Chromium-free technologies open up manifold opportunities

For decades, yellow and green chromating have been the technologies of choice for the corrosion protection of metals. Rising costs for health, safety and the environment as well as changing market demands have resulted in a situation where chromium-free alternatives are increasingly gaining a foothold in the market. A comparison of old vs. new technologies shows why: The eco-friendly technologies show better results in key aspects.

Two chromium-free processes from Frankfurt-based Chemetall GmbH, Gardobond X 4707 and Oxsilan AL 0510, were selected for the comparison of chromating vs. alternative technologies. Both are established processes that have been used in plants around the world for several years already. Gardobond X 4707 is based on zirconium and titanium as coating components and was developed specifically for the treatment of aluminum. A totally new approach was made with Oxsilan, a technology suited for multi-metal applications. In addition to zirconium, silanes form the basis of this eco-friendly process replacing chromating and zinc-phosphating processes. Cross-linking between the Oxsilan layer and paint components during drying and/or application of the powder, wet or e-coat paint system affords optimum paint adhesion and corrosion protection. While the Oxsilan technology is suited for all conventional metals such as steel, stainless steel and aluminum, chromating can be used for the substrate aluminum and small volumes of galvanized steel.

Downsides of chromating

The main disadvantage of yellow and green chromating lies in the toxicity of the metal salts used. According to the GHS Regulation, the chromium concentrates used are classified as acutely toxic, hazardous for the environment, caustic, flammable and as an aspiration hazard. Over and above this, chromium-containing baths exhibit an acute aquatic toxicity. Consequently, they have been placed in the highest water hazard class 3. The concentrates of the chromium-free alternatives, by contrast, are only caustic. The treatment baths proper are no longer classified as hazardous and are therefore placed in water hazard class 1.

Economic consequences

Especially the differences regarding the hazardousness have a strong impact on the economic viability of the processes. Neutralising, precipitating, separating and disposal of the chromium-contaminated water accounts for a major part of the overall process costs. Add to this the high costs for disposal as well as for regular analysis and controls by the environmental protection authorities.

Parameter/ process	Gardobond® x 4707	Oxsilan® AL 0510	Yellow chromating	Green chromating
Bath temperature	Room temperature to 30 °C	20–40 °C	20–40 °C	20– 50 °C
Treatment time	30–120 sec.	30–120 sec.	60–180 sec.	30–180 sec.
Application	Dip, Spray, Cascade	Dip, Spray, Cascade	Dip, Spray, Cascade	Dip, Spray, Cascade
Coating weight		5 - 50 mg/m² Zr	100–300 mg/m² Cr	20–200 mg/m² Cr
rinse	6 – 40 mg/m²			
no-rinse	6 – 40 mg /m²			
Substrates	Aluminum, magnesium	Steel, galvanized steel, stainless steel, aluminum, magnesium, cast iron, etc.	Aluminum, galvanized steel	Aluminum, galvanized steel

Table 1 (left) Comparison of general process conditions.

Process	Drying temperature
Chromating	80°C
Gardobond X4707	
no-rinse process	120 °C
rinse process	180 °C
Oxsilan AL 0510	180 °C

Table 2 Comparison of general process conditions.

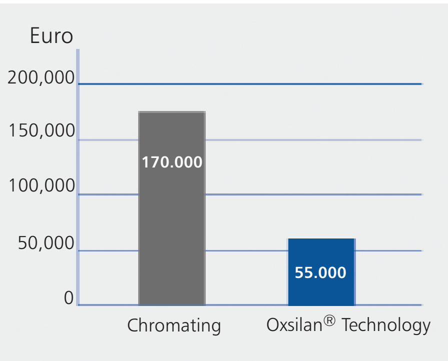

Fig 1 Water and wastewater costs for the coating of 1 million sqm substrate by chromating and with Oxsilan. Water/Waste Water Costs Chromating Oxsilan technology.

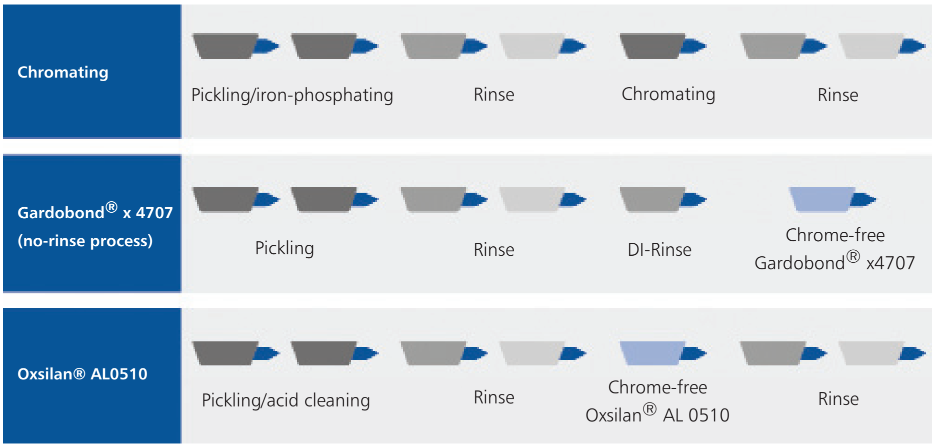

Fig 2 Comparison of typical process sequences.

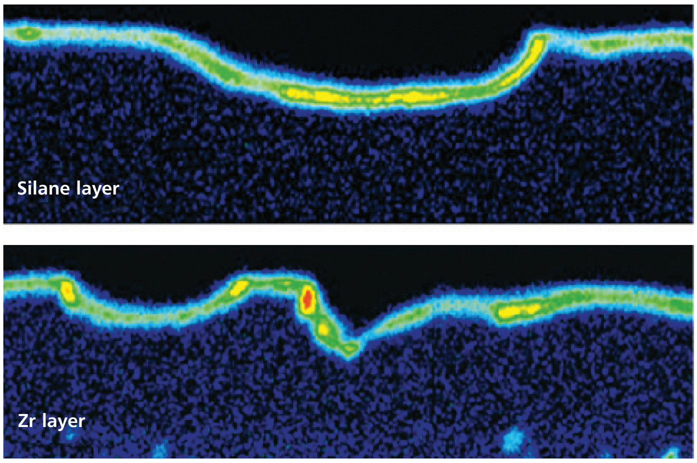

Fig 3 Microprobe examination on an aluminum section coated with Oxsilan.

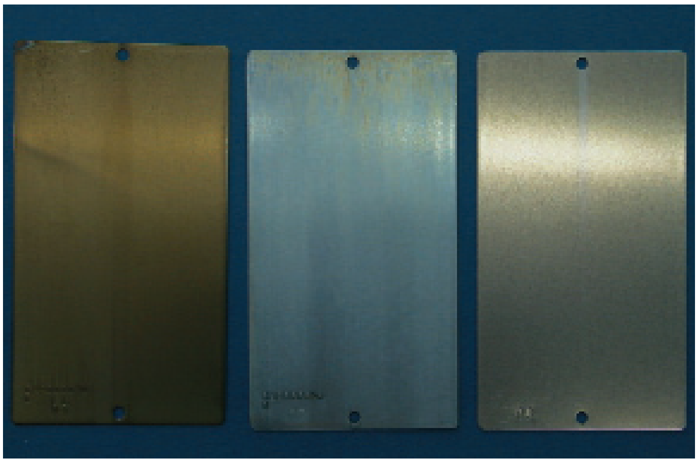

Fig 4 Sheets pretreated with Oxsilan: steel, galvanized steel and aluminium (f.l.t.r.)

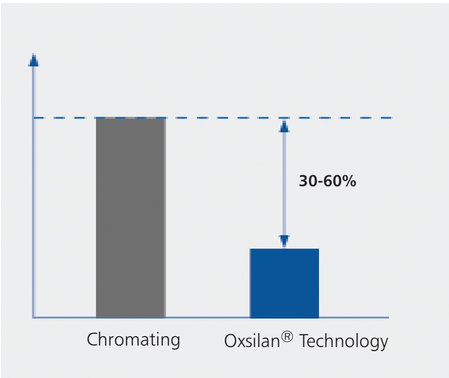

Fig 5 Comparison of the total process costs: the Oxsilan technology allows realising savings potentials of 30 – 60 percent compared against chromating

Fig 6 Comparison of the different pretreatment processes.

	Yellow chromate	Green chromate	Gardobond® x 4707	Oxsilan® AL 0510
Economic viability	--	--	++	++
Health risk for operators	--	--	++	++
Corrosion protection	++	o	o	++
Multi-metal applications	o	o	--	++
Reliable process	++	++	++	++
Approved/meets specifications of	GSB	AAMA	Qualicoat	

Chromium-containing baths need to be cleaned at regular intervals. The downtimes as well as the chromium-containing sludge that forms, including its treatment and disposal, additionally affect the economic viability of the process. Besides the economic side also the hazard potential of chromium represents a negative aspect from the viewpoint of health protection. The operators need to take extensive precautions for handling the material. In view of the fact that they pose no health hazard, such measures are obsolete when using the chromium-free variants. Also their storage is significantly easier and safer.

A comparison of the pretreatment costs based on an annual throughput of one million square metres of metal substrate shows that chromating leads to three times higher costs for water and waste water than Oxsilan.

Difference in terms of process sequence

In terms of the process sequence there is difference between the chromium-containing and chromium-free technologies. The substrates must be pre-cleaned and rinsed before the conversion coating can be applied.

Comparison of typical process sequences

In chromating processes, the aluminum substrates are pre-cleaned by means of acid or alkaline pickling. After chromating, the parts are treated in a multi-stage rinse to rinse off the toxic chromating solution. The conductivity value of the pretreated parts after dripping and before application of the adhesive water dryer must be less than 30 μS/cm. Steel and galvanised steel are subjected to iron-phosphating with subsequent rinsing. For application of the Oxsilan AL 0510 technology, an acid cleaning is sufficient as a pretreatment of steel or galvanized steel. With this cleaning process, at the same time also laser edges and scale residues can be removed. Aluminum substrates are subjected to acid pickling. Just like in the case of the chromating processes, a rinsing step is required upstream and downstream of the pretreatment. For application of the Gardobond X 4707 process, several rinsing steps using DI water are required after acid pickling. When using a no-rinse process, rinsing after conversion coating can be omitted but it must be ensured that, before application of the process, the conductivity value of the pretreated parts after dripping is less than 30 μS/cm. As the process is sensitive with regard to carry-over, no-rinse processes are less suited, especially for older plant types.

Volume of rinsing water is the same

In terms of the rinsing water consumption there is no significant difference between the processes. Due to the higher solids content, chromating processes require substantially more DI water that the alternative processes. In the case of the chromium-free processes, more attention needs to be paid to the rinsing steps upstream of conversion coating. Here, the Oxsilan technology is significantly more robust than conventional processes, which is why the conductivity value of the dripping water upstream of the treatment with Oxsilan can be increased from 30 μS/cm to 200 – 250 μS/cm. As a result, substantially less DI water is required. For a substrate area of 100 square meters, chromating requires about 80 liters of deionised water. Chromium-free processes

Fig 7 Gardobond® X 4707 for the passivation of aluminum sections in a vertical plant.

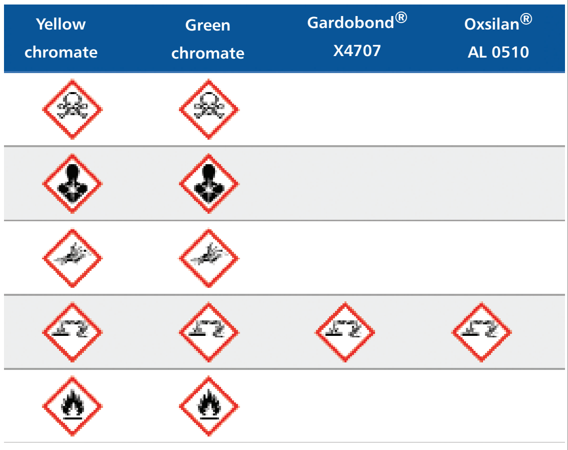

Fig 8 Classification of the concentrates according to GHS.

require similar quantities. What counts in this context is that the rinsing waters from chromating processes are contaminated with chromium.

Higher drying temperatures allow for higher productivity

The eco-friendly technologies are able to withstand high drying temperatures. They allow for higher cycle times and materially reduce the risk of gas emissions after coating. Particularly in the case of aluminum sections using a polyamide plastic as a thermal barrier, the high temperatures can contribute to avoiding gas emissions during powder or wet painting. Also annealing, e.g. of cast iron or hot-dip galvanized parts, can be performed directly in the adhesive water dryer after pretreatment.

All technologies offer excellent corrosion protection

In terms of corrosion protection, all four technologies provide similar results. The GSB and Qualicoat standards for aluminum are fulfilled by the chromating processes in the same way as by the two chromium-free alternatives presented. Microprobe analyses of the cross-sections of substrates treated with Gardobond and Oxsilan show highly homogeneous cohesive coatings on the metal. They exhibit a uniform coating thickness across the surface regardless of edges or other surface irregularities. On galvanized steel, Oxsilan affords similar corrosion protection values as a chromating technology.

On steel, Oxsilan opens up completely new application opportunities. Chromating and conventional chromium-free processes are not suited for steel or yield poor corrosion protection values. When using adequate paint systems, the Oxsilan technology, by contrast, provides a corrosion protection of > 1000 h neutral salt spray testing on steel and galvanised steel. In this context, it makes no difference at which shares aluminum, galvanized steel or steel are pretreated. Multi-metal operation is possible.

Analytical scope the same for all processes

One argument frequently used against chromium-free processes is the alleged extra work for chemical analyses and greater expenditure for laboratory equipment. When looking at the time required for chemical analyses, it is almost identical for all processes contemplated. In the case of chromium-containing processes, the chromium points are titrated and the pH, conductivity value and free fluoride content (in the case of green chromating) are measured once per shift. When using Gardobond X 4707 and Oxsilan AL 0510, the effective ingredient points are determined by titration or photometry, among others, and the pH and conductivity value are measured. A fluoride measurement is only required in exceptional cases. The interval between the measurements is largely identical and all processes allow for automatic metering.

Quality assurance by determination of the coating weight

Quality is further assured by determining the coating weight, i.e. by a quantitative measurement of the conversion coating applied on the part or test panel. Chromium-containing coatings are gravimetrically removed by means of nitric acid. Then, the mass loss is determined by measuring the weight difference. In the case of chromium-free processes, the coating applied is in most cases determined photometrically. Another reliable method is the XRF analyser gun. Within just 30 seconds it measures the Gardobond X 4707 or Oxsilan layers generated on the substrate. With the XRF gun, measurements can be made directly on the part, thus allowing for a batch-independent, non-destructive analysis.

Visual check of the coating

A visual check after the adhesion water dryer is frequently performed to assess the pretreatment. In such a visual check, a wiping-proof, uniform yellow iridescent layer in the case of yellow chromating and a wiping-proof uniform green iridescent layer in the case of green chromating is what we are looking for. Parts pretreated with Oxsilan exhibit a distinct color change after the pretreatment. On steel and galvanized steel, it affords a yellowish-bluish and on aluminum a yellowish iridescent coloring of the surface. No color change of the surface is visible in the case of Gardobond X 4707. Due to the slight picking loss, the appearance of the pretreated parts is just slightly more matte.

Alternative processes

Economic viability, process reliability, quality, long service life and reliable delivery are vital criteria in a highly competitive marketplace. Over the years, eco-friendly processes have been continually optimised and now represent a viable alternative to the chromating technologies. Already 15 years ago, Chemetall launched the Gardobond X 4707 process. Today, this process is used in more than 50 plants in the wheel and household appliance industry worldwide, in the same way as for the treatment of aluminum sections and sheets for construction applications. The Oxsilan technology is already used at over 300 companies around the world, among them more than 50 from the automotive industry. Meanwhile, Daimler, Opel, PSA, Renault and Hyundai have converted their component or car body pretreatment lines in different plants to the eco-friendly technology. The Oxsilan technology suited for multi-metal treatment will leverage new potential in many companies. Commercial-scale applications have shown that the conversion also pays off in economic terms. This is demonstrated in a comparison of mean values. The sometimes drastically higher costs for the disposal of the process chemicals in the case of chromating is set to have a stronger effect in the years to come as even optimists do not expect prices to decline in this field. ■

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