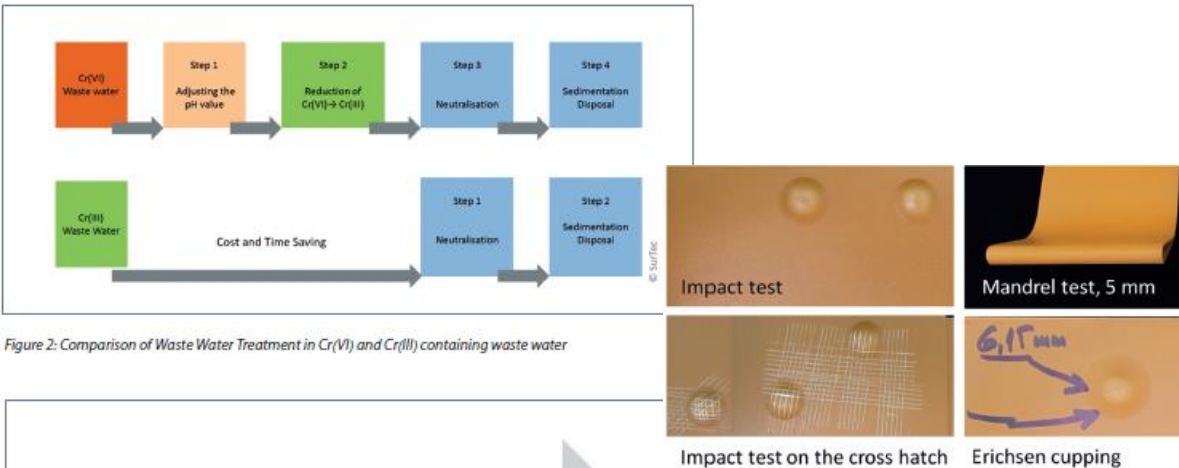
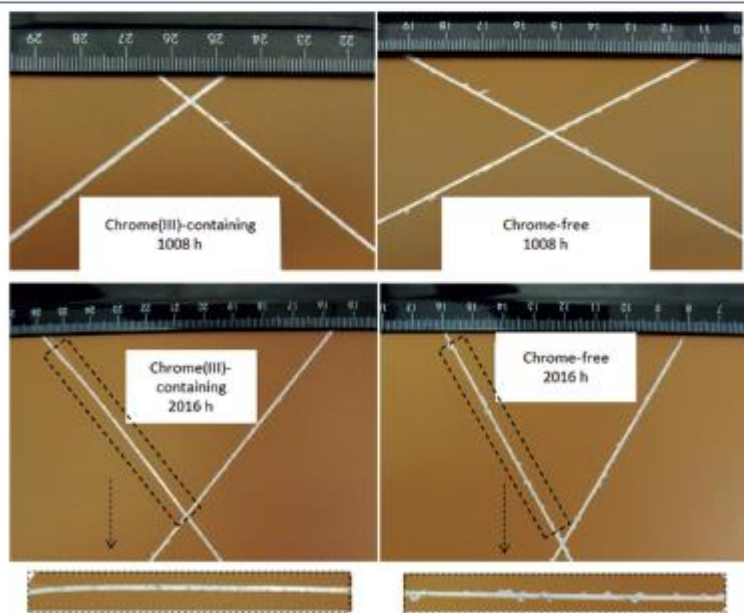


Figure 3: Process sequence for Cr(III)-containing Conversion layer including Pre-treatment. This is a No-rinse process therefore rinsing after the conversion treatment is not necessary.

Test	Chrome(III)-containing, no rinse SurTec 653	Chrome-free, no rinse
Paint	Polyester powder coating	
Impact test, 60 cm	No fissures No delamination	No fissures No delamination
Cross hatch test	Gt0	Gt0
Impact test, 60 cm onto cross hatch	Gt0	Gt0
Mandrel test 5 mm mandrel	No fissures No delamination	No fissures No delamination
Erichsen cupping ≥ 5 mm	6,15 mm	6,45 mm

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Figure 5: Tabular overview of the paint adhesion results for Cr(III)-containing and chrome-free systems



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Figure 6: Appearance of samples after 1008 h and 2016 h ASS

Filiform test

As preparation prior to the Filiform test, in each case, two scratches were made with a Sikkens stylus on the pre-treated and painted specimens. These ran perpendicular to one another and Cross-wise, respectively alongside the direction of the casting marks.

Subsequently the scratches were inoculated with 38% hydrochloric acid in compliance with Qualicoat, and were then moved to a test chamber set at 40°C and 82% relative humidity.

As in the case of the mechanical tests, also in the Filiform test indicated no difference between the Chrome(III) containing and the Chrome-free system. After a test period of 1000 hours in the chamber no Filiform thread could be detected in either system.

Acetic salt test (ASS, according to DIN EN ISO 9227)

The samples were again scratched with a Sikkens stylus in the shape of an Andreas Cross, exposed to the ASS for 1008 or 2016 hours and finally assessed.

The results are summarised in Figure 7 and Figure 6 shows what the samples looked like after the long periods of exposure.

After 1008 hours both the chrome-free and the chrome(III) containing no-rinse process SurTec 653 complied with the Qualicoat standards. However, the Cr(III) containing pre-treatment performed better and the superiority of the corrosion protection became all the more visible, the longer the duration of the test was. After 2016 hours, it was evident that the underfilm corrosion in case of the Cr(III) containing pre-treatment was only half as large as in case of the chrome-free layer. SurTec 653, fulfilled the Qualicoat standards even after 2016 hours ASS.

SUMMARY

The approaching restriction of chrome(-VI) compounds in the surface treatment technology and in the pre-treatment of aluminium does not necessarily lead to chrome-free technologies. The positive corrosion protection characteristics of chrome(III)-containing conversion coatings should not be sacrificed. In the above study it was shown that both alternative systems, with and without Cr(III), comply with the standard of the European Quality Association QUALICOAT. In direct comparison and in view of the corrosion

protection section, however, the chrome (III) containing process was clearly superior. Through the use of chrome(III) as in SurTec 653 one can be assured of higher process reliability. While chrome-free systems barely fulfil the quality requirements, the Cr(III) containing system clearly surpasses these requirements. Slight variances in the industrial coating process and differences in the quality of the aluminium can be better offset by using chrome(III). Under registration number A-111, SurTec 653 is registered as an alternative pre-treatment system by QUALICOAT. [n](#)

	Blister Formation limit: SO	Length of blister [mm] target ≤4 mm	Depth of infiltration Target ≤ 4 mm	Infiltrated surface target ≤16 mm2/10 cm
Results after 1008 h				
SurTec 653 Chrome(III)-containing System	SO	1	1	0,9
Chrome-free System	SO	2	2	11,4
Results after 2016 h				
SurTec 653 Chrome(III)-containing System	SO	1	1	4,7
Chrome-free System	SO	2	1	17,9

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Figure 7: Tabular summary of the Corrosion test results

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