SPECIAL EDITION

Chrome-free technologies open up many opportunities.

Gardobond® X 4707 & Oxsilan® AL 0510

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Gardobond® X 4707 and Oxsilan® AL 0510
Chrome-free technologies open up many opportunities

For decades, yellow and green chromates have been the technologies of choice for the corrosion protection of metals. Concerns over health and safety and the environment, as well as changed market demands have resulted in an increasing call for chrome-free alternatives. A comparison of the old vs. the new technologies shows why: eco-friendly technologies show better results in many key areas.

Two chrome-free processes from the Frankfurt-based Chemetall GmbH, Gardobond® X 4707 and Oxsilan® AL 0510, were selected for a comparison of chrome vs. alternative technologies. Both these Gardobond® and Oxsilan® processes have been used for several years in many plants around the world.

Gardobond® X 4707 is based on zirconium and titanium and was developed specifically for the treatment of aluminum. A totally new approach was made with Oxsilan®, a technology suitable for multi-metal applications. In addition to zirconium, silanes help to form the basis of this eco-friendly process replacing chrome and zinc-phosphates. The Oxsilan® coating bonds with the paint during the drying and/or application of the powder, wet or e-coat paint systems to give excellent paint adhesion and corrosion protection. Furthermore, the Oxsilan® technology can be used on all conventional metals such as steel, stainless steel and aluminum, whereas chromate can only be used on aluminum and small volumes of galvanized steel.

Comparison of general process conditions

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

Downsides of using chromates

The main disadvantage of using yellow and green chromates lies in the toxicity of their metal salts. The chromium chemicals are carcinogenic and mutagenic with classifications of very toxic, dangerous to the environment, oxidizing and corrosive. Over and above this, chromium-containing baths exhibit an acute aquatic toxicity. Consequently, they have been placed in the highest German water contaminating class 3, in contrast chrome-free alternatives are only caustic. The treatment baths for these are no longer classified as hazardous and are therefore placed in the German water contaminating class 1.

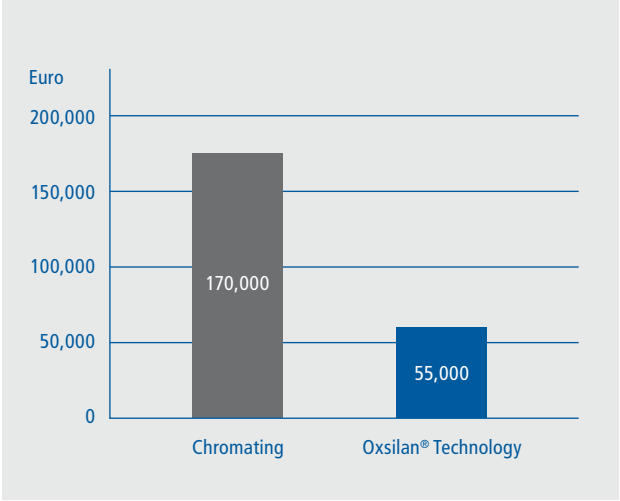
Economic consequences

It is especially worth noting that the different hazard ratings between the processes have a major financial impact. Neutralization, precipitation, separation and disposal of the chrome-contaminated water accounts for a major part of the overall process costs. And even further costs must be added, i.e. the charges incurred for the regular analysis and controls by the environmental protection authorities.

Chromate-containing baths need to be cleaned at regular intervals. The loss of production time as well as the treatment and disposal of the chromate-contaminated sludge waste also affects the economic viability of the process. Besides the economic concerns there is also the hazard potential of chromium itself which needs to be taken into account. Operators working with such material need to take extensive safety precautions when handling it. On the other hand chrome-free variants do not require such stringent safety measures to be taken as they pose a much reduced danger to health. Furthermore their storage is significantly easier and safer.

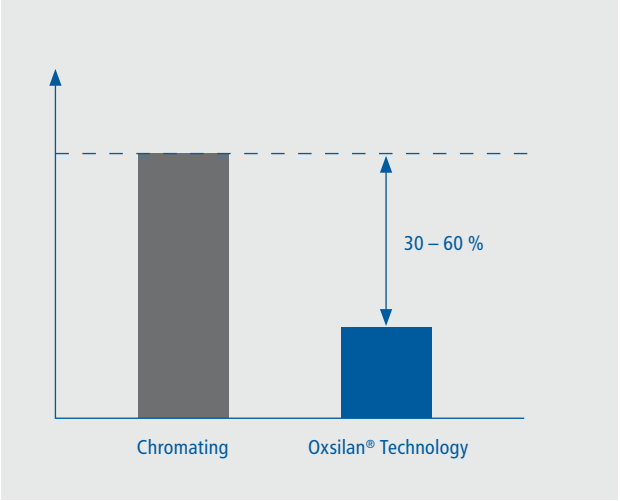
A comparison of the pretreatment costs based on an annual throughput of one million square meters of metal substrate shows that chromating leads to water and waste water costs being three times higher than for Oxsilan®.

Water and waste water costs



Water and waste water costs for the coating of 1 million sqm substrate by chromating and with Oxsilan®.

Total process costs



Comparison of the total process costs: Oxsilan® technology can potentially give real savings of between 30 – 60 percent compared to chromates.

Process Comparison
Similar process sequence, excellent corrosion protection

With regard to the process sequence there is little difference between the chrome-containing and chrome-free technologies. The substrates must be pre-cleaned and rinsed before the conversion coating can be applied.

In chromate processes, the aluminum substrates are pre-cleaned by means of acid or alkaline pickling. After chromating, the parts are then put through a multi-stage rinse to rinse off the toxic chromate solution. The conductivity of the drip off water from the pretreated parts must be less than 30 µS/cm before entering the adhesive water dryer. Iron-phosphating follows a similar process sequence of cleaning, coating (this sometimes is combined in one stage), and rinsing. When using Oxsilan® AL 0510 technology, acid cleaning is sufficient as a pretreatment for steel or galvanized steel. Also, this cleaning process can act as etch, pickle and desmut.

Aluminum substrates are treated with acid pickling instead. Just as in the case of the chromating processes, a rinsing step is required before and after the pretreatment. For the Gardobond® X 4707 process, several rinsing steps using DI water are required after acid pickling. It can also be used in a no-rinse process, when the final rinse stage after the conversion coating is omitted but it must be ensured that, before the coating is applied, the conductivity of the drip off water is less than 30 µS/cm. No-rinse processes are very sensitive to carry-over, so they are less suited for older pretreatment plants.

Comparison of typical process sequences

Volume of rinsing water is the same

In terms of rinse water consumption there is no significant difference between the processes. Due to the higher solids content, chromate processes require substantially more DI water than the alternative processes. In the case of the chrome-free processes, more attention needs to be paid to the rinses before the conversion coating. Here, the Oxsilan® technology is significantly more robust than conventional processes, which is why the conductivity of the drip off water prior to the Oxsilan® pretreatment can be increased from 30 µS/cm to 200 – 250 µS/cm. As a result, substantially less DI water is required. A substrate the size of 100 square meters, which has been treated with a chromate coating, requires about 80 liters of deionized water. Chrome-free processes require similar quantities. However what really matters is that the rinse waters from chromate processes are contaminated with chromium.

Higher drying temperatures, increased productivity

The eco-friendly technologies are able to withstand high drying temperatures. This allows for higher cycle times and can help to avoid gas emissions after coating. Particularly in the case of aluminum sections using a polyamide plastic as a thermal barrier, the high temperatures can reduce gas emissions during the stoving of the powder coating or wet paint.

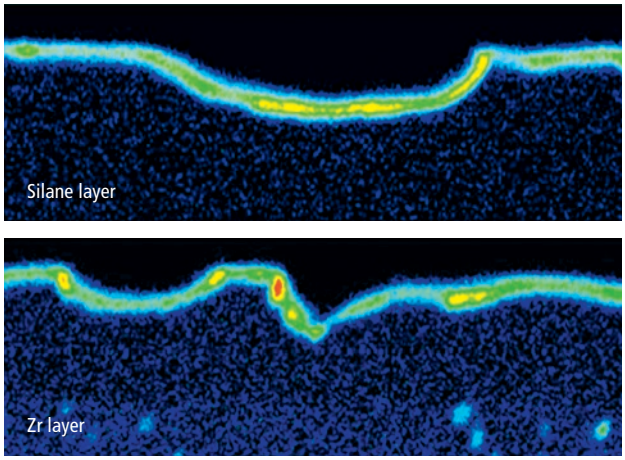
Comparison of the drying temperatures

Process	Drying temperature
Chromating	80 °C
Gardobond® X 4707	
no-rinse process	120 °C
rinse process	180 °C
Oxsilan® AL 0510	180 °C

All technologies offer excellent corrosion protection

In terms of corrosion protection, all four technologies perform well. The GSB and Qualicoat standards for aluminum are met by the chromating processes and also by the two chromium-free alternatives presented. Cross-section analyses of substrates treated with Gardobond® and Oxsilan® show highly even cohesive coatings on the metal. They display a uniform coating thickness across the complete surface of the metal regardless of edges or other surface irregularities. On galvanized steel, Oxsilan® gives similar corrosion protection to that of chromate technology.

On steel, Oxsilan® opens up completely new application opportunities. Chromate and conventional chrome-free processes are not suitable for use on steel or give poor corrosion protection. In contrast, Oxsilan® technology in combination with normal paint systems gives a corrosion protection of > 1000 h neutral salt spray testing on steel and galvanized steel. Consequently, multi-metal substrates can be processed on the same line.



Microscopic examination of an aluminum section coated with Oxsilan®

Quality Assurance
Simple and fast

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

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

Analytical scope the same for all processes

One argument frequently used against chrome-free processes is the alleged extra chemical analysis work and greater expenditure on laboratory equipment. When looking at the time required for chemical analyses, it is almost identical for both chrome and chrome-free processes. In the case of chrome-containing processes, the chromate points are titrated and the pH, conductivity value and free fluoride content (in the case of green chromate) are measured once per shift. When using Gardobond® X 4707 and Oxsilan® AL 0510, the pointage is determined usually by titration or photometry and the pH 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. Chromate-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 chrome-free processes, the coating applied is in most cases checked photometrically. Another reliable method is the XRF spectrometer. In just 30 seconds it can measure the Gardobond® X 4707 or Oxsilan® coating on the substrate. With the XRF spectrometer, measurements can be taken 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 process is often made to assess the quality of the pretreatment. In such a visual check, a wipe-proof, uniform yellow iridescent layer in the case of yellow chromate and a wipe-proof uniform green iridescent layer in the case of green chromate is what we are looking for. Components pretreated with Oxsilan® exhibit a distinct color change after the pretreatment. On steel and galvanized steel, it gives a yellowish-bluish and on aluminum a yellowish iridescent coloring to the surface. No color change on the surface is visible in the case of Gardobond® X 4707. As a result of the pickling stage, the pretreated parts just appear slightly more matte.

	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 INTERNATIONAL, AAMA, QUALICOAT			

Comparison of the different pretreatment processes

Yellow chromating	Green chromating	Gardobond® X 4707	Oxsilan® AL 0510
			
			
			
			
			

Classification of the concentrates according to GHS

Alternative processes are well-established worldwide

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 optimized and now represent a viable alternative to the chrome technologies. Chemetall has launched the Gardobond® X4707 process approx. 15 years ago. Today, this process is used in more than 50 plants in the wheel and household appliance industry worldwide, as well as for the treatment of aluminum sections and sheets for the construction industry.

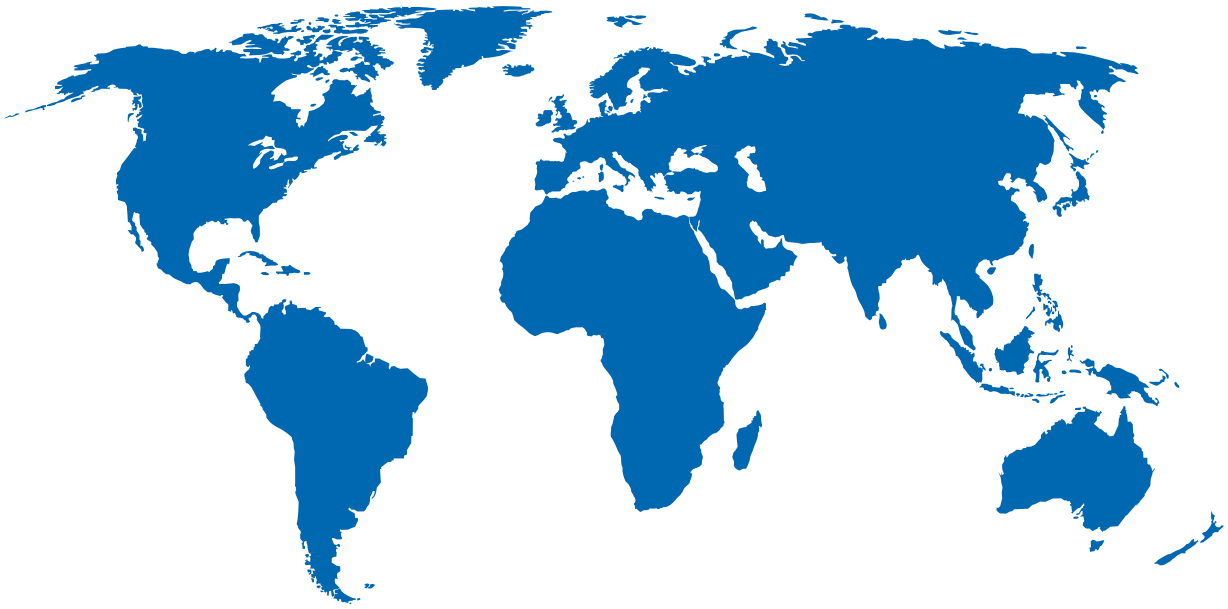
Oxsilan® technology is now used at over 300 companies around the world, including among them more than 50 automotive companies. Meanwhile, Daimler, Opel, PSA, Renault and Hyundai have converted their component or car body pretreatment lines in different plants to the eco-friendly technology.

The robust Oxsilan® technology which is suitable for use in multi-metal pretreatment lines will leverage new potential in many companies. Commercial-scale applications have already shown that conversion to this process also pays off in economic terms. This is demonstrated in a comparison of mean values (see fig. „Total process costs"). Even the most optimistic people assume that the high waste management costs often incurred for chromate process waste will rise even further in the years to come.

Chemetall at a glance

Chemetall is a leading global surface treatment company, headquartered in Frankfurt, Germany. With our 2,100 employees, 40 subsidiaries and 22 production sites, we are a financially strong and fast growing company with a long-term orientation. Our aim is to further strengthen our quality and innovation leadership. With our own sales offices, production facilities, service teams, laboratories and warehouses at locations all around the world, we are operating in close proximity to our customers.

The chemical treatment of metal surfaces is our core competence: Our products are developed for cleaning, giving corrosion protection, sealing, improving paint adhesion, and facilitating the forming and treatment of metals. Our globally established technologies are used in the most diverse industry sectors and have played a leading role in shaping metal treatment.



Headquarters and Regional Head Office Europe, Middle East, Africa, South America
Chemetall GmbH
Trakehner Straße 3
60487 Frankfurt am Main
Germany
Phone: +49 (0) 69 7165-0
surfacetreatment@chemetall.com

Regional Head Office North America
Chemetall US, Inc.
675 Central Avenue
New Providence, NJ 07974
USA
Phone: +1 908 464 6900
chemetall.americas@chemetall.com

Regional Head Office Asia-Pacific
Chemetall Asia Pte Ltd.
12 Loyang Crescent
Singapore 508980
Phone: +65 6885 7900
cm.asia@chemetall.com

www.chemetall.com

CM-SE0075ENG-04.2014