GSB INTERNATIONAL
INFO

Coated steel or aluminium piecework must withstand a variety of environmental influences. GSB Quality Seals provide internationally accredited product assurance.

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Editorial

"We can only see a short distance ahead, but we can see plenty things there that needs to be done."
(Alan Turing)

Just as things develop in Europe, 2016 may be a year, in which also in our industry a technological change is needed. The so called "Sunset" for the chromating comes nearer. The introduction of sustainable, environmentally friendly practices and processes requires a considerable expenditure of time. Just a simple exchange of the bath treatment will not be successful.

To recognize fundamental changes and to be prepared for, even if this takes years or decades to become effective with their scope and consequences, protects against unpleasant surprises and secures the future. Our organization has recognized these things and has assumed the changes at an early stage. A number of pretreatment processes of different manufacturers are already available, process reliable and competitive, which meet the high demands of the GSB International. Many member companies have already applied these processes partly for more than 10 years and use them successfully.

Hans-Jürgen Alfort
Chairman of the board GSB International

Chromium-free surface pretreatment for aluminium

Documentation of state of the art
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Content

Uniklinikum Mainz (PBS Schreiner, Grebenau)

Preface

Preface

In the early 1990s, the State of Berlin issued the ban on the use of aluminium as a building material, against which the General Association of the Aluminium Industry (GDA) filed a successful opposition. However, this was associated with the requirement that chromium-free processes must be used in future for the surface pretreatment.

GSB International has faced this challenge for more than 15 years, and has worked extensively on the introduction and approval of chromium-free pretreatment processes. In close co-operation with pretreatment chemical manufacturers and coating companies, approval procedures for alternative systems were developed and then implemented in the quality guidelines. Only in 1994 was approval granted for a chromium-free pretreatment process to ensure that member companies could continue to serve their markets with alternative processes with a high quality level. Therefore, since that time, proven chromium-free pretreatment processes have become available that behave in a stable way under production conditions, have shown high corrosion resistance in long-term weathering tests and are commercially competitive.

Since its foundation over 30 years ago, GSB International has pursued a consistent strategy of developing quality-assured products, with due consideration of environmentally friendly technologies and procedures. The selection of the processes and operating sequences remains exclusively within the corporate responsibility of each individual member company. As in the past, GSB International does not specify any requirements in the quality standards that exceed the regulatory framework.

At the end of 2010, the ECHA placed chromium (VI) oxide and other chromium (VI)-containing compounds on the list of substances of very high concern (SVHC list) because they are carcinogenic and mutagenic. This raises the very important question of the future of chromating as a pretreatment process for aluminium in construction. Nevertheless, this problem has been known since the 1990s in the industrial sectors in question.

Our organisation therefore acted in a timely manner to find alternative chromium-free pretreatment processes.

Khan Shatyr Project – Kasachstan (Alumil-Milonas Aluminium Industry S.A., Kilkis, Greece)

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1. Introduction
1.1 Current situation

On June 1st, 2007, the REACH regulation came into force to replace the existing chemicals legislation in the European Union (EU).

The REACH regulation has established a certification procedure for substances of very high concern. As of 30th June 2011, there are 53 substances included on the candidate list (SVHC list) for certification. The objective of the EU Commission is to expand the list to 136 substances by the end of 2013. Publication in the „candidate list" does not result in mandatory certification but rather far-reaching information requirements in the supply chain. REACH requires companies to inform their business customers if their products contain more than 0.1 per cent of a chemical identified in the list.

At the end of 2010, the European Chemicals Agency (ECHA) added chromium (VI) oxide and other chromium (VI) compounds to the candidate list for substances of very high concern (SVHC list).

The list of substances subject to mandatory certification now contains 6 substances, for which the companies concerned must submit certification applications by 2013. The inclusion process is currently under way for a further 13 substances. This also applies to chromium (VI) oxide, chromic acid and other chromium (VI) compounds. After inclusion in Annex XIV of the REACH regulation, a certification must be applied for prior to each use. The EU Commission makes the decision regarding the certification.

The possible consequences are:
- Chromate-containing surface pretreatment processes may continue to be used. The required registration of the chemicals with the ECHA is very expensive, which may lead to an increase in the process costs.
- Relocation of production to non-REACH countries. The import of chromate-containing products without registration with the ECHA is prohibited. Here also, the required registration can lead to price increases.
- The use of chromate-containing surface pretreatment processes is prohibited without exception.
- According to current knowledge, a final decision by the European Commission is anticipated within the next 5 years.

Health endangerment
Toxicological significance is ascribed to chromium (VI) compounds, which have the potential to cause cancer. Their classification as compounds with carcinogenic and mutagenic potential has been known for many years.

Metallic chromium and trivalent chromium compounds, such as the chromium (III)-phosphate that makes up the green chromating layer, are not irritant, mutagenic or carcinogenic. However, the production of process chemicals always starts from chromium (VI) compounds. Thus, the handling of hazardous chemicals is assumed here, and particular caution is required.
Chromium (III) compounds are not included in the SVHC list, and therefore can still be used without restriction.

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2. Statutory provisions
2.1 Architecture and construction

The relevant national building codes and rules do not currently prohibit the use of chromium-containing surface pretreatments.

However, individual cities and districts have switched over in their tenders to the mandatory prescription of chromium-free pretreatments.

As early as 1990, the Building/Living Senate in Berlin, in the 40th Official Journal, prohibited the use of building materials posing a high health and environmental hazard, and thus banned the use of window and door profiles made of aluminium. At the meeting of February 19th, 1998 (document 13/2002) in the context of the lifting of the restriction on the use of aluminium in the regulatory area of public sector and publicly funded construction, the Berlin Senate declared that aluminium is only allowed if
- a pledge of commitment by the manufacturer for product-related recycling and
- a declaration by the contractor on the chromium-free passivation for coloured aluminium components exist.

There is therefore no differentiation between chromium (VI) and chromium (III) compounds, but the use of chromium is generally prohibited.

The decision of the Berlin Senate had a nationwide impact and so other cities, such as Munich, also introduced the same or similar regulations.

The certification systems for sustainable construction (LEED, DGNB, etc.) also provide, in their evaluation rules for building, positive points for the use of chromium-free surface pretreatment processes for aluminium. For this reason, architects are increasingly inviting tenders for chromium-free surface pretreatments.

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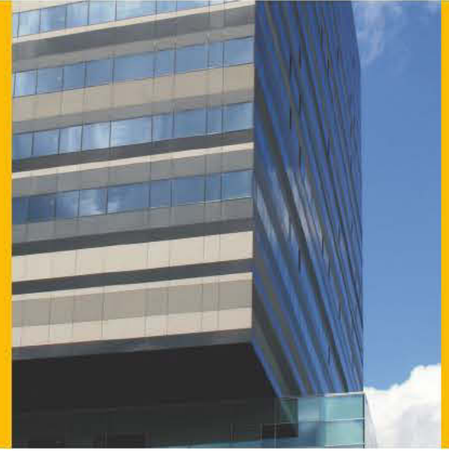


Mövenpick Hotel,
NL-Amsterdam City Center

Other European countries, like Spain, France and Greece, already have a market share of more than 60 % made up of chromium-free pretreatments. In 2011, China enacted a ban on the use of chromium (VI)-containing pretreatments in architecture.

Other markets

Other markets have already gone one step ahead. By virtue of the Directive on End of Life Vehicles (2000/53/EC, July 1st, 2003/ July 1st, 2007), the use of Cr (VI)-containing compounds has long been prohibited. Some car manufacturers have generally rejected chromium-containing compounds in pretreatments and in the processes for surface pretreatment of aluminium.

The same applies to electrical appliances. Here the guidelines
- ROHS (EU Directive 2002/95/EC on Restriction Of The Use Of Certain Hazardous Substances In Electrical And Electronic Equipment, July 01st, 2006) and
- WEEE (EU Directive 2002/96/EC on Waste Electrical And Electronic Equipment, July 01st, 2006)

should be highlighted.

Even in the aerospace industry, chromic acid anodisation is being replaced by tartaric acid anodisation. New projects are generally only tendered for with tartaric acid anodisation.

3 GSB International
3.1 General information

These developments prompted GSB International to test chromium-free pretreatment processes in observance of the high and proven quality standards and to incorporate them into the quality standards as a GSB International-compatible pretreatment.

3.2 State of the art at the time of the foundation of GSB International in 1976

For more than 50 years, in the pretreatment of aluminium, chromating has performed the tasks of improving adhesion for subsequent coating and serving as a barrier layer against substances diffusing through any organic layer, such as water vapour or corrosive atmospheric gases. This applies to coating with liquid and powder coats.

We primarily differentiate between yellow and green chromating. Whereas the yellow chromate layer, which primarily consists of chromium oxide (Cr203), still contains Cr(VI) ions, no chromium (VI) ions can be detected any more in the green chromating layer, which primarily consists of chromium phosphate (Cr(III)PO4). Chromium-containing conversion layers created both in the dipping and spraying processes deliver comparably good results in relation to adhesion promotion and corrosion inhibition. In all chromating processes, thorough rinsing to remove the adhering treatment solution is necessary. This requires the preparation of chromate-containing rinse water to prevent chromate from entering the waste water.

Certification procedures of GSB International

In addition to inhibiting corrosion and improving paint adhesion, for all certified and used paint systems, the equipment suitability, processing properties and process stability of the pretreatment process are particularly important.
This led the Technical Committee (TC) of GSB International, in developing a certification process for alternative, chromium-free pretreatment chemicals, to propose a multi-stage sequence:

Stage 1:
- Application of the chemical suppliers to GSB International for certification of the relevant pretreatment system.
- Presentation of the system and discussion with the Technical Committee (TC)

For this purpose, the following documents must be prepared:
- Presentation of individual results based on GSB QR AL 631
- Submission of tested sample sheets
- Submission of current product data sheets and material safety data sheets
- Names of reference objects, if applicable
- Evidence of product suitability for dipping plants and/or spraying equipment
- Evidence of product suitability for powder and/or liquid coats
- Plant experience

Stage 2:
The pretreatment, coating and testing according to GSB QR AL 631 of the sample plates is performed in a test institute to be named by the TC.

As a reference, a commercial yellow chromating has been used so far. A chromium-free „master process" is being tested. The samples pretreated with the reference material are coated and tested the same way.

As a reference material, a reference powder coat determined by the TC is used. The tests and requirements are summarised in section 8.2.6 of GSB QR AL 631.

Stage 3:
If the results of stage 2 are positive, a plant test is performed at a coating company that is a member of GSB International.
Stage 3 must be performed in a production plant; here, the material must be pretreated with a surface area of at least 500 m². 25 m² from the middle and end of the pretreatment lot respectively must be coated and exposed as an object of natural weathering. The consent of the TC for the coating company and the object is required.

The documentation of the plant test is created by an observer appointed by the TC.

After a positive evaluation of the results of field tests in accordance with section 8.2.6 of GSB QR AL 631, the preliminary certification for the pretreatment system is granted. Only the findings from the field tests confirm the plant suitability and process stability of the alternative treatment processes.

Stage 4:
Sample material from the pilot test (stage 3) is weathered for three years in a near-shore industrial climate (preferably in Hoek van Holland in the Netherlands). Once the natural weathering results have been obtained, if the progression is positive, the final certification may be granted and authenticated for the pretreatment system.

Extension test
The certified alternative pretreatment chemicals, like the coating materials, are subject to an annual extension test. The test samples required for the extension test, in the form of ready-coated profiles or sheets, are removed by the tester from a coater who is routinely using the pretreatment chemical to be tested. In the event of positive test results, the certification is extended by one year.

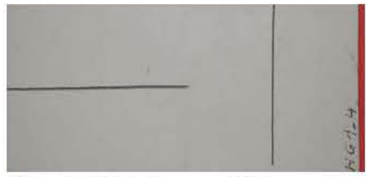
Expanded certification criteria
For alternative pretreatment processes, increased care in degreasing, pickling and rinsing with completely deionised water (DI) prior to the conversion treatment is crucial. The quality of the product „coated material" is essentially dependent on the pretreatment, the coating material and the careful application of the coating. Therefore, in the currently valid quality guidelines, expanded certification criteria have been included.

Thus, in 2007, GSB International introduced the status of „premium coater". The most important quality criterion for the premium coater is the precise definition of the pretreatment process with product testing.

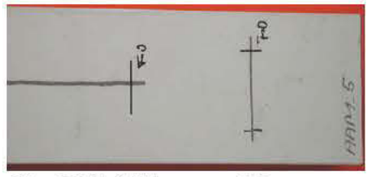
Here, for the first time in a quality community, the entire pretreatment process is documented, stored and monitored by means of corrosion tests on coated products. Process changes must always be communicated. Another aspect is the increased documentation of self-monitoring for the premium coater.
With the premium segment for the coater and the coating material, there is increased security for the life expectancy of constructed façade sections. For the first time, the detailed definition and monitoring ensures additional security, which is not the case with national and international standards.

3.5 Extension of natural weathering

Since the beginning of the natural weathering tests in Hoek van Holland, GSB International did not end the exposure after three years, but extended the test period to ten years. The samples removed after ten years were documented and handed over to the respective pretreatment manufacturers for storage.



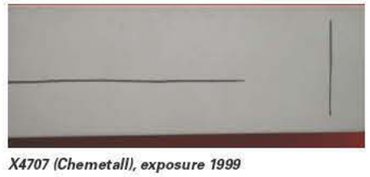
Alodine 4830 (Henkel) exposure 1999



Alfipas 745 (Alufinish), exposure 1998

Alficoat 748 (Alufinish), exposure 2001

Nabutan STI 310 (Nabu), exposure 1998



X4707 (Chemetall), exposure 1999

3.6 Certified systems

Alternative pretreatment systems, chromium-free (Rinse and No-Rinse)

Company	Internet	System	Certification
Henkel KGaA	www.henkel-technologies.de	Alodine 4830/31 (powder coat area)	Stage 4
		Alodine 400	Stage 4
NABU-Oberflächentechnik GmbH	www.nabu-stulln.de	Nabutan STI / 310 (powder coat area)	Stage 4
		Nabutan 900	Stage 2
Alufinish GmbH & Co. KG	www.alufinish.de	Alfipas 745/746 (Pulverlackbereich)	Stage 4
		Alficoat 748 (powder coat area)	Stage 4
		Alfipas 7816	Stage 3
Chemetall GmbH	www.chemetall.com	Gardobond X 4707 Oxsilan AL 0510	Stage 4 Stage 3
Chemische Werke Kluthe	www.kluthe.com	Deccordal AI230A	Stage 4
CHEMAL GmbH & Co. KG	www.chemal.com	Non-Chrome B.K.-3990	Stage 4
MacDermid GmbH	www.macdermid.com	Iridite CF (powder coat area)	Stage 4
AD Chemicals B.V.	www.adinternational.com	Precoat Cr-free (powder coat area)	Stage 3
Surf Chem - Skylodimos Bros.		SurfPass Ti NOC (powder coat area)	Stage 3

Alternative pretreatment systems, chromate-free (Rinse and No-Rinse)

Company	Internet	System	Certification
Henkel KGaA	www.henkel-technologies.de	Alodine 5992	Stage 3
SurTec International GmbH	www.surtec.com	SurTec ChromitAl 650 TCP (powder coat area)	Stage 3

Weathering in Hoek van Holland

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4. Pre-anodisation

Another environmentally friendly alternative passivation of the aluminium surface is the generation of thin aluminium oxide layers, referred to as pre-anodisation.
Pre-anodisation has been successfully used in the construction industry for several years. It is applied especially with locations of buildings near the coast, in aggressive industrial climates or application areas particularly susceptible to filiform corrosion, such as indoor swimming pools.

Earlier studies initiated by GSB International have shown that filiform corrosion can only be prevented with a pre-anodisation beyond the required warranty periods. This has in fact been confirmed in outdoor weathering studies by the Forschungsinstitut für Pigmente und Lacke e. V. (FPL) (Research Institute for Pigments and Paints), of Stuttgart, Germany, as well as by the Forschungsinstitut für Edelmetalle und Metallchemie (FEM) (Research Institute for Precious Metals and Metallochemistry), of Schwäbisch Gmünd, Germany.

Since 1995, the pre-anodisation layer, produced under defined conditions, has been certified by GSB International as a pretreatment process for aluminium. It should be implemented in accordance with the provisions of section 8.3 of the quality guidelines GSB AL 631.

Anodic oxide layers can be produced only on a metal connected as the anode, which is immersed in an electrolyte. By the action of the electric current generated during the electrolysis at the anode, atomic oxygen is liberated, which reacts with the aluminium, forming alumina. This is solidly anchored to the metal surface. The layers consist of an impermeable barrier layer and a porous outer layer, the achievable thickness and pore diameter of which depend on the current density, time, temperature and acid concentration. The pore density is about one billion pores per mm2 of external surface.
To prepare the adhesive artificial oxide layer, sulphuric acid is generally used as the electrolyte. The layer thickness can be adjusted via the process parameters of temperature, current density and time. Highly suitable layer thicknesses have been found to range between 5 and 8 µm.

The following are considered to be the properties of the layer and the process:
- Very good corrosion resistance
- Variable adjustment of layer thicknesses
- Special plant technology is required
- Only achievable with dipping

The anodic oxidation of aluminium, both in terms of the quality of the passive layers formed, and also their technical importance, has a leading position in the surface pretreatment of aluminium. The very good corrosion resistance, even under difficult operating conditions, and the good environmental compatibility, are factors that favour the increasing use of these intermediate layers. The application of pre-anodisation is a pre-requisite for the awarding of the GSB International quality label „Sea Proof Plus".

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5 Summary

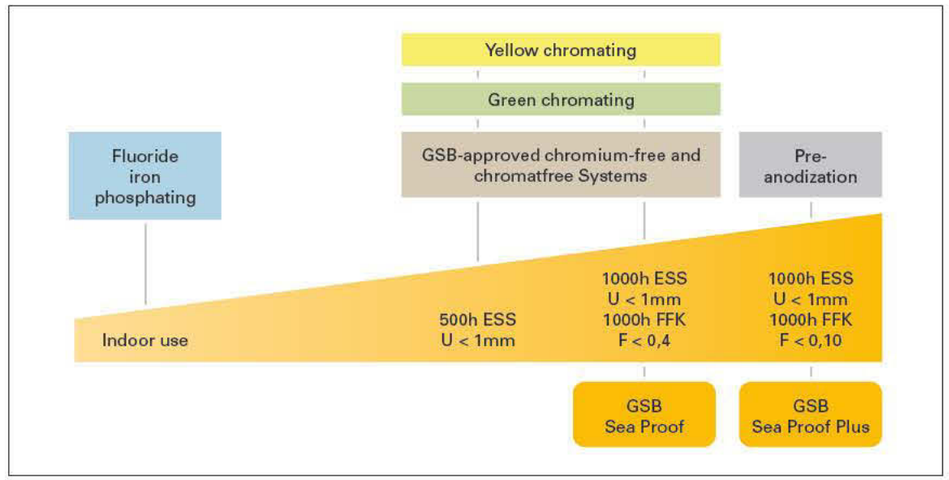
- Since its introduction 50 years ago, chromating has grown steadily into a safe process for the pretreatment of aluminium. Only through this safe process technology could electrostatic powder coating develop to include coloured design of aluminium in the construction industry in the last forty years, in addition to proven electrochemical oxidation.
In particular, the high process safety and high corrosion protection achieved are very highly prized in the market.

- The classification of chromium (VI) compounds as compounds with carcinogenic and mutagenic potential has been known for many years. Therefore, their inclusion in the candidate list (SVHC list) comes as no surprise to the affected industries.
The use of chromating for the pretreatment of aluminium, however, continues to be legally permitted until a final decision by the European Commission is reached.

The relevant national building codes and rules, such as the REACH Regulation, also do not rule out the application of this surface pretreatment process at the current time.
There is no absolute clarity regarding how chromium (III) compounds will be classified in the future. This also includes green chromating, which still possesses a certification for coatings that come into contact with food products. However, the production of process chemicals always starts from the basis of chromium (VI) compounds.

- It is important to note that it is already a requirement of some individual cities and districts that a chromium-free pretreatment be enforced for the use of aluminium in public buildings. This raises the question of what is actually to be understood by the term „chromium-free". This requirement is not consistent with the national building codes and the REACH chemicals ordinance, and represents a tightening of the requirements profile. Harmonisation and an unambiguous interpretation would be in the interest of all parties involved.

- Since 1994, chromium-free pretreatment processes have been certified for the coating of aluminium according to GSB International guidelines QR AL 631. The market now has a wide range of available choices of definitively certified processes. Several million square metres of coated alu-



Requirements for chromate-containing and chromium-free surface pretreatments

Uniklinikum Frankfurt am Main
(PBS Schreiner, Grebenau)

minium with chromium-free pretreatment are the hard evidence of the process safety of this pretreatment process.

- The chromium-free process used must be adapted to the production parameters of the respective plants; and also vice versa. A systematic and continuous bath monitoring of the chromium-free pretreatment is required. According to the current state of the art, this is more challenging than in the case of chromating.

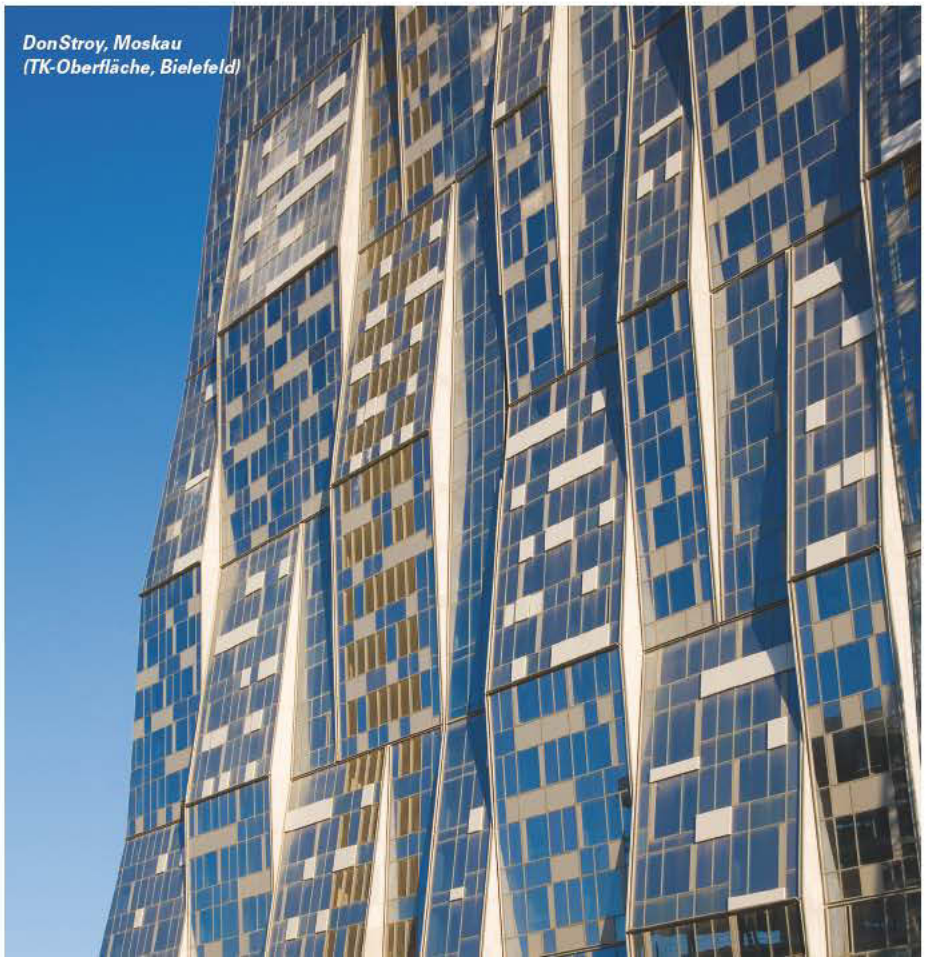
- The health protection of employees is much more thoroughly guaranteed with the use of chromium-free pretreatment processes.

- The increased durability of chromium-free processes compared to chromating is an important economic factor.

- Pre-anodisation is the chromium-free process that offers the best corrosion protection and the highest resistance to filiform corrosion. This chromium-free process has been used successfully more than 20 years in regions with particularly aggressive climates.

- According to the present results, chromium-free pretreatment processes are classified as being comparable in their corrosion protection to chromating processes. There are studies that have confirmed the higher filiform resistance of chromium-free processes compared to chromium-containing processes.

- Also in other industrial sectors, chromium-free pretreatment has now established itself. Chromium-free pretreatment, despite the existing objections, results in increased sustainable protection of the environment and humans.



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