Survey on technical and economic feasibility of the available alternatives for chromium trioxide on the market in hard/functional and decorative chrome plating

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Contents

Survey on technical and economic feasibility of the available alternatives for chromium trioxide on the market in hard/functional and decorative chrome plating

Abstract

In this report, information was gathered regarding the technical and economic feasibility of alternatives to the use of chromium trioxide for functional and/or decorative chrome plating.

Published analyses of alternatives (AoA) for chromium trioxide, which are part of the applications for authorisation under REACH (EC) No. 1907/2006, were evaluated to gain an overview on possible alternative processes. By participation at a BAuA workshop on perspectives of substitution of chromium trioxide contacts to relevant actors were established. Current literature was investigated and 34 expert interviews with suppliers and users of alternatives as well as with users of chromium trioxide were conducted to identify possible alternatives and to discuss advantages and drawbacks in detail.

Plating metals or plastics with chromium trioxide is a technically stable, well established and therefore economic process that can create surfaces displaying a variety of different properties which can simultaneously fulfil multiple technical and aesthetical requirements. Until today no one-to-one replacement to chromium trioxide has been discovered for functional chrome plating, which meets all requirements at once. The same holds in quite a few cases for the deposition of thinner chromium surfaces on metals or plastics from chromium trioxide – generally referred to as "decorative chrome plating" – but where it has to be appreciated as well that these surfaces often serve important additional functions besides purely aesthetic aspects.

However, in this survey available alternatives were identified that are technically and economically feasible – sometimes in one or few uses only, but sometimes even in larger areas of application. Some of the alternatives are long-established technologies with known strengths and weaknesses. And there are developments underway that expand the fields of application and specifications of these processes.

Key words:

chromium trioxide, substitution, SVHC, REACH, alternatives, hard chrome plating, decorative chrome plating

Studie zu technisch und wirtschaftlich verfügbaren Alternativen zum Einsatz von Chromtrioxid bei der Hart-, Funktional- und Dekorativverchromung

Kurzreferat

Mit diesem Bericht wurden Informationen über technisch und wirtschaftlich machbare Alternativen zum Einsatz von Chromtrioxid in der Hart- und Dekorativverchromung zusammengestellt.

Dazu wurden zunächst die Analysen der Alternativen (AoA) geprüft, welche ein Teil der Autorisierungsanträge für die zulassungspflichtigen Verwendungen von Chromtrioxid gemäß der REACH-Verordnung (EG) Nr. 1907/2006 sind. Zusätzlich erfolgte eine Auswertung der aktuellen Fachliteratur. Durch Teilnahme an einem Workshop der BAuA zu Perspektiven der Substitution von Chromtrioxid konnten Kontakte zu relevanten Akteuren geknüpft werden. Insgesamt wurden 34 Experteninterviews mit Anbietern und Verwendern von Alternativverfahren sowie mit Anwendern chromtrioxid-basierter Verchromungsverfahren geführt, um Vorteile und Grenzen der Alternativen detailliert zu ergründen.

Die Verchromung von Kunststoffen oder Metallen mit Chromtrioxid ist ein technisch stabiler, etablierter und wirtschaftlicher Prozess, der Oberflächen mit einer Vielzahl nützlicher Eigenschaften erzeugt, die verschiedene technische und ästhetische Anforderungen erfüllen. Bis heute existiert kein Eins-zu-eins-Ersatzverfahren, das alle bestehenden Anforderungen gleichzeitig erfüllt. Dies gilt sowohl für die Funktional- oder Hartverchromung, als auch für die als Dekorativverchromung bezeichnete Aufbringung dünnerer Chromschichten, bei der allerdings keineswegs nur dekorative Aspekte eine Rolle spielen.

In dieser Untersuchung wurden jedoch Verfahren identifiziert, die sowohl technisch als auch wirtschaftlich sinnvolle Alternativen darstellen – manchmal nur in Bezug auf sehr spezielle Anwendungsfälle, aber durchaus auch mit breiteren Anwendungsbereichen. Bei einigen dieser Alternativverfahren handelt es sich um etablierte Technologien mit gut bekannten Stärken und Schwächen. Allerdings gibt es jüngste Entwicklungen, die Anwendungsfelder dieser Alternativverfahren zu erweitern.

Schlagwörter:

Chromtrioxid, Substitution, SVHC, REACH, Alternativprüfung, Hartverchromung, Dekorativverchromung

1 Introduction

Since its invention about 100 years ago chrome plating has become an important industrial process with regard to surface treatment of metal and plastic materials. The process is mainly based on galvanic deposition of metallic chromium from aqueous solutions of hexavalent chromium compounds.

In 2013 chromium trioxide (CrO_3, EC-Nr. 215-607-8, CAS-Nr. 1333-82-0) one of the most important substances with regard to galvanic chrome plating has been identified as a substance of very high concern (SHVC) in the context of the European Union Regulation 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

Importers or downstream users (in this case: galvanisers and suppliers of respective chemicals) therefore have been obligated to apply for an authorisation according to article 62 if they want to start or continue using or distributing chromium trioxide in the European Union (EU).

Since inclusion of chromium trioxide into Annex XIV of REACH ("Authorisation List") more than 50 applications for authorisation have been received by the European Chemicals Agency (ECHA), many of them with regard to the application of chromium trioxide for functional or decorative chrome plating.

In this survey, information was to be gathered regarding the technical and economic feasibility of alternatives to the use of chromium trioxide for functional and/or decorative chrome plating in order to be able to determine their potential to substitute chromium trioxide and to assess their technical or economic limitations in the respective application areas. However, the analysis of the socioeconomic impact of using alternatives to chromium trioxide-based processes was not within the scope of the study.

Chromgruen and VDI Technologiezentrum (VDI TZ) have been assigned by the German Federal Institute for Occupational Safety and Health (BAuA) to carry out this survey in December 2018.

2 Methodical approach and project activities

The project is structured into three work packages:

1. Identification of available alternatives to chromium trioxide in the relevant application areas
2. Assessment of their technical eligibility based on relevant parameters and gathering of information on their economic feasibility
3. Identification and description of appropriate examples for successful substitution of chromium trioxide in functional and decorative chrome plating

The following approach and objectives were pursued:

- Evaluation of the published analyses of alternatives (AoA) for chromium trioxide, which are part of the applications for authorisation under REACH
  objective: to gain an overview on possible alternative processes for hard or decorative chrome plating with chromium trioxide
- Participation at BAuA workshop on perspectives of substitution of chromium trioxide
  objective: to get in touch with relevant actors
- Literature research and expert interviews with suppliers and users of alternatives as well as with users of chromium trioxide
  objectives: to identify possible alternatives and to discuss advantages and drawbacks in detail
- Documentation of the findings in a consistent form
  objectives: to provide a structured overview of alternatives on the market and select appropriate examples for a presentation to a wider public

These steps are described in the following sections in more detail.

2.1 Evaluation of the published analyses of alternatives for chromium trioxide

Entry point for this task are the applications for authorisation according to REACH which have been submitted to ECHA. 36 applications for authorisation regarding chromium trioxide covering 61 uses as presented on ECHA's website have been screened. These applications amongst others contain analyses of alternatives (AoA) where application areas and the respective technical and economic criteria are described by the applicants. 28 uses focus on functional or decorative chrome plating or on a combination of both. In eight cases the analysis of alternatives is described together with the socio-economic analysis.

These documents were used to identify

- relevant actors as potential interview partners
- application areas of chromium trioxide in functional and decorative chrome plating
- technical and economic criteria in these application areas
- potential alternatives.

Additionally, the use "*etching of plastic surfaces as pre-treatment for decorative chrome plating*" was examined as it is inextricably linked to the respective plating process.

2.2 BAuA Workshop „Perspectives of Substitution of Cr(VI)“

Members of the project team have participated in the workshop in order to gain technical input and to establish contacts for interviews. It was possible to establish contacts to several providers of alternative processes for hard chrome plating like e.g. trivalent chrome based hard chrome plating, plasma nitriding and laser cladding. All lecturers were successfully approached in order to conduct expert interviews. Additionally, contacts to users of chromium trioxide and to representatives from relevant industry associations were established. The presented alternatives were evaluated in depth subsequently.

2.3 Literature research and interviews

Starting with the analyses of applications for authorisation and the evaluation of BAuA's workshop the technical and economic feasibility of potential alternatives as discussed there have been analysed based on literature and expert interviews with suppliers and users of alternatives as well as with users of chromium trioxide.

2.3.1 Literature research

Literature search was confined to scientific review articles from recent years focussing on alternatives for chromium trioxide-based plating processes. As the study was focussed on processes with a high technology readiness level (TRL), literature describing new scientific approaches for substitution of chromium trioxide was not included. Furthermore, review articles older than five years were excluded, because it can be supposed that this literature has been taken into account in the AoA of the application documents. Due to the same reasons a focus was put on technical journals like e.g. mo Magazin für Oberflächentechnik, JOT – Journal für Oberflächentechnik, ZVOreport, Galvanotechnik formed the core base of the project.

2.3.2 Expert interviews

Expert interviews were conducted in order to allow for recent, practical, and specific information and experiences to be included in the project. Major advantages of this method are the specific focus as well as the time budget the expert is spending on the subject as compared e.g. to a questionnaire-based survey. Also important is the option to ask additional clarifying questions, if need be in follow-up phone calls or emails.

Interview partners were selected in a deliberate way as opposed to a random selection from a given population. Therefore, this method of qualitative analysis does not allow for representative conclusions. Also, as participation was voluntary, it had to be accepted if it was not possible to find interview partners for certain applications. Potential interview partners were identified from literature. Already existing contacts from past activities were utilized as well. At the end of the first project phase about seventy potential interview partners (companies or persons) had been identified. This list was then further complemented with about 400 additional addresses, which were retrieved from public B2B suppliers database (“wer liefert was”). The frequency distribution of the different technologies does not reflect their respective assumed importance, but is a consequence of available information (Table 2.1).

Tab. 2.1 Investigated complementary company addresses

Technology	**Number of Companies**
Chemical Vapour Deposition (CVD)	19
Physical Vapour Deposition (PVD)	152
Carburisation	33
Nitriding	103
Boriding	6
Electroless Nickel Plating	85
Sum Total	**398**

As a result of a preliminary expert interview with representatives of the surface coating industry association ZVO e.V. one of the interview partners conveyed additional contacts to experts, most of them being either plating companies or end customers of plated products both with hands-on experience in alternatives to hexavalent chrome plating.

In spite of the activities described above it was not possible to conduct targeted interviews with users or suppliers of chemical vapour deposition, boriding and electroless nickel plating. But it should be pointed out that in none of the other interviews any of these technologies were mentioned as essential for getting a comprehensive overview of relevant alternatives.

Finally, 34 interviews have been conducted where in some cases multiple alternatives have been discussed (Table 2.2). A more detailed list is given in the appendix.

Tab. 2.2 Overview on conducted interviews

Alternative	**No. of interviews (multiple responses possible)**
Cr (III) based decorative coating	7
Cr (III) based functional chrome coating	9
Cr(VI) free etching	3
Laser Cladding (EHLA)	5
Case hardening	12
Thermal spraying	11
Varnishes and films	1
Physical Vapour Deposition	9

Interviews were conducted in person or via phone calls. In order to ensure a consistent interview quality a guideline was designed where all relevant aspects were included. It was based on a complemented list of technical and economic criteria which were seen as relevant for the feasibility of the respective alternatives. Interviews were planned with a time frame of 60 to 120 minutes.

The following aspects were discussed:

1. Short description of alternative
2. Application area
3. Relevant technical requirements for the product
4. Technical restrictions

5. Legal or normative requirements
6. Design requirements
7. Risk assessment
8. Production costs
9. Costs for protective measures
10. Use related data
11. General economic aspects
12. Implementation obstacles

If necessary, follow-up questions were discussed via eMail or telephone. Interview results are presented anonymously as citations (Interview XX) in the relevant chapters.

2.4 Documentation of the findings in a consistent form

Results from the analyses of applications for authorisation were complemented and/or updated by literature and expert interviews. They are presented in the following chapters.

Practical relevant case studies of substitution of chromium trioxide in functional as well as decorative chrome plating were identified and prepared for publication on the SUBSPORTplus website.

3 Application areas of chromium trioxide in chrome plating

Due to the status of the authorisation process for chromium trioxide as an SVHC it seems safe to assume that all relevant application areas of chromium trioxide in functional and decorative chrome plating are covered by respective applications for authorisation. Analyses of alternatives included in applications for authorisation (AoA) were downloaded in January 2019 to March 2019 and evaluated subsequently.

3.1 Functional chrome plating

The following Table 3.1 shows an aggregation of the sectors and main product categories as described in the applications for authorisation. A detailed list can be found in the appendix.

Tab. 3.1 Sectors and main product categories of functional chrome plating

Sector	Main product categories
Aerospace	coating, maintenance, repair and overhaul work of aircraft engine components
Automotive	engine valves
	piston rings
	piston rods
	filament guiding parts, special work pieces
General Engineering	heavy industrial items (of paper machines, vehicles, marine equipment, textile machines etc.) e.g. valves, riddle drums
	civilian firearms barrel bores and auxiliary parts
	mechanical and electromechanical cylinders, cam- and padlocks, electromechanical lock cases and architectural hardware
	interior coating of continuous casting moulds
	coating of forming tools
Manufacture of Printing Equipment	printing cylinders of rotogravure printing processes
	rolls and rollers
	mandrels
	sheet guiding cylinder jackets
Metal Precision Parts	sugar sieves
	sheet-guiding cylinder jackets
Construction & Industry, Power Generation, Railway and Maritime	piston rings for two-stroke and four-stroke large bore engines
Defence industry	military armament steels parts
	steel weapon barrels
	small- and medium-calibre firearms barrel bores and auxiliary parts

Sector	Main product categories
Steel and aluminium industry	work rolls
	feed rolls
Textile and carbon processing industry	filament guiding parts, special work pieces
Plastic industry	coating of injection moulding tools
	coating for extrusion tools
Oil, petroleum, chemicals industry	interior and exterior coating of highly strained parts
	interior coating of transport pipes

3.2 Decorative chrome plating

The following Table 3.2 shows an aggregation of the sectors and main product categories as described in the applications for authorisation. A detailed list can be found in the appendix.

Tab. 3.2 Sectors and main product categories of decorative chrome plating

Sector	Main product categories
Automotive Sector	interior: brand labels, ornaments, gear lever knobs, trim strips, decorative frames, rear-view mirrors, door openers exterior: brand labels, ornaments, trim strips, rims, front skirts, rear-view mirrors, radiator grills, door openers
Cosmetic Sector	perfume caps, lipstick caps, jar caps, nail files, nail scissors, shavers
Furniture construction	chairs, kitchen furniture interior
General Engineering	precision parts & electrotechnical parts, microscopes, laser optics, mechanical engineering parts, military applications, solar & photo cells, antennas
Store construction	clothes rails, shelves, racks for shops
White Goods Sector/ kitchen	washing machine door frames, interior parts in fridges, display frames, knobs, oven shelves, coffee machine parts
Sanitary Sector	bathroom taps, shower heads, towel rails, hoses, soap dishes, mirror frames

3.3 Etching of plastic substrates

Relevant sectors and main product categories are mostly the same as in section 3.2, but of course only plastic products are concerned. A detailed list can be found in the appendix.

3.4 Economic relevance and value chain of the chrome plating industries

Galvano and surface technologies have a very broad application range and are used for products in nearly all industrial branches. Operating characteristics, service life and customer perception of products are largely determined by the performance and properties of surfaces. Furthermore, surface technology shapes the appearance of a variety of everyday objects.

According to the Federal Statistical Office of Germany, a total of 965 companies with more than 20 employees were registered in the sector "surface finishing and heat treatment" in Germany. The nearly 60,000 employees in this sector generated sales of around 8.3 billion euros in 2017. The branch is highly fragmented and dominated by small and medium-sized enterprises (SMEs). According to the branch’s inter-trade organisation ZVO (Zentralverband Oberflächentechnik) electroplating is the largest segment within surface finishing with about 30 percent of total industry sales. It is stated that the value share of galvanic surfaces would be 5 to 15 percent - measured by the total value of the final product. The value added of surface finishing at the customer companies is assessed to be more than 20 percent (ZVO, 2019).

Chrome plating is of significant importance for the electroplating market. For example, in North America the chrome plating industry holds an estimated 40 percent share of the overall automotive electroplating market. North America is assessed as the largest market for the chrome plating industry with a share of 32 percent of overall revenues of the electroplating industry. Europe is the second-largest market, accounting for 27.5 percent of revenues (GRAND VIEW SEARCH 2018).

Figure 3.1 shows a simplified depiction of the value chain of chrome plating.

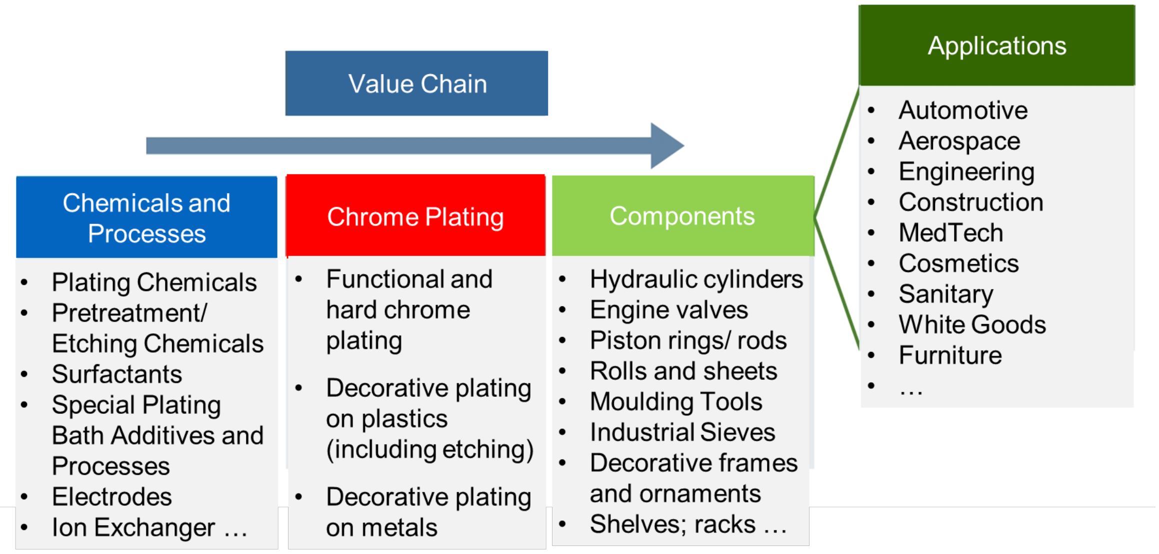

Fig. 3.1 Value chain of chrome plating industry

Within the value chain the chrome plating industry often acts as a job coater between component manufacturers and OEMs on one hand and chemicals and process suppliers on the other. However, some component manufacturers are running inhouse electroplating process lines. While conventional chromium (VI) processes mainly use standard chemicals, the know-how of chemicals and process suppliers in the conversion to chromium (III) electrolytes is gaining in importance due to the need for special additives and more complex processes.

Some figures depicting the economic relevance of the chrome plating industries are summarised in Table 3.3. They can help to roughly estimate the economic importance of electroplating industry. As can be derived from the assessments of (Interview 29) trivalent chromium-based finishes already have a significant market share in the decorative finishing segment, while functional hard chrome plating currently is based only on hexavalent chromium processes.

Tab. 3.3 Figures for assessments of market value of electroplating and chrome plating chemicals and services

Market (region)	**Market value (year)**	**Source**
Chrome plating chemicals (Germany)	Decorative chrome plating • Cr(VI): 1-2 m € (2018) • Cr(III): 1-2 m € (2018) Hard chrome plating • Cr(VI): 5-10 m € (2018)	Interview 29
Metal finishing chemicals (world, forecast)	15.3 bn $ (2024)	Global Industry Analysts (2019a)
Electroplating Services (Germany)	2.5 bn € (2017)	ZVO (2019)
Electroplating Services (world, forecast)	17.4 bn $ (2024)	Global Industry Analysts (2019b)
Cr(III) finishing market (world)	255 m $ (2016) (83 % thereof plating)	Global Industry Analysts (2017)

3.5 Detailed description of alternatives

In the following sections potential alternatives are listed based on the analyses of alternatives from applications for authorisation. Subsequently, selected applications are described in more detail, which have been assessed in practice based on literature research and expert interviews. For better readability these sections are structured uniformly:

1. Process Overview
2. Technical Requirements
3. Design Requirements
4. Legal and normative requirements
5. Economic and Cost Issues
6. Risk Characterisation
7. Additional findings (if available)
8. Conclusion

Due to the short timeframe of this project in conjunction with the diversity of chrome coating applications and their sometimes highly specialised requirements this description cannot be considered as exhaustive.

4 Potential alternatives for chromium trioxide based functional chrome plating

4.1 Overview

Using chromium trioxide in functional chrome plating has multiple positive effects based on the characteristics of the coating deposited from chromium trioxide. Key functionalities of coatings, produced by chromium trioxide-based electroplating, especially are good corrosion resistance and excellent wear and abrasion properties combined with hardness, shape retention and very low adhesion. Therefore, functional chrome plating with chromium trioxide has been used for a wide range of applications for more than 50 years.

It is very difficult to find a single alternative, neither a substance nor a technology, which replaces the multi-functionality of chromium trioxide generated coatings simultaneously. Until today no one-to-one replacement to chromium trioxide, which meets all the requirements and is economically feasible, has been discovered. In other words: there is no drop-in alternative so far.

Section 4.10 gives a non-exhaustive list of applications where no potential alternatives could be identified. But for individual applications competitive options have been developed. Classic complementary technologies such as thermal spraying and laser cladding have been used as alternative technologies not only in small niches, but in more and more applications. Also, there are vacuum technologies like PVD or DLC (Diamond-Like Carbon) in the market, which can compete with hard chrome in certain areas. Functional chrome plating with a chromium (III) electrolyte is also possible for some materials. The latter achieves resistant chromium layers, but has considerable disadvantages compared to the use of chromium trioxide due to additional manufacturing steps and additional heat treatment.

The following Table 4.1 gives an overview of potential alternatives as were analysed in the AoA documents. They can be categorised as follows:

I. Alternative galvanic processes
II. Vacuum processes
III. Spraying processes
IV. Case hardening processes
V. Laser and discharge processes
VI. Others

The order implies no ranking. Alternatives that are considered as “most promising” (Category I) in the AoA are indicated by leading and trailing asterisks. A detailed list with attribution to the respective application can be found in the appendix.

Tab. 4.1 Potential alternatives for functional chrome plating

Identification in AoA	Description
ALTERNATIVE GALVANIC PROCESSES	
Black nickel electroless plating	Chemical deposition of Ni from NiP electrolytes in combination with an oxidising acid solution

Identification in AoA	**Description**
Co-Sn plating	Galvanic deposition of Co-Sn alloy
Cr(III) based plating	Galvanic deposition of Cr from trivalent chromium compounds
Cu electroplating	Galvanic deposition of Cu
Electrolytic black zinc nickel	Galvanic deposition of Zn/Ni alloys
Galvanic Coating Process	Coating with alternative material (blanked out in AoA)
High phosphorus electroless nickel	Deposition of a nickel–phosphorus composite coating from aqueous solutions onto a substrate without the use of electric current. Typical composition of the high phosphorus nickel coating is 87-90% Ni and 10-13% P. Also known as "Kanigen electroless nickel".
High phosphorus electroless nickel + PTFE	Same as above but with PTFE added to the plating solution enabling the polymer to be co-deposited.
Iron-phosphor coating	Conversion coating process
Nano-crystalline cobalt phosphorous alloy coating	Deposition of nano-crystalline Co-P (nCoP) alloys either with pulse electroplating process or chemically
Ni and Ni alloy coatings (Ni-B, Ni-P; Ni-W)	Electroless or electrochemical deposition of Ni or Ni alloys
XXXX Electroplating	"XXXX": blanked out in AoA
Zinc - Diffusion Process with Passivation	Details blanked out in AoA
Zinc-based materials (zinc, zinc-tin, zinc-aluminium, zinc-nickel based passivation, non-electrolytic zinc plating)	Diverse Zn or Zn alloy coatings
VACUUM PROCESSES	
Chemical vapour deposition (CVD)	Range of deposition methods, typically under vacuum, where the substrate is exposed to one or more volatile precursors which react on the surface and produce the desired deposit. Coatings can be polysilicon, SiO_2, Si_3N_4, metals, graphene, diamond
Physical vapour deposition (PVD)	Variety of vacuum processes starting with the coating material in a solid (or rarely in a liquid) form placed in a vacuum or low-pressure plasma environment. The coating material is vaporised and deposited, atom by atom, onto the surface of the substrate in order to build up a thin film. PVD coating materials are e.g.: titanium nitride (TiN), titanium-aluminium nitride (TiAlN), zirconium nitride (ZrN), chromium nitride (CrN), chromium carbide (CrC), silicon carbide (SiC), titanium carbide (TiC), and tungsten carbide (WC).

Identification in AoA	**Description**
Diamond Like Carbon (DLC) coatings	PVD (see above) coating of combined bond types of graphite and diamond. DLC forms an amorphous diamond-like carbon layer, with hardness properties > 2,000 HV.
SPRAYING PROCESSES	
Atmospheric Plasma Spraying - MCrAlY // Refractory oxides	Thermal spray process
High velocity thermal process	Coating powder is injected into a flame that accelerates the powder particles to high velocity (usually sub-sonic). The heat of the flame melts the high-speed powder particles, which hit the substrate and flatten in pancake-shaped “splats”. As they overlay each other, these splats form a coherent and low porosity coating. Included are HVOF and the Detonation gun (D-gun) and Super D-gun processes. Possible powder materials include pure metals (Cu, Al, Zn, Ni, Mo, W, ...), alloys (NiCr, NiAl, NiMoAl, NiCrSiB, CoCrMo, Inconel (trademark of certain NiCr alloys), Stellite (CoCr alloys), carbides (WC-Co, WC-CoCr, WC, Co-Cr, Cr_3C_2-NiCr, ...)
Wire flame spraying	Coating material in form of a wire, which is fed continuously into an oxygen-acetylene flame. The melt is removed from the tip of the wire as a droplet by atomising gas and shot onto the substrate.
Plasma spraying	Thermal spray process which uses highly energetic plasma as a heat source with possible powder materials similar to HVOF (pure metals, alloys, and carbides).
CASE HARDENING PROCESSES	
Carburising, Carbonitriding, Cyaniding, Nitriding, Nitrocarburising, Boronising	N, N and C or B are diffused into ferrous metal surfaces, either in salt baths, gas phase or plasma-assisted
LASER AND DISCHARGE PROCESSES	
General laser and weld coating technology	summarises the following processes: Laser alloying, Laser cladding electrospark deposition (ESD)/ electrospark alloying, Explosive cladding
Alternative texturing methods	Comprise different technical approaches, such as Electrical Discharge Texturing (EDT), Electrical Discharge Coating (EDC, with e.g. TiC or WC), laser texturing (LT), electro-beam texturing (EBT) or shot-blast texturing (SBT).
OTHERS	
Change of base material (stainless steel)	self-explanatory
Chemical Coating Process	details blanked out in AoA

Identification in AoA	Description
Forged steel work roll grades (without Cr coating)	self-explanatory
Ion Implantation	Ions of one element are accelerated into a solid target, thereby changing the physical, chemical, or electrical properties of the target. Applied in tool steel toughening and surface finishing e.g. for prosthetic devices
Lubricant Varnish Coating Process	Coating with solid lubricants such as MoS_2 or graphite
Plain valves	No Coating
Plastic coating	Powder coating deposited by dipping or spraying. Polymers are PTFE or solid lubricants
Sol-Gel Process	Colloidal solutions ("sol") evolve towards gel-like diphasic systems containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks.
Synthetic Material-Teflon-Coating Process	PTFE based coating process

It was possible to conduct expert interviews with regard to at least one “Category I” process in each of the groups[1] described above, but not every single “Category I” alternative was covered.

Processes/technologies on which no expert interviews were conducted are:

Ni and Ni alloy coatings,
Nano-crystalline cobalt phosphorous alloy coating,
Chemical vapour deposition and
Plasma spraying.

Although each of these were described in at least one AoA as a promising alternative, none of them were explicitly mentioned by any of the interview partners.

Major disadvantages of these technologies as described in the AoA are briefly delineated as follows:

- Ni and Ni alloy coatings (diverse branches)
  - Insufficient hardness requires additional heat treatment, which is not feasible for certain parts.
  - For some applications layer thickness is too low.
  - Coefficient of friction is too high.
  - High sensitivity to process fluctuations affects the layer quality and adhesion which leads to a reduced reliability.
- Nano-crystalline cobalt phosphorous alloy coating (diverse branches)
  - Insufficient hardness
  - For some application: insufficient wear resistance and anti-adhesion properties
  - Process relies on cobalt dichloride (Acute Tox. 4, Skin Sens. 1, Resp. Sens. 1, Muta. 2, Carc. 1B, Repr. 1B, Aq. Acute 1, Aq. Chronic 1). Some cobalt compounds are in the candidate list as SVHC.
  - Technical readiness level too low.

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[1] Except for group “Others“ which included no “Category I” alternative.

- Chemical vapour deposition (CVD)
    - Does not enable a continuous process but is limited to a batch production process and therefore low production volumes
    - Process temperature too high.
    - Slow deposition rates of the DLC layer (approximately 150 µm/h for CVD compared to 900 µm/h for functional chrome plating), leading to even higher cycle times
    - Investment and running cost lead to an estimated cost per part factor which is 70 times higher compared to functional chrome plating using chromium trioxide.
- Plasma spraying
    - Insufficient corrosion resistance
    - Not feasible for complex geometries and small parts
    - Produces porous coatings, which can lead to an increased susceptibility to corrosion
    - Process temperature is too high for most parts.

4.2 Laser cladding (extreme high-speed laser material deposition)

4.2.1 Process overview

Extreme high-speed laser material deposition (EHLA) is a special variant of laser cladding, which has been developed by Fraunhofer Institute for Laser Technology (Fraunhofer ILT) in Aachen, Germany [2]. The process has been in industrial use since 2017 (Interview 14). Therefore, the EHLA process is not mentioned in the analyses of alternatives of the applications for authorisation for chromium trioxide-based plating. Conventional laser cladding produces a molten bath on the substrate surface by laser radiation and a filler material is then deposited as a wire or as a powder into the molten bath. In the EHLA process the powder is melted before it hits the component. This allows for thinner layers and a higher feed rate.

EHLA is characterised by elevated welding speeds of 20 to more than 200 m/min, which is by a factor of 10 to 100 faster compared to conventional laser cladding. In addition, the energy of the laser beam is coupled primarily into the powder on its way to the substrate. Most important is a fine powder focus and a longer interaction time on the particles' trajectories through the laser beam. Therefore, heat input into the substrate can be reduced resulting in layers with a small dilution zone, as well as a small heat affected zone between layer and substrate and consequently low distortion of the coated component.

By relative movement of the heat source and the substrate a molten metallurgically bonded, dense pore and crack-free layer is produced. Resulting layers have a certain roughness and must be post-processed mechanically. A variety of metals and alloys may be used as coating materials e.g. iron-, nickel- or cobalt-based alloys, depending on the required performance and properties of the coating.

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[2] A video describing the process can be found here: https://www.youtube.com/watch?v=V8H_XjDqXKA

While conventional laser cladding uses grain sizes of 45 – 90 µm, the EHLA process uses finer grain sizes of approximately 20 – 50 µm, similar to 3D printing. Process temperature must be above the melting temperature of the respective materials. Heat input is locally limited to a small area, so that – at least for larger components – no impairment in terms of dimensional stability is to be feared. The method can be used locally and it works continuously. Layer thickness can be adjusted by varying the rotational speed of the component to be coated. Multifunctional coatings can be produced by subsequent deposition steps with different powders. Gradient coatings can be achieved by using a combination of different powders with separately controllable powder conveying units. The process requires a local shielding gas atmosphere, which is typically assured by injecting Argon through the nozzle. Dust and fume extraction are advisable in the proximity of the process (Interview 13).

Tab. 4.2 Comparison of conventional laser cladding with EHLA process (CANDELA-RUIZ 2019)

Parameter	**Conventional Laser Cladding**	**Extreme high-speed laser deposition welding (EHLA)**	**Factor**
Feed speed	0,5 – 2 m/min	> 100 m/min	50
Deposition rate	50 cm²/min (locally) 100 cm²/min (surface)	Up to 1000 cm²/min	10-20
Heat impact zone	> 500 – 1000 µm	5-10 µm	100
Coating thickness	> 500 µm	10 – 250 µm	50
Surface roughness	100 – 200 µm	10 – 20 µm	10

The EHLA process is applied for mechanical components with increased requirements in terms of wear and corrosion protection. The process is not a one-to-one replacement for chromium trioxide-based coatings, but serves as an alternative for applications where special property profiles are required (FRAUNHOFER-ILT 2017).

The method is used successfully on hydraulic cylinders in the off-shore sector (for example for dredging vessels). These types of hydraulic cylinders conventionally are typically coated by thermal spraying either with ceramic layers or Ni/Cr layer systems as the corrosion protection of hard chrome plating is often not sufficient. In addition, due to the trend towards ever longer and thinner design, hydraulic cylinders are subject to mechanical deformations resulting in special demands on the adhesive strength of the coatings. In case of hard chrome coatings, bending of the piston rod damages the layer structure. As nickel is much tougher than chromium, tensions at nickel/chromium interfaces can lead to microcracks and then corrosion (Interview 14).

In addition to this established industrial application, further applications are currently being investigated as part of R & D work in the area of general engineering, for rolls in the paper and steel industry, in the aerospace sector and in the automotive sector (brake discs in passenger cars).

To date the process is mainly implemented in bilateral research projects and there are hardly any published examples (Interview 13).

4.2.2 Technical requirements and limitations

Due to the variety of metals and alloys that can be used a broad spectrum of technical properties can be achieved (see Table 4.3, (Interviews 13, 14, 15, 16, 17).

Tab. 4.3 Summary of technical properties of the EHLA process

Property	**Evaluation**	
Corrosion resistance	By selection of the filler materials a wide range of properties can be represented. Depending on materials composition a higher corrosion and wear resistance than for chromium trioxide coatings can be achieved for example for off-shore applications.	+
Chemical resistance		
Wear resistance		
Adhesion of the coating	By fusion metallurgical bonding a higher adhesion than in chrome coatings is achieved. In standard laser deposition welding, there is a danger of crack formation (Interview 16). In a similar process this is met by inductive pre-warming (Interview 17). Because of the lower heat impact of the EHLA process, the generation of brittle metal phases can be avoided. So, the risk of crack formation is lower than for conventional laser cladding (CANDELA-RUIZ 2019).	+
Hardness	Hardness properties can be adjusted by incorporating ceramic particles in the metal matrix. However, a comparison with other methods is difficult because no mixed hardness is measurable.	✓
UV/Light resistance	Depending on used materials, for engineering applications usually not relevant.	✓
Temperature resistance	The temperature load by the laser is locally limited, with larger components, the thermal load is low.	✓
Coating thickness	Can be adjusted between 25 and several hundred µm. Layer thickness is adjustable by feed rate and the application of multiple layers.	✓
Nickel leaching	Depending on used materials, for engineering applications not relevant.	✓
Repairability	The process can be used as repair technology for worn out components.	✓
Geometry	There are constraints concerning the geometry of the components. Suitable for rotationally symmetrical components with a thickness of a few cm to 1 m. The flexibility depends on the handling technique (e.g. lathes). Due to the masses to be moved only components up to 10 m in length and 10 t in weight are suitable for the process. For planar, non-rotationally symmetric surfaces, the process is still in trial. These can be clamped on a rotary carrier. Interior coatings, especially of deeper boreholes are not feasible (Interviews 16 and 17).	–

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

4.2.3 Design requirements

There are usually no design requirements to be fulfilled for invisible parts in the engineering sector. To some extent it may be relevant, if the process is used to coat brake discs, which are partly visible. To achieve sufficient optical properties for visible parts, finishing treatment would be required.

4.2.4 Legal or normative requirements

Usually there are no special legal requirements to be fulfilled by the process. Worker protection focusses on shielding of laser radiation. Certain applications require release controls regarding the materials/powders used (e.g. food safety).

4.2.5 Economic and cost issues

The costs of the system and the process scale with the size of the plant and the materials used.

Investment costs
The system can be divided into two subsystems:

- Optical and laser components
- Peripherals (powder feeding system, handling system, housing, local shielding gas atmosphere, etc.)

The costs for the optical laser component ranges between 100,000 to 200,000 €. The peripherals consisting of the powder handling and feeding unit, the sample handling as well as other peripherals for shielding and protection varies between approx. 300,000 to 1,000,000 €. There are some providers of turnkey plants. Other companies act as integrators for various components and can make individual compilations. Investment costs are comparable to those of thermal spraying processes (Interviews 13 and 15).

Another estimate was given to be about 2.5 – 3 m € for a standard laser deposition welding plant including robotics (Interview 16).

Process costs
Depending on layer thickness, coating speed is 0.5 to 3 m² per hour. Coatings are expensive relative to the total product. However, for the application “hydraulic cylinders for off-shore components” the EHLA process can be deployed economically profitable taking into account the superior performance and durability in comparison to hard chrome plating. The EHLA process is easy to integrate, which makes logistics easier and cheaper and ensures independence from the coater (Interview 14).

Two interview partners characterised material costs of standard laser deposition welding as being "very high" (Interviews 16 and 17).

Parameters of laser power can be controlled very precisely. The handling system usually runs stable because no external forces act on the component. The powder nozzle of the powder feed is subject to wear and must be replaced at certain intervals. Powder quality may vary depending on the manufacturer. Energetically, the process is highly efficient, the yield of laser radiation is 30 to 50%.

Electricity costs are estimated to be low compared to electroplating (energy saving approx. 80% to 90%). The powder yield is about 90%, residual material is suction cleaned and can be recycled partly (Interview 13). The overall materials and energy efficiency are quite high in comparison to other procedures. System lifespan depends on the application. Maintenance of the laser is required yearly resulting in a high availability of the beam source. Cooling filters and desiccants are exchanged. Costs of the protective measures result from personal protective equipment, exhaust devices and wet scrubbers (Interview 14).

Fraunhofer ILT and RWTH Aachen University hold a patent for the EHLA process in Germany, which was not extended to Europe. Possibly a new patent is to be applied for next expansion stages. The EHLA process is used by companies on a license basis. Fraunhofer ILT runs cooperation projects with companies to implement EHLA for industrial processes, after implemented EHLA already several times in the industry for different applications (Interview 13).

According to a recent publication three plants have been sold to a Chinese company for the coating of offshore hydraulic cylinders (5 m long, 1.5 m diameter). The authors state that China plans to regulate Chromium VI following European standards (FECHT & ITASSE 2018).

For customers, there are usually no fundamental acceptance problems. Most companies are familiar with the application of powders and lasers. Where EHLA gets into play often there is no working alternative available. No specially qualified staff is required for the process. Skilled workers can be trained to handle the process.

The establishment of a process line from order to production would take about six months. New coating solutions may require additional recertification processes by the customer. Qualification and sampling could be carried out in application centres of system providers as well as Fraunhofer ILT (Interviews 13 and 15).

4.2.6 Risk characterisation

Radiation protection (laser) and dust generation during powder handling and surface finishing (grinding) are the main issues regarding occupational safety and health. Laser protection walls (about 2,5 m high) and goggles are used. Welding specialists who operate the systems also wear respiratory protective masks, possibly with overpressure, overalls and gloves. Only a few workers have access to the system, which is dust and vapour extracted and works computer-controlled. The process is monitored by sight windows or cameras. Aerosol measurements show higher concentrations during post-processing by grinding than during the coating process. After welding all residual powder is removed from the component. Personal protective measures have to be applied as well (Interview 14).

The process uses no chemicals or solvents other than the applied metal alloys. However, the resulting welding fumes, which contain inhalable dusts and toxic substances, must be taken into account. The composition of the welding fume corresponds approximately to the chemical components of the filler material. For nickel-based alloys, which contain more than ten percent cobalt at the same time – depending on their respective content in the welding fume – nickel oxide or cobalt oxide are considered to be the leading components in welding fumes. With chromium-containing alloys, the formation of hexavalent chromium compounds cannot be excluded (ARBEITSSCHUTZ SCHWEIßEN 2019). It is therefore state of the art to siphon off the produced welding fume close to the process or close to the release point of the emission. Compared to other deposition welding processes, EHLA produces significantly fewer welding fumes based on optical assessment. Compared to laser welding processes for cutting or joining, significantly lower beam intensities are used (Interview 13).

4.2.7 Conclusions

The EHLA process has become a competitive and environmental friendly alternative in the field of wear and corrosion protection coatings for special applications in recent years. EHLA cannot be regarded as a one-to-one replacement for chromium trioxide-based coatings, but serves as an alternative for applications where special property profiles are required. The process is restricted to rotational symmetric components.

Since 2017 EHLA has been in industrial use in the field of hydraulic cylinders for offshore applications, where hard chrome coatings are not a viable alternative. The strengths of the process are highly adhesive coatings through a metallurgical bond to the base material as well as optimised wear and corrosion protection through dense coatings as well as targeted selection of the coating alloys. Just like conventional laser cladding EHLA can be used as repair technology for worn out components. The process extends the application possibilities of laser cladding to large parts with small layer thicknesses. An advantage is the integrability in production lines due to the relatively low space requirements. Investment costs are comparable to those of thermal spraying. From a health and safety point of view, a big benefit is, that no processing chemicals or solvents are used. Only the coating material is applied as powder and is physically treated by laser radiation. Protection measures are comparable to conventional laser cladding, whereby the powders used are somewhat finer-grained (grain sizes of approximately 20 – 50 µm instead of 45 – 90 µm for conventional cladding). The reworking effort is lower due to the precisely controllable layer thickness. Currently, the process is being investigated for other applications in which rotationally symmetric components with high wear/corrosion protection requirements have to be protected by thin protective layers e.g. for paper or printing rolls, possibly also brake discs in the car.

4.3 Salt bath nitriding

Nitriding is one of a large variety of techniques summarised as case hardening. Case hardening is a well-known method for hardening steel surfaces and there exists a great variety of processes like boronising, carburising, carbonitriding, cyaniding, nitriding and nitrocarburising. Especially the diverse nitriding and nitrocarburising processes are discussed as potential alternatives for certain hard chrome plating use cases.

There are three major variants of the process:

- salt bath nitriding/nitrocarburising with nitrogen/carbon coming from a mixture of cyanide or cyanate salts in NaCl (T = 550-590°C)
- gas nitriding/nitrocarburising where NH_3/CO/CO_2 serve as N/C source (T = 500-550°C)
- plasma nitriding with a mixture of nitrogen and hydrogen (T = 420-500°C)

The following description was given by a hardening company using salt bath nitriding (Interview 23).

4.3.1 Process overview

Salt bath nitriding is a heat-treating process that diffuses nitrogen into the surface of a ferrous metal to create a case-hardened surface. Salt bath nitriding is performed in baths of molten cyanide salts at temperatures of about 570°C. A slight additional carburisation occurs due to the carbon content of the cyanide bath. In comparison to gas nitriding the process is much faster, because of the high surface activity of the salt bath and because of faster heating: in one to two hours a surface hardening depth of 0.5 mm is produced as compared to about 50 hours with gas phase nitriding. Strength reduction of a case-hardened part is much lower as compared to gas phase nitriding (Bargel, Schulze 2018, pp.226–227).

The processes have been marketable for many years. Products are e.g. piston rods, engine valves (non-automotive), hydraulic manifolds.

4.3.2 Technical Requirements and Limitations

Due to the variety of metals and alloys that can be used a broad spectrum of technical properties can be achieved.

Tab. 4.4 Summary of technical properties of salt bath nitriding process

Property	Evaluation	
Corrosion resistance	500 h salt spray test	✓
Hardness	depending on substrate 1,500–1,600 HV	+
Temperature resistance	< 500 °C	–
Coating thickness	depending on substrate	0
Process temperature	30K lower than final tempering temperature (in case of tempered parts)	–
Base material	Iron	–
Surface roughness	RA or RZ values can be specified	0
Others	no bulk parts	–

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

4.3.3 Legal or normative requirements

Parts, which are case hardened by salt bath nitriding are actually used in the food sector e.g. for stirring units in bakeries. Therefore, food law compliance was assumed by the interview partner.

4.3.4 Design requirements

Due to the functional nature of the surfaces, appearance is of lower importance, but blotchiness is an indicator of processing errors.
Matte black colours can be achieved if need arises (e.g. weapons industry).

4.3.5 Risk characterisation

Gas as well as plasma nitriding are closed system processes while salt bath nitriding is performed in open systems.
Exposure is possible in form of skin contact (sputtering) as well as inhalation, and there are physico-chemical hazards as well (fire, explosion, gases under pressure).
In case of salt bath nitriding during one shift one worker is responsible for the ovens where he spends three to ten times (in sum between 45 to 180 minutes) at the salt bath, which is ventilated/exhausted.
The fact that cyanide salts are used is a critical aspect of this process, but there are also alternative baths with less toxic cyanates in use.

4.3.6 Economic and cost issues

Process quality could not be compared to chrome plating, but it was stated that salt bath nitriding has a higher scrap rate than gas/plasma nitriding.

Energy costs are estimated to be higher.

Costs for OSH measures are comparable to chromium trioxide chrome plating (personal protection, exhaust system) but waste management is supposed to be more expensive. Interviewee indicated that about 15 tonnes waste salt has to be disposed of as toxic waste with annual costs of about 50,000 €.

While in some AoA it was stated that nitriding does not allow for repair, interviewee contradicted in parts stating that repairability can be achieved if stacking is done beforehand.

4.3.7 Conclusions

Salt bath nitriding is a long-established process which can be (and essentially is already) an alternative to functional chrome plating for some special applications. It is of course restricted to ferrous base materials, which are nitrable.

As main obstacle for an implementation the interviewed user sees the lacking know-how as the process differs in many aspects and is based on a different technology. In addition, the use of molten cyanides in open system has to be taken into account when evaluating this alternative.

4.4 Salt bath nitrocarburising

Salt bath nitrocarburising is another case hardening process. The following description is mainly based on an interview with a supplier and user of this technology (Interview 26).

4.4.1 Process overview

An automated salt bath nitrocarburising process consists of the following steps. After degreasing and cleaning parts are preheated and then put into the salt bath. Thereafter an optional oxidising step can be applied in order to increase corrosion resistance. Finally, parts are rinsed and cleaned.

Optionally they can receive a mechanical finishing and/or be impregnated with oil. Chemicals for the nitrocarburising step are alkaline cyanate and alkaline carbonate, which are periodically regenerated with amino compounds. In the optional oxidation step the parts are treated with a mix of alkaline hydroxide, alkaline carbonate & alkaline nitrate. The nitrocarburising process takes between 15 min to 10 h, with standard time at 1 or 2 h.

Branches where nitrocarburising processes are applied are automotive, industrial vehicles, construction equipment, handling, aeronautic, railway, general engineering, firearms, household appliance, material transformation, energy. Regarding products examples from automotive were named: brake system, differential component, engine, gas spring, gearbox, shock absorber, wiper system, turbocharging.

4.4.2 Technical Requirements and Limitations

Tab. 4.5 Summary of technical properties of nitriding process

Property	**Evaluation**	
Corrosion resistance	Up to 600h in NSST (ISO 9227). Potentially more depending application.	+
Chemical resistance	Similar to hard chrome	✓
Abrasion resistance		
Adhesion of coating	Optimal not a coating but a material modification	+
Hardness	Depending on the substrate: Low carbon steel approx. 550 HV High alloyed steel approx. 1,200 HV	0
Temperature resistance	Up to process temperature, therefore ~ 570 °C	–
Layer thickness	depending on process and substrate: 1 to ~30 µm	–
Base material	Ferrous materials	–
Geometry	Max. ⌀1,000 x 3,000 mm, suitable for complex or small geometries	✓
Process temperature	480 – 630°C, standard temperature ~570 – 590°C	–

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

4.4.3 Legal or normative requirements

Legal requirements regarding e.g. food or medical applications have not been tested, but regarding OEM norms the process is recorded on IMDS database.

4.4.4 Design requirements

There are no special design requirements. The surfaces are of homogenous grey or black appearance.

4.4.5 Risk characterisation

Salt bath nitrocarburising is an open system process. Chemicals used are sodium cyanate (CAS No. 917-61-3, Acute Tox. 4/H302, Aquatic chronic 3/H412) and potassium carbonate (CAS No. 584-08-7, Eye irrit. 2/H319, Skin irrit. 2/H315, STOT SE 3/H335). Substances are handled in powder form (approx. 50 to 500 µm) or as pellets. Exposure risks results from handling the solids, but especially from the molten salt bath. In general, there is one worker per production shift, but the process is automated. The operator is present in front of the bath at approximately 25 % of working time. Direct contact with chemical components is less than 1 hour per shift.
Due to the high temperatures specific protection are needed for operators in vicinity of bath area.

4.4.6 Economic and cost issues

An overview of some cost aspects is given in Table 4.6. Percentages are listed in regard to overall production costs.

Tab. 4.6 Overview of costs for salt bath nitrocarburising

Cost type	Values
Overall production costs	0.40 to 1.0 €/kg
Performance/ process time	500 – 1,500 kg/h
Process quality/% waste/scrap	negligible (main risk lies in part handling)
Material cost	20 – 40 %
Labour cost	15 – 25 % excluding loading and unloading of the parts
Energy cost	10 – 20 %
Quality control cost	< 5 %
Investment cost	10 – 20 %
Waste management cost	5 – 10 % (including recycling operations)

Costs for protective measures resulting from personal protective equipment (glasses, safety shoes, operating clothes) are seen as negligible.

Use related data were described in comparison to hard chrome coating as follows. Service life is usually equivalent or better (no peeling/flaking during assembling or running). Maintenance rate is seen as equal. Regarding repairability two options are described – either direct reprocessing or pre-treatment (brazing and machining to correct dimensions) before reprocessing.

Salt bath nitrocarburising has widely spread market availability and is seen as competitive both to gas nitriding and to hard chrome coating. The described solution is patented and has to be licensed.

There are several implementation issues. A new production line has to be established, as it is not possible to upgrade a hard chrome process. On the other hand, the spatial requirements of the process are in general lower. A line for an average performance of 1,000 kg/h needs 300 m^2 per 6 m height.

Regarding waste management there are current research activities to improve material recycling.

4.4.7 Additional findings

One interview partner from a galvanising company (Interview 8) reported the following feedback from his customers regarding nitriding/nitrocarburising:

- Case hardening processes are not applicable for guns.
- The processes require special steels, which are more expensive.
- For hydraulic components even with additional oxidation the necessary corrosion resistance is not met.

4.4.8 Conclusions

Salt bath nitrocarburising is a long-established process which can be (and essentially is already) a technically and economically feasible alternative to functional chrome plating for some applications. It was described that e.g. for engine valves, the distribution is 65% hard chrome, 35% nitriding/nitrocarburising.

While it was stated that with additional oxidisation high corrosion resistance is achievable there are applications where this is not sufficient.

However, it is restricted to base materials where this kind of surface treatment is chemically possible. Even if changes of base material are a technical option this may lead to higher costs.

4.5 Plasma nitriding

Plasma nitriding is a third case hardening process. The following description is mainly based on an interview with a supplier and user of this technology (Interview 24).

4.5.1 Process overview

The special process was designed as a hard chrome alternative for forming tools. It is part of an integrated service chain from logistics, pre-treatment (cleaning, paint removal, laser hardening, micro polishing), plasma nitriding, post-treatment (polishing and varnishing if wanted). During pre-treatment the tools are processed (e.g. closing of borehole, manual micropolishing for reducing roughness peaks).

In the following plasma nitriding step a mixture of nitrogen and hydrogen gas is ionised in a vacuum. At a processing temperature of 530°C nitrogen diffuses into the substrate and creates the wear protection.

For smaller parts and so-called tailored blanks (parts consisting of different materials and sheet thicknesses e.g. a vehicle door) sometimes plasma nitriding is combined with a PVD treatment. In this case the cast segment is plasma nitrides while the hardened steel part is coated by PVD. Plasma nitriding in this case takes about two days due to slow heating and cooling down phases. This slow temperature changes of 25 to 30°C per hour avoids the build-up of material tension. The structure of the cast material is not changed.

The company is trying to establish the process in other branches (e.g. kitchen sinks, fertiliser spreaders in agriculture, large pinions in general engineering, large cranks or large components for freezers).

4.5.2 Technical Requirements and Limitations

Tab. 4.7 Summary of technical properties of plasma nitriding

Property	**Evaluation**	
Corrosion resistance	Not relevant as tools are working in a small oil film (minimal lubrication) and there is no corrosive atmosphere.	0
Chemical resistance	Not relevant	0
Wear resistance	In this application most important: protection against abrasive wear (four times higher than hard chrome coating).	+
Adhesion of coating	Not relevant: no coating but surface modification.	0
Hardness	Base material about 30 HRC Diffusion zone: 55 – 60 HRC Compound layer: up to 1,100 HV (like hard chrome)	0
UV-/Light resistance	Not relevant	0
Temperature resistance	Not relevant (low temperature at cold working)	0
Layer thickness	Thickness of compound layer: 8 – 15 µm Compound layer is more homogenous than hard chrome layer.	–
Geometry	No restriction, dimensionally stable because of very slow heating and cooling	✓
Materials	All nitrable materials can be hardened; but proportion of ferrite must be low. The higher the ferrite proportion the slower the nitriding process.	–

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

In the past the company has also offered hard chrome coating, which was provided by a contractor but some customers complained about yellow efflorescence of hexavalent chromium in pores, cavities and cracks of the cast material. Pictures of this effect have been shown to the interviewer.

4.5.3 Legal or normative requirements

There are no specific legal requirements. OEM requirements are met.

4.5.4 Design requirements

There are no relevant aesthetic requirements.

4.5.5 Risk characterisation

As it is a closed vacuum process there is no exposure during the processing.

4.5.6 Economic and cost issues

An overview of some cost aspects is given in Table 4.8.

Tab. 4.8 Overview on economic and cost issues of plasma nitriding

Cost type	Values (relative to hard chrome coating)
Overall production costs	Overall in Europe slightly higher, in Asia lower
Performance/ process time	Depends on cast quality; necessity of paint stripping and re-varnishing is also a relevant factor; process time in general is one day more than for hard chrome coating
Process quality/% waste/scrap	No scrap
Labour cost	plasma nitriding requires costlier manual polishing
Energy cost	Slightly higher or equal
Quality control cost	< 5 %
Investment cost	Similar (comparison of new lines)

A detailed cost comparison has been made by the interview partner for seventeen sets of tools (all hull parts for a five-door car). Costs for plasma nitriding were 450,000 € and therefore 150,000 € higher than hard chrome plating, but tools with hard chrome coatings do last for only 200,000 to 250,000 parts. This means that – depending on production volume – once or twice a year re-chroming is necessary. Wear resistance of plasma nitriding on the other hand is higher, lasting either permanently or for about five years (about 1 million parts), thus leading to lower lifecycle costs. In a span of five years hard chrome plating leads to costs of about 3 m Euros as compared to 450,000 € for plasma-nitriding. Additionally, for single-tool moulds costs for downtimes must be calculated several times in case of hard chrome coatings. Furthermore, post-processing of hard chrome coated moulds is more costly, because of layer irregularities at the radii, esp. at so-called pull rods where small cusps can be formed.

4.5.7 Additional findings

Plasma nitriding can also be used in combination with DLC coatings, which can significantly improve the corrosion resistance and enables water and oil repellent surfaces (Interview 27).

4.5.8 Conclusion

The described process is applied to diecast single-tool thermoforming moulds for car body parts (hoods, doors, fenders). Part sizes are up to 10 m length. The process is technically and economically viable, but at least until today only feasible for a special application. Exposure is negligible for this vacuum process.

One interview partner from a galvanising company (Interview 8) reported the following feedback from his customers regarding nitriding/nitrocarburising:

- Case hardening processes are not applicable for guns.
- The processes require special types of steel, which are more expensive.
- For hydraulic components even with additional oxidation the necessary corrosion resistance is not met.

4.6 Thermal spraying (HVOF)

Thermal spraying describes coating techniques where melted materials are sprayed onto a surface. While there are many variations which are subsumed under the term "thermal spraying" the following description focuses on high velocity oxy fuel (HVOF), which has been named in several AoA as a potential alternative to hard chrome coating.

4.6.1 Process overview

In the HVOF process the part to be coated is rotated while the spray gun moves back and forth along the rotation axis. Coating powder material is injected into a high-velocity flame, which accelerates the powder to sub-sonic speed and melts the particles. The coating material hits the rotating surface of the base material and forms overlaying batches. As a result of the rotating part and the axillary motion of the spray gun a coherent coating with low porosity is created. Combustion fuels are e.g. hydrogen, propylene, acetylene, propane or kerosene. There is a range of coating materials like metals (Cu, Al, Zn, Ni, Mo, W), alloys (NiCr, NiAl, NiMoAl, NiCrSiB, CoCrMo) or carbides (WC-Co, WC-CoCr, WC).

In the following the process is detailed as carried out at a manufacturer of aerospace landing gear (Interview 20). The process is applied on low-alloyed high-tensile steel aviation shock absorbers in individual and small series production (overall about 95% of all parts are still hard chrome coated). It basically consists of three steps. First the parts have to be prepared by surface wrinkling and masking. Then follows the surface treatment by HVOF. Finally, the parts are whetted to create a smooth surface. The surface is coated by a tungsten chromium cobalt carbide powder (WCCoCr 86/10/4). Kerosene serves as fuel, oxygen and hydrogen are process gases. Fuel and process gases are injected into a combustion chamber where ignition takes place. Powder is injected into the gas stream and flows through a barrel from where it is sprayed onto the surface. Jet velocity at the exit is above the speed of sound.

4.6.2 Technical Requirements and Limitations

Requirements and limitations for aviation parts

Technical requirements are set by the customers (civil or military). Standard test regulations are DO-160 by Radio Technical Commission for Aeronautics (RTCA).

Tab. 4.9 Summary of technical properties of HVOF process for aviation parts

Property	Evaluation	
Corrosion resistance	Salt spray test (RTCA DO-160) is fulfilled	✓
Wear resistance	Better than chrome	+
Hardness	Higher than chrome (but problematic for post-processing)	+
Geometry	Parts must be rotationally symmetric. Only outside machining possible (line of sight process). Internal machining heavily restricted.	–
Process temperature	Parts to be coated have a low annealing temperature. Therefore, elaborate cooling is necessary.	–

Component masking	Masking is more expensive than for chrome coating, because metal protection caps are needed, which are less precise.	–

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

Microcrack properties of chrome coatings are beneficial, because this provides good corrosion as well as wear resistance with good lubrication properties. In case of HVOF new materials had to be found, which could pose as friction partners for the carbide layer (Interview 20).

Requirements and limitations for piston rods

One interview partner (Interview 19) purchases HVOF coated piston rods (ca. 5 % of all products). He named the following technical and economical properties (Table 4.10).

Tab. 4.10 Summary of technical properties of HVOF coatings for piston rods

Property	**Evaluation**	
Corrosion resistance	Salt spray test results (DIN EN ISO 9227) are comparable to hard chrome coatings (but: different requirements for different use cases)	✓
Chemicals resistance:	No special tests but products need resistance against oils, greases, cleaners and sulphur. There is no problem here with HVOF, but if necessary, a more expensive coating (WCr) must be used.	✓
Wear resistance	At best comparable to hard chrome.	✓
Adhesion of coating	Comparable to hard chrome. In case of lower quality coatings spalling can result (but this holds for hard chrome as well). Additional melting of the coating is critical as it could lead to warpage.	✓
Hardness	Due to its very high hardness HVOF coatings can cause abrasion at the sealings. Depending on the use case HVOF coatings with lower hardness can be applied (600 bis 700 HV).	✓
UV-/Light resistance	No problems from sunlight exposure of piston rods.	✓
Temperature resistance	No problems at the relevant working temperatures of about 100 ° C.	✓
Layer thickness	Post-processing (whetting) leads to diverse layer thicknesses. Therefore, coatings must have relatively high thicknesses, which is expensive.	–
Seal compatibility	All coatings have to be tested. HVOF coatings are dust attracting, which can cause scoring and reduce service life. Hard chrome on the other hand is stain resistant.	–
Repairability	In extreme conditions (e.g. mining) repairability of HVOF coatings is better than hard chrome.	✓

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

4.6.3 Legal or normative requirements

All products in the aerospace sector need approval of the Federal Office of Civil Aeronautics, of European Union Aviation Safety Agency (EASA) and if necessary, by other authorities.

4.6.4 Design requirements

The coating is a pure functional layer. No specific design requirements.

4.6.5 Risk characterisation

The process works in a closed system, which minimise inhalation risks. Chemicals are powders and gases. Overspray remains in the cabin.

4.6.6 Economic and cost issues

Throughput is higher than chrome plating, but the process in general is more expensive:

- Spraying powder is very expensive.
- There is about 50% overspray, which cannot be reused in production.
- The process is more complex than chrome coating.
- Work costs are higher due to individual/small series production.

There were relatively high investment costs, because the HVOF coating plant was acquired in addition to an existing galvanic plant and there were expenses for testing and meeting the relevant aviation approvals.

Customer requirements for service life and maintenance are fulfilled. There are no experiences regarding repairability, because product lifetime is long (30 to 50 years). But in general, dechroming is easier than removal of a HVOF coating.

Market availability is low due to single sourcing.

Major implementation obstacles are additional space requirements and capacity building.

One interview partner (Interview 19) who purchases HVOF coated piston rods described the following economic aspects. Costs for the finished coating are about three times higher than hard chrome. Regarding service life he found that seal abrasion can be higher. Therefore, comprehensive tests are needed. The market availability is sufficient for now as only few parts are HVOF coated, but a complete substitution would require a higher number of high-quality suppliers.

4.6.7 Additional findings

One interview partner from a metal finishing company (Interview 8) stated that they are outsourcing a small part of their production where a customer requires HVOF coating of rolls. But this represents only about 5 % of their production. Especially rolls for paper mills or high-quality films production have to be hard chrome coated, because of the specific smoothness ($R_{max} \leq 0.0025$), anti-adhesive and dust-resistant properties as compared to a coating prepared by HVOF or other thermal spraying processes.

This conforms with the results of another interview (Interview 21) with a user of thermal spraying process for cylinders in the printing industry. The interview partner stressed that several types of cylinders could be sprayed, but that printing cylinders have to be hard chrome coated as even after post-processing sprayed surfaces are less smooth than chrome coatings. Fine particulate emissions are a problem, especially if chrome (chromium trioxide generation) or nickel-based powders are used. Overspray accounts for 40% of used material. Substitution of a complete galvanic line would lead to 30% higher investment costs (20 instead of 15 m €). Material costs as well as energy costs are estimated to be several times higher than for hard chrome.

4.6.8 Conclusions

HVOF or other thermal spraying processes are applicable in use cases where no smooth surfaces are needed. Higher costs are accepted in cases where hardness and wear resistance are an issue. Besides the cost factor there are geometric restrictions as only rotationally symmetric parts can be coated and interior machining is not possible.

4.7 Thermal spraying with inductive heating

This section describes a thermal spraying process where the applied coating is additionally treated by an inductive heating step, which is applied at one surface treatment company that has been interviewed (Interview 17).

4.7.1 Process overview

The parts are pre-treated mechanically by means of abrasive blasting. Then thermal spraying is conducted with an acetylene-oxygen flame and a self-flowing nickel base alloy (NiCrBSi). Afterwards the part is inductively pre-heated and the coating is fused at high temperature. Finally, the surface is finished by turning and grinding. Pre-heating takes place at about 300 °C while melting is carried out at about 1,000 °C. 1 m^2 coating takes about 160 minutes.

Treated products are piston rods mainly for mobile port cranes.

4.7.2 Technical Requirements and Limitations

The following table lists the technical properties of thermal spraying and inductive coating.

Tab. 4.11 Summary of technical properties of thermal spraying and inductive coating

Property	**Evaluation**	
Corrosion resistance	> 1000h NSST, created layer is vapour and gas proof	+
Chemical resistance	Limited by main alloy component nickel	✓
Wear resistance	Lower than chrome, but nor limiting, as nickel has better tribological properties in the specific friction paring (plastic seal)	✓
Adhesion of coating	Ca. 400 N/mm^2 (due to the micrometallurgical bond).	✓
Hardness	450 – 600 HV	–

Property	Evaluation	
Temperature resistance	Tinder resistant to about 900 °C	✓
Layer thickness	500 µm	✓
Surface roughness	$R_a < 0,2$	✓
Geometry	Parts must be rotationally symmetric. Diameter up to 1,000 mm possible. No interior coating possible. No coating of thin-walled tubes possible.	–
Process temperature	High melting temperature can lead to warpage.	–

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

4.7.3 Legal or normative requirements

There are no special legal or normative requirements.

4.7.4 Design requirements

Surface is similar to chrome but slightly gold coloured.

4.7.5 Risk characterisation

The processes work in open systems, which are ventilated. One person controls the process remotely.

Chemicals are powders (Nickel: STOT RE 1 (H372), Skin Sens. 1 (H317), Carc. 2 (H351), Nickel-Boron: Acute Tox. 4 (H302)) and gases (acetylene, oxygen). Also, the inductive field poses an electron-magnetic hazard.

4.7.6 Economic and cost issues

All estimates are given in relation to a comparable hard chrome process.

Productivity with regard to throughput is lower as additional steps are needed.

Process quality is comparable.

Material costs, labour costs, energy costs and process costs are higher.

Investment costs are similar to a galvanic line.

Environmental and safety expenditures have to be made with regard to exhaust ventilation and exhaust filters, personal protective equipment (fireproof clothings) and waste disposal of filter dusts.

Overall sales prices are about three times higher than hard chrome, but service time is significantly higher and repairability is also better. Therefore, the process is competitive to hard chrome plating as well as to “general” thermal spraying.
Major obstacle is the necessary know how for implementation.

4.7.7 Conclusion

Thermal spraying with inductive coating is relevant in use cases where on one hand thermal spraying is principally applicable and competitive (geometry etc.), but where additional requirements regarding adhesion of coating, corrosion protection, surface roughness and service time are given. While process costs are overall significantly higher this can be countered by longer product lifetime. Therefore, the process is competitive where the relevant constraints do not apply.

4.8 Physical vapour deposition

4.8.1 Process overview

Physical Vapour Deposition (PVD) is a vacuum process where a coating is physically deposited from the vapour phase. A suitable material (e.g. metals like titan, chromium aluminium) is vaporised in high vacuum at an electric arc while a reactive gas (e.g. nitrogen) flows in. A negative electrical potential is applied to the parts charged in the vacuum chamber so that the metal vapour reacts with the gas and the reaction product, e.g. metal nitride deposits on the surface. Evaporation and removal by means of impact ionisation in one process step leads to very hard, wear-resistant, corrosion-resistant and extremely uniform precise layers with high adhesive strength.

4.8.2 Technical Requirements and Limitations

Relevant technical properties have been described by a company that supplies the technology and applies it as well (Interview 32) and by a user of PVD technology (Interview 34). They are summarised in Table 4.12.

Tab. 4.12 Summary of technical properties of PVD process

Property	**Evaluation**	
Corrosion resistance	No or only reduced corrosion resistance	–
Wear resistance	Higher than chrome	+
Hardness	1,000 – 4.000 HV	+
Coefficient of friction	Lower than hard chrome coatings	–
Layer thickness	2 – 5 µm	–
Process temperature	100° – 300° C (< 250°C for 95% of applications) (Interview 32) 450 – 550°C (Interview 34)	–
Repair/reloading	High thickness coating is not possible in contrast to excess chrome plating with subsequent regrinding of worn-out parts.	–
Post-treatments	Parts geometry is closely traced therefore no post-treatments needed.	+
Geometry	Geometries with holes with small internal diameter difficult to coat, size restricted by vacuum chamber	–
	Treatment of complex geometries comparable to hard chrome process	✓

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

Due to low layer thickness and process temperature there are high requirements regarding hardness, ductility and temperature resistance of the base material (Interview 34).

4.8.3 Legal or normative requirements

By one process supplier (Interview 32) compliance with food as well as medical law requirements were named as the relevant certifications were available.

4.8.4 Design requirements

One process supplier states that multiple colours are possible – from light grey to dark black for DLC coating, and other colours for other PVD processes (brown, gold, blue, green) (Interview 32).

4.8.5 Risk characterisation

PVD is mainly a closed systems process. Exposure to chemicals is possible during the degreasing phase (where alkaline soaps are used) (Interview 32) and during maintenance (also see 5.6).

4.8.6 Economic and cost issues

Performance is described to be equivalent to hard chrome coating as the process is fully automated. The same is stated regarding process quality and scrap rate. Overall costs are described to be on average about 10 percent higher. (Interview 32)

Investment costs for a new plant are estimated to be about 20 to 30 % higher than for a chrome plating plant, but depending on the process. (Interview 32)

Costs for protective measures are generally seen as low due to the closed system process. Environmental costs with regard to emissions or waste are also seen as negligible (< 1%). (Interview 32)

Service life as compared to hard chrome plating is estimated to be higher, because of higher wear resistance. This leads to lower maintenance rates and repairability needs (Interview 32).

In general, there is a competitive market with regard to PVD plant supply (Interview 32).

Major obstacles for implementation are larger required space and missing essential knowledge for process conversion (Interview 32).

One PVD coating company (Interview 34) describes the process as economically feasible for machine parts, cutting gear, forming tools, etc. which require high wear resistance but no or only low corrosion resistance. They also state to see only minor options to replace hard chrome coatings.

4.8.7 Additional findings

One hard chrome plating company (Interview 6) comments that PVD is unsuited for their uses, because of a high heat input into the material (250°C surface temperature) and that it is not possible to produce glossy surfaces. The coating relies on a preceding hardening or on hard metals as base materials. If base materials of insufficient hardness are used, hard top coats will be pressed into the base material or even sheared off. Therefore, mainly high-quality hardened steels or expensive hard metals (WC-Co) are coated by PVD. Steel hardening as well as the subsequent vapour deposition often leads to warpage. Additional restrictions result from limited part sizes depending on vacuum chamber dimensions. Narrow and deep boreholes cannot be coated. Even if the base material is hardened for many applications, the required wear volume is lacking as a consequence of the thin top layer. For this type of wear loads, a thick hard chrome layer is advantageous, because it can have a layer thickness of millimetres – provided a suitable parts geometry. Costs are five to ten times higher. Coated parts cannot be reprocessed.

Similar statements were given by another surface treatment company especially with regard to high glossy surfaces for film production and print rolls (Interview 8):
- Wear volume with PVD is too low.
- Hardened base substrate required top layer is too thin to be self-supporting.
- Warpage can occur because of high temperatures.
- Process has high energy use and high costs.
- Process is severely size restricted.

One producer of sanitary equipment (Interview 2) stated that PVD coated sanitary parts often show edge piling and regularly fail climate cycling tests (varying temperature and humidity).

Both was confirmed by tool manufacturers (Interview 9) who explained that especially these deficiencies were problematic for the quality of their products. As additional drawbacks lacking stain resistance, low throughput, necessary investment and overall 30 – 40 % higher costs were named.

4.8.8 Conclusions

PVD with its diverse coating materials (e.g. metals or carbon as DLC) can be applied as a substitute for hard chrome coating where restrictions regarding geometry, material properties or corrosion resistance do not apply. The process is carried out economically for machine parts, cutting gear or forming tools, which require high wear resistance but no or only low corrosion resistance. However, application for sanitary products as well as high-end manual tools is seen as neither economically nor technically feasible.

4.9 Trivalent chromium based hard chrome plating

The following description is based on interviews with two solution providers for trivalent chromium-based processes, which were introduced in 2014 and 2017, respectively (Interviews 5 and 30).

4.9.1 Process overview

Basically, the two trivalent chromium-based processes as described by the interview partners are very similar. After several preparative steps (degreasing, pickling and electrocleaning) a nickel subcoat is introduced in order to achieve higher corrosion protection. Finally, the trivalent chromium-based coating is deposited. Adequate rinses between all steps are mandatory.

Although the base principles are very similar there are also some differences regarding relevant process parameters of the trivalent chrome process step (Table 4.13).

Tab. 4.13 Process parameters of two trivalent hard chrome processes

Parameter	Process 1 (Interview 30)	Process 2 (Interview 5)
Bath temperature	48 – 55°C	20 – 45°C
Plating speed	0.5 – 1 µm/min	0,6 - 2,0 µm/min
Cathodic current density	35 – 50 A/dm^2	40 – 120 A/dm2
Anodic current density	> 8 A/dm^2	No information
Chrome electrolyte	No information	$CrCl_3$
Boric acid used	No	Yes, but process without H_3BO_3 in preparation
Complexing agents	Yes	No information
Other additives	No information	conducting agent, wetting agent

According to (Interview 30) the process is applicable in the following branches: automotive, hydraulics, rotogravure. Coated products are shock absorber rods, engine valves, hydraulic rods, brake pistons, rotogravure printing cylinders.

(Interview 5) states that hydraulic cylinders, linkage pins, shock absorbers, ball valves are typical products to be coated. Additionally, in this process an inductive heat treatment (350 – 700°C) is utilized to achieve higher hardness.

The main differences of trivalent chromium processes in comparison with chromium trioxide plating are:

- Plating bath uses chromium (III) sulphate or chromium (III) chloride instead of chromium trioxide.
- Boric acid (H_3BO_3), which is included in the candidate list for authorisation, is used as a buffer in this process not just for the nickel-plating step but also for chrome plating, and in a higher concentration (80 g/l as compared to 40 g/l for nickel plating).
- There are up to two additional electrolytic passivation baths, which are not needed in a chromium trioxide bath (due to "auto-passivation").
- There is no need for a reductive flush, which is necessary in a chromium trioxide process.
- Lead anodes are not usable. MMO anodes are needed.
- Ion exchangers are needed in order to control concentrations of iron and nickel ions.
- Trivalent chromium-based coating takes longer than chromium trioxide-based coating for the same layer thickness.

- The chromium coating relies on a nickel subcoat in order to reach comparable corrosion protection.
- Additional heat treatment is necessary in order to reach comparable hardness.

4.9.2 Technical Requirements and limitations

(Interview 30) lists the following technical properties in comparison to hexavalent hard chrome coating (Table 4.14).

Tab. 4.14 Summary of technical properties of trivalent hard chrome coating process (Interview 30)

Property	**Reference (hard chrome)**	**Evaluation**	
Corrosion resistance NSS	96–240 h	>> 240 h with Nickel	+
Corrosion Resistance to chlorides	bad	very good	✓
Abrasion resistance Taber test	1.2–1.5 mg/1,000 cycles	1.6–2.1 mg/1,000 cycles	–
Adhesion	very good on steel	very good on nickel	✓
Hardness not heat treated	900 – 1,100 HV	750 – 850 HV	–
Layer thickness	10 – 300 µm	10 – 300 µm	✓

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

(Interview 5) names slightly different values (Table 4.15).

Tab. 4.15 Summary of technical properties of trivalent hard chrome coating process (Interview 5)

Property	**Evaluation**	
Corrosion resistance	1,000 h NSST (with electroless Nickel) >120h (without Nickel)	+
Chemical resistance	Acid resistance excellent	+
Abrasion resistance	Taber-wear index 1,03	+
Adhesion of coating	Heat-treated excellent, without heat good	
Hardness	1,700 – 1,800 HV0.1 (with heat treatment), 900 – 1,200 HV0.1 (without heat treatment)	+
Temperature resistance	See: heat treatment	
Layer thickness	Up to 200 µm growth rate: 0.6 – 1.2 µm/min, but slower at > 100 µm	–
Geometry	With special anodes complex geometries possible	
Process temperature	heat treatment at > 500°C; restricts some base materials.	–
Dimensional stability	Process has to be optimised on a case-by-case basis based on available data on different geometries, shapes and materials	–

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

4.9.3 Legal or normative requirements

For the mentioned products there are no special legal requirements, but OEM norms can apply.

4.9.4 Design requirements

For the mentioned products there are no special design requirements. Surface colour after coating is described by (Interview 5) as grey, matt finish, which can be polished to mirror-like finish.

4.9.5 Risk characterisation

Regarding exposure conditions the processes are comparable to hexavalent hard chrome coating, but the risk is lower due to replacement of chromium trioxide with trivalent chromium. On the other hand, nickel and – at least in one process type – boric acid (SVHC) are introduced into the process.

4.9.6 Economic and cost issues

(Interview 30) gives the following data relative to the chromium trioxide-based plating process unless stated otherwise:

Cost type	**Comparison (per part)**
Performance/processing time	Equal to hard chrome
Process quality/scrap rate	
Energy cost	
Labour cost	
Performance	
Process cost	Depends on the application and on the corrosion and wear resistance requirements
Investments	More tanks are required for pre-treatment

(Interview 5) lists similar data with regard to the plating process.

Cost type	**Comparison**
Performance/ processing time	similar
Process quality/scrap rate	cleaner process e.g. no slur removal necessary
Labour cost	similar/lower
Energy cost	lower (lower current density, less need for air filtration)
Process cost	Lower/similar
Investment cost	similar equipment as in Cr_6-plating is used
Service life	Electrolyte has been working for over 3 years at industrial scale with additions of bath components made according to instructions.
Maintenance rate	Daily tracking of bath properties (pH, conductivity, element concentrations)

Both processes are available on the market and there is sufficient delivery security. (Interview 30) declares that the process is working under industrial conditions in EU, America and Asia and that many evaluations have been made for several applications. (Interview 5) describes that the process is in use for coating hydraulic cylinders since 2014 at one manufacturer. At another plant in Europe the process is in use for three years. Several application tests are underway, amongst others coating of moulds for epoxy resin parts are tested. Major implementation obstacles in general are seen in larger required space and missing customer specifications.

4.9.7 Additional findings

One interview partner (Interview 11) had done tests in the early marketing phase of one of the processes. They made the following statements:

- Corrosion resistance was sufficient, due to nickel sub-coating.
- After heat treatment hardness was comparable to chromium trioxide-based coating (1,200 HV).
- Layer thickness is seen as a problem, because additional plating is not possible with the trivalent chromium process.
- Anti-adhesive properties were not acceptable. One of the major products (hydraulic cylinders) needs good dry run properties, which result from oil adhesion due to micro cracks of the chromium layer deposited from chromium trioxide.
- Nickel leaching is expected.
- Some branches will not accept the process either because of normative requirements, which regulate bath details (aerospace, military), legal restrictions regarding nickel leaching (food, medical industry).
- The use of boric acid as a buffer substance is seen as a problem, but it might be substituted by other weak acids (e.g. succinic or lactic acid).
- Exemplary economic assessment for a piston rod lead to the following conclusions:
    - The process takes about twice as long (even without inductive hardening)
    - Accordingly, labour costs are higher.
    - Material costs are higher.
    - trivalent chromium bath is much more sensitive to contamination (while a chromium trioxide-based bath can operate with foreign ion concentrations of up to 20 g/l Cu , trivalent chromium-based baths are restricted to concentrations below 10 µg/l Cu).
    - Bath service time is much shorter (chromium trioxide ~5 years, trivalent chromium ~3 months).
    - Process costs are higher because anodes are more expensive (e.g. iridium tantal mixed oxides on titan or niob as carrier material).
    - All chromium tanks would have to be replaced because of chromium trioxide contamination.
    - Waste water treatment will be more problematic as the complexing agent blocks trivalent chromium precipitation.

- General economic estimates were as follows:
    - Supply problems are expected for mixed metal oxide anodes.
    - Dependency from only a few suppliers is seen as a problem while the existing chromium trioxide baths can be made basically "from scratch" by the users as there are no complex chemical additives involved.
    - Implementation problems especially result from missing customer acceptance and missing OEM specifications.
- In summary the process was evaluated as not yet marketable, but the company keeps testing other suppliers.

One interview partner (Interview 12) describes his experiences with some test coatings as follows:

- Only one of five tested parts was acceptable.
- Corrosion resistance was sufficient, but only with nickel sub-coating.
- Hardness was higher than chromium trioxide-based coating (> 1,600 HV).
- Coating thickness was between 10 – 100 µm with the target value being 200 µm.
- Interior or partial coating is not possible with the trivalent process.
- Due to heat treatment (which was necessary for the intended hardness) there was unacceptable discoloration and no dimensional stability. Parts had to be polished.
- The black/dark blue colour of the coated parts is rather inacceptable.
- Production costs are expected to be five times higher.
- The existing plant cannot be used for the trivalent chromium process. Investment costs for a new plant are estimated to be about 750,000 €.
- Pre-treatment (nickel sub coating) is more elaborate than for the chromium trioxide process.
- In summary the assessment was that the process is not yet fully marketable.

4.9.8 Conclusions

As the identified trivalent chromium-based processes all rely on a nickel sub coating and at least one of them on boric acid as a buffer substance the improvement regarding exposure to chromium trioxide is associated with some relevant drawbacks.

Technical problems are seen especially in the reduced hardness as compared to the chromium trioxide-based coating, which requires additional inductive hardening. This leads to temperatures that can be detrimental for coated parts, especially if size accuracy is a relevant feature.

These disadvantages are combined with higher overall costs, especially because of higher requirements regarding bath sensitivity and therefore maintenance.

Information gained on this process are inconsistent. Interviewed companies, who tested at least one of the processes, reported not to get adequate results, while suppliers report that their processes are marketable. No regular users of at least one of the trivalent chromium based hard chrome processes could be identified and interviewed. This would be necessary in order to reach a final conclusion.

4.10 Applications with no identified alternatives

Based on the conducted interviews for some applications there are currently no alternatives for hard chrome coating available. The following examples are non-exhaustive and are only meant to provide an idea of the multi-dimensional requirements that some applications pose with regard to substitution.

Inner coating of gun barrels

This application requires simultaneously a sufficient resistance regarding mechanic, chemical and thermal stresses. Hard chrome layers protect the steel barrel which has no sufficient resistance to these stresses. Additionally, wear resistance must be high enough to withstand the erosive forces of shootings. Otherwise flight stability of bullets would be reduced over time (Interview 8, Interview 16). Another interview partner (Interview 11) named existing military standards as major obstacles for hard chrome replacement as in many cases utilisation of hexavalent chrome was mandatory.

Textured press plates for furniture and flooring industries

The production of high-quality laminate surfaces with wood like structures requires caul plates with a multitude of properties. These plates, which have dimensions of more than 20 m^2 are made from steel in a multi-step procedure (> 200 single work steps). According to one interview partner (Interview 10) until today hard chrome plating is the only option to create surfaces of the required quality. The top layer must be wear resistant and polishable at the same time. It has to preserve the underlying structures, which are both highly intricate and very fine (15 µm – 1,000 µm). In order to produce wood structure laminate surfaces that align with the underlying colourings the pressing process must be extremely accurate. The press plate has to compensate for tiny aberrations of the different layers when pressed with ~500 bars at 180°C. As in some cases the plastic layer contains corundum particles sufficient abrasive wear resistance is crucial. Plate production costs about 150,000 to 300,000 € per part. Therefore, the comparably easy repairability of chromium layers is essential.

Very large hydraulic cylinders which operate under dynamic stress

Regarding hydraulic cylinders some interview partners pointed to the fact that it has to be distinguished between cylinders that are positioned vertically and those that operate horizontally or inclined (Interviews 6 and 8). While the former do not perceive dynamic stress in the latter case dynamic forces can lead to bending or torsion. These forces can not only lead to deformations but to spalling or flaking if the adhesion of the layer is too weak. Therefore, in use cases like these only hard chrome coatings can provide layers that fulfil these additional requirements.

Very large parts in general (with specific technical requirements)

One interview partner gave several examples for tools or moulds that require high hardness, wear resistance, corrosion resistance etc., and which are of dimensions so that processes like PVD or plasma-nitriding – irrespective of detailed technical requirements – where not feasible, because of their size constraints. These parts were more than 10 m in length or several meters in diameter with masses of more than 10 tonnes. There are chrome bath lines available to treat parts of this size, but no other technology. Another interview partner (Interview 11) pointed to another advantage of hard chrome plating regarding very large parts that are larger than the available tanks. It is possible to do partial chrome plating by first coating roughly half of the part and then the other part with additional machining of the overlap in order to achieve identical overall layer thickness.

5 Potential alternatives for chromium trioxide based decorative chrome plating

5.1 Overview

Compared to hard chrome plating there has been significant technical improvement in decorative chrome plating in recent years, so that the essential functional and decorative properties required (e.g. a bright chrome-like appearance) are met. In addition, the two most promising alternatives - trivalent chromium plating and PVD based processes - are now also commercially available, in various industrial sectors in use and also comparable in terms of economic efficiency.

The following Table 5.1 gives an overview of potential alternatives as were analysed in the AoA documents. They can be categorised as follows:

I. Alternative galvanic processes
II. Vacuum processes
III. Lacquering techniques
IV. Others

The order implies no ranking. Alternatives that are considered as “most promising (Category I) in the AoA are indicated by leading and trailing asterisks. A detailed list with attribution to the respective application can be found in the appendix.

It was possible to conduct expert interviews regarding all “Category I” processes.

Tab. 5.1 Potential alternatives for decorative chrome plating

Identification in the AoA	**Description**
ALTERNATIVE GALVANIC PROCESSES	
Chromium free electroplating	The basis of all multi-component coating systems is generally copper. The copper layer does not provide adequate corrosion protection. Further subsequent protection is needed. Therefore, multi-component coating systems (Cu, Sn, Zn, Ni, Co), gold and platinum electroplating, zinc electroplating are used.
Trivalent chromium electroplating	Galvanic deposition of Cr from trivalent chromium compounds
Currentless (electroless) nickel plating	Auto-catalytic plating process of NiP without external electrical power
Satin & black anodised aluminium	Anodising is an electrolytic process used to increase the thickness of the natural oxide or to enhance the formation of an oxide layer on the surface of the metal parts. Alternative substrate, which could potentially replace the whole electroplating process.

VACUUM PROCESSES	
Chemical vapour deposition (CVD)	CVD describes a range of deposition methods, typically under vacuum, where the substrate It is exposed to one or more volatile precursors which react on the surface and produce the desired deposit. Coatings can be polysilicon, SiO_2, Si_3N_4, metals, graphene, diamond
PVD based processes	General name for a variety of vacuum processes starting with the coating material in a solid (or rarely in a liquid) form placed in a vacuum or low-pressure plasma environment. The coating material is vaporised and deposited, atom by atom, onto the surface of the substrate in order to build up a thin film. Relevant PVD coatings are PVD metal: vacuum based deposition of a metal coating/layer (chrome, aluminium) Lacquer + PVD systems: two- or three-layer systems with an initial lacquer applied on the substrate, a subsequent PVD layer (of TiN, TiCN, TiAlN, CrN, ZrN, WC, ZrC, ZrOC, SiC, or TiC) and in case of the three-layer-system, a topcoat
Diamond Like Carbon (DLC) coatings	PVD type coating of combined bond types of graphite and diamond. DLC forms an amorphous diamond-like carbon layer, with hardness properties > 2,000 HV.
LACQUERING TECHNIQUES	
Powder Coating	The application of powder coatings is based on electrostatic attraction without use of solvents. The substances used for powder coatings are organic polymers with thermosetting properties.
Wet lacquering/colour painting	Liquid coating materials are applied either as clear or as coloured lacquer.
OTHERS	
Stainless steel (alternative substrate)	self-explanatory

5.2 Decorative plating on plastics with trivalent chromium

The alternative for decorative plating on plastics uses electrolytes based on non-toxic trivalent chromium instead of carcinogenic hexavalent chromic acid. Trivalent chromium-electrolytes substitute only the final step of the overall plating process which comprises a multitude of pre-treatment, washing and plating steps. Chromium trioxide based chromic acid is conventionally also used in the etching step during the pre-treatment of the plastics. That means that a substitution of chromium trioxide in the plating process will not eliminate chromium trioxide from the complete process. Alternatives for substitution of chromic acid in the etching process are discussed separately in chapter 5.3. However, it has to be stated, that a change of the etching pre-treatment will have a significant impact on the performance of the whole process and cannot be addressed separately from the overall plating process (FGK 2015).

Chromium plating of plastics is used to generate metal-like decorative coatings with cool-touch properties for many applications in the field of automotive, consumer products (e.g. perfume caps), sanitary or furniture construction. Applications for the automotive sector have to be emphasised due to their high-quality requirements as well as economical relevance for the German industry. The Plating on Plastics for Automotive Applications (PoPAA) is addressed by an application for authorisation of chromium trioxide of an industry consortium of the Fachverband Galvanisierter Kunststoffe (FGK) led by Gerhardi Kunststofftechnik GmbH. Here the PoPAA process is described as follows:

„PoPAA is performed to produce a surface that meets the high requirements predefined by the OEMs regarding functionality (e.g. being highly durable under aggressive and demanding conditions) and aesthetics (high-class, valuable, top-quality appearance). Furthermore, PoPAA is used for a selective coating of parts which are fabricated of two, three or even more plastic materials (so-called 2K- or 3K-parts). These 2K/3K parts are the result of a special moulding technique which allows the simultaneous injection of different plastic materials of which at least one component is not able to be coated with the PoPAA process. This is of particular importance to European suppliers to retain a competitive technological advantage over non-EEA suppliers e.g. from Asia or the NAFTA countries. Over the last years the increasing demand for multicomponent applications has made this a rapidly growing market.“ (FGK 2015).

5.2.1 Process overview

The plating process on plastics typically involves numerous steps, such as etching as pre-treatment and several intermediate purging and plating steps followed by the chrome electroplating process (main process). Process steps include pickling, neutralising, Pd-activation, chemical nickel, pre nickel, acid copper, semi-gloss and gloss nickel, microporous nickel, copper (ca. 50 µm), nickel (ca. 20 µm) and finally a thin chromium layer (only a few tenth of microns).

In the development of trivalent chromium electrolytes, it has to be distinguished between two main variants, one based on chloride and one based on sulphate compounds. The main characteristics of both variants concerning electrolyte composition and process parameters are shown by an example provided by Coventya as a provider of plating chemicals. The process of chromium plating on plastics has been described with a simplifying schematic sketch (Figure 5.1: process steps displayed in different colours from left to right. Area of one box implicates the part of each step of the overall period of time).

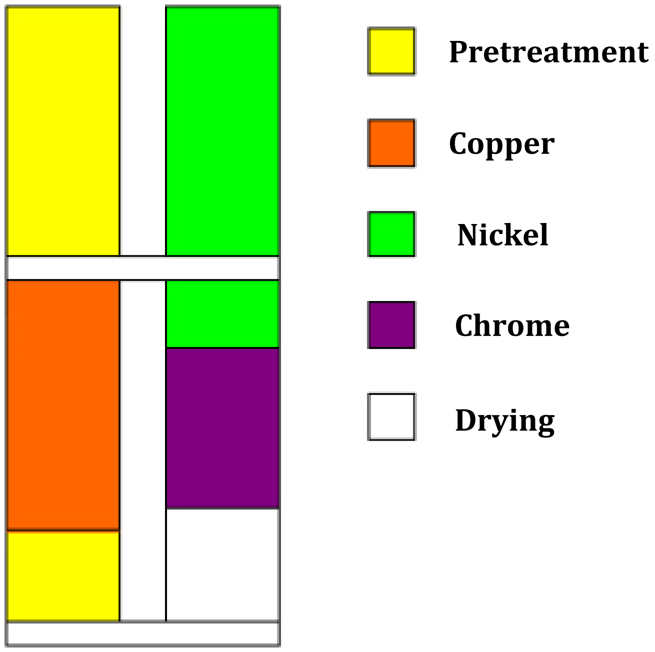

Fig. 5.1 Principal sketch of chromium plating on plastics

While changing from hexavalent to trivalent chromium most of the galvanic process steps remain the same. However, a switch to trivalent chromium requires some adaptions and additional process steps due to a completely different electrochemical process.

Tab. 5.2 Characteristics of trivalent chromium electrolytes composition and process parameters (Coventya 2016)

Parameter	**Chloride**	**Sulphate**
Chrome (g/l)	24	6
Iron (mg/l) (tolerable concentration)	< 60	< 70
Boric Acid (g/l)	60	90
Surface tension (mN/m)	40 – 45	
pH	2.6	3.5
Temperature (°C)	32	50
Current density (A/dm^2)	10	4
Anode material	Graphite	Mixed metal oxides (MMO)
Agitation	Air	
Plating rate (µm/min)	0.08 – 0.13	0.04 – 0.06

While a chromium (III) chloride-based electrolyte operates without organic additives, a sulphate-based process requires special additives, which are responsible for example for colour, gloss, opacity and layer thickness. Since some of the substances may interfere in their action, it is necessary to have a precise dosage adjustment (JORDAN 2013). Due to lower foreign metal ion deposition and therefore better optical properties, the sulphate process is favoured by the automotive industry in contrast to the chloride process. Overall the sulphate process has prevailed. Major bath chemicals suppliers are backing this (Interview 29).

With regard to passivation, further developments based on self-assembled monolayers (SAM), coatings or novel electrolytic coatings are already in industrial application or in trial (Coventya 2017).

Main differences between trivalent and chromium trioxide plating are:

- Electrolyte composition .
  Hexavalent chromium electrolytes contain chromium trioxide in a sulfuric acid solution with additional components like surfactants and catalysts. The chromate anion is reduced in a complex multistep process at the cathode and deposited as chrome metal. Trivalent chromium electrolytes usually contain chromium salts (sulphate, chloride) as well as complexing agents, buffers, catalysts and surfactants to achieve the required performance for plating. Most of these additives have to be dosed manually to the electrolyte bath. For some applications chromium sulphate electrolytes are preferred to chloride electrolytes due to better and more stable optical properties of the coatings. The deposition of metallic chromium takes place from cationic chrome sulphate (or chloride) complexes. In order to avoid a co-deposition, foreign metal cations have to be removed by use of ion exchangers. Due to less oxidising conditions, less stable and therefore less toxic surfactants can be used for wetting of components (HSO 2015, Interviews 28 and 29).
- Additional process step for surface passivation.
  Although chromium is less noble than iron in the chemical sense, it is almost as corrosion resistant to air and water as a precious metal. A few nanometres thick, invisible oxide layer separates the metal from the atmosphere, so that further oxidation by diffusion is impeded by this passivating layer. With chromium trioxide electrolytes this passivation layer is generated by the oxidative chromic acid while trivalent chromium electrolytes cannot produce such a passivation. Thus, plated surfaces are highly active e.g. the interior of steel pipes can easily form rust (JORDAN 2013). Therefore, the passivation has to be generated in an additional process step using for example phosphates or polyphosphates or other kind of organic substances. The formation of chromium phosphates on the surface can cause a bluish blushing. Research and development on advanced passivation systems is still going on. COVENTYA (2017) reported good results using an organic immersion coating forming self-assembled monolayers on the surface by a process, which is in industrial use in Germany since 2017. One process supplier stated that there is no need for an additional bath as the chromium trioxide process requires a reduction bath, which is no longer needed in case of the trivalent chromium process (Interview 4).
- Additional time for layer building.
  Chromium deposition is slower in the trivalent chromium-based process (five minutes). As the cycle time of the total process is about 3–4 minutes it is advised to install two trivalent chromium baths (Interview 4).
- Anode material.
  Anode materials are often expensive and have to be carefully adopted to the process. For chloride processes graphite anodes and for sulphate processes mixed metal oxide anodes are used. The stability of the anodes varies between several weeks and a few years (Interview 28).
- Bath maintenance
  Analytical efforts are much higher for adequate control of bath composition with all its additives. Analysis of layer thickness and colour has to be performed on a daily basis. Quality maintenance of a trivalent chromium bath takes about 14 hours per week, compared to 2 hours per week for the chromium trioxide bath (FGK 2015).

- Longer bath lines.
  As trivalent chromium plating baths are very sensitive to impurities an ion exchanger (special resin) and a number of additional basins/baths are needed to enable adequate rinsing processes to reduce impurities as much as possible. This is necessary for both the pre-treatment bath technology as well as the trivalent chromium plating step. Clearly, modifications of serial production lines, especially for processing of large parts, is a very costly process. Several companies stated during the consultation that the building conditions simply do not allow for the installation of further baths. The companies carrying out these operations explained that new buildings would have to be constructed (FGK 2015).
- Bath temperature management.
  According to a supplier of bath chemicals chromium trioxide baths must be cooled because of the high level of hydrogen release. This is not necessary in the trivalent chromium process (Interview 4).
- Additional differences to the chromium trioxide-based process are (SCHÜTTE, 2015):
  - significantly lower amount of chromium (7–10 g/l vs. 250–400 g/l)
  - lower odour (ammonia and chloride free process)
  - simplified waste water treatment

5.2.2 Technical requirements

The essential technical requirements for plating on plastics with trivalent chromium electrolytes are currently achieved even for the automotive industry. Meanwhile quality management laboratories of the OEM accept trivalent chromium coatings and the price and optical properties are more or less the same. However, with physical measurements different colour values can be observed. Sometimes different departments of OEM can have different quality requirements (Interview 28). Coating colours can be adjusted in a certain range between darker and lighter shades. Lightness value of up to 84 are achievable while the standard chromium layer from chromium trioxide is > 80 (Interview 4).

Tab. 5.3 Summary of technical properties of trivalent chrome plating on plastic

Property	Description/ test methods	Evaluation	
Corrosion resistance	The corrosion resistance of metallic chrome coatings from trivalent chromium electrolytes is dependent on numerous parameters, such as the type of electrolyte used (trivalent chromium sulphate based or trivalent chromium chloride based), the underlying layer system (copper, nickel intermediate layer, etc.) and whether the coating is provided with a subsequent passivation. Common tests: exterior 480 h NSST, 96 h CASS EN ISO 9227, Russian mud resistance (FGK 2015)	Comparable to chromium trioxide (Interview 28), (HSO 2019) NSST 480 to 1000 h, CASS 48 to 96 h (Interview 29) Russian mud resistance: chloride process better performance, sulphate equal (COVENTYA 2016)	✓

Property	**Description/ test methods**	**Evaluation**	
Chemical resistance	Chemical resistance refers to the sensitivity of optical properties of the coating when contacted with chemicals (e.g. fatty acids from fingerprints, skin creams etc.). It is usually tested according to drop tests (OEM specification)	Achieved (Interview 28)	✓
Wear resistance	Wear resistance of chromium coating is important because wear adversely affects the optical properties (scratches etc.), corrosion resistance as well as the Nickel-leaching. There are different types of wear mechanisms and test methods thereof e.g. touching (ABREX-Test), Wiping or polishing (Taber Abraser-Test) Brushing, (Amtec Kistler Test), Scratching (Scratch Tester). There is no existing standard for Cr-plated surfaces. Wear is also depending on thickness, grain structure. Most test show similar results.	Lower than Cr(VI) but alright (Interview 28) Similar results depending on test methods (COVENTYA 2016)	✓
Adhesion of coating	The adhesion of the layer depends essentially on the pre-treatment of the plastics (pickling).	Works only with chromium trioxide pickling (Interview 28)	✓
Hardness	In the decorative coating, the thin Cr layer is not critical to the hardness of the overall coating.	No difference (Interview 28) 750– 800 HV 0,05 (LIEBERT 2019)	✓
UV/Light resistance	No difference, same properties of deposited Cr	Achieved (Interview 28)	✓
Temperature resistance	No difference, layer composite similarly composed	Achieved (Interview 28)	✓
Coating thickness	For decorative coatings, only very thin Cr layers (a few µm) are required, which can be achieved with both processes.	No difference (Interview 28)	✓

Property	Description/ test methods	Evaluation	
Nickel leaching	Depends on porosity and thickness of the layer. Abrasion and leaching test according to EN 12472 and EN 1811:2011	Higher leaching than chromium trioxide-coatings, but within specifications of nickel guideline (Interview 28) For microporous coatings no significant nickel leaching can be observed neither for chromium trioxide nor for trivalent chromium (DAHLHAUS 2019)	✓

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

5.2.3 Design requirements

Regarding design requirements the optical and haptic properties are most relevant. Concerning the haptic properties both variants trivalent chromium as well as chromium trioxide are more or less the same, because both variants deposit elemental chromium layers and therefore provide a cool (metallic) touch.

Due to a different process (deposition of cations) the optical properties of trivalent chromium-based coatings are very sensitive to co-deposited impurities. A yellowish/brownish shade of the coating can be caused by catalysts, such as sulphur or iron, that are normal compounds of trivalent chromium electrolytes. Besides that, there are impurities (for example coming from the rack, the substrate, or the production surroundings) that enter the trivalent chromium electroplating bath as impurities. The co-deposited impurities cause a tarnishing of the layer. Even smallest quantities of impurities can lead to this effect. As reported in an application for authorisation of chromium trioxide, it was not possible to adequately maintain process conditions that prevent tarnishing. Besides the yellowish colour, trivalent chrome plated products from different suppliers were not of the exact same colour. Different trivalent chromium coated parts assembled together (for example, in the interior of a car) would show a slightly different colour and would not match exactly (FGK 2015).

From the assessment of the interviews and the literature analysis meanwhile it can be stated that stable colour values can be achieved within an acceptable colour range e.g. L-value: 83 to 85; b-value -0,5 to -1,5; a-value: -0,4 to -0,8 (LIEBERT 2019). However, there is need for an ion exchanger to remove impurities from the bath. One interviewee stated trivalent chromium-coatings need higher cleaning efforts to sustain optical properties (e.g. need of polishing after carwash due to stains caused by different surface energy resulting from passivation steps with organic chemicals) (Interview 28).

One supplier of bath chemicals stated in the interview that a trivalent chromium bath has higher throwing power than conventional chromium trioxide baths. This leads to a more homogenous metal distribution. Burn marks in zones of higher current density are not found. Auxiliary anodes or screens are rarely needed, even with parts of complex geometry. Boreholes or other openings do not have to be plugged in contrast to conventional chromium trioxide baths (Interview 4).

From a design point of view also new functions like touch displays or illumination are relevant. This can be achieved with chromium plating processes (both chromium trioxide and trivalent chromium) by selective etching of multiple component injection moulded parts. With this process, specific parts of the components can be spared out from plating to realise the desired functionality. There is a know-how lead of German manufacturers in this technology field (Interview 28).

5.2.4 Legal or normative requirements

There are no specific legal requirements for the use of trivalent chromium electrolytes. However, if the pre-treatment is performed with hexavalent chromic acid an authorisation under REACH is required for the process. The matching of OEM specifications for the coating systems is most relevant. Furthermore, in the automotive sector there are legal obligations to guarantee long periods of product delivery of the same product.

5.2.5 Economic and cost issues

Exchanging chromium trioxide in the PoPAA process with trivalent chromium electrolytes comes with important process changes that influence the economic feasibility. A detailed cost analyses has been performed within the analyses of alternatives within an application for authorisation (FGK 2015). Some relevant factors are as follows:

- Additional baths for adequate rinsing (more rinsing is required to minimise the carryover of impurities in the bath process) and passivation;
- Re-qualification and certification of processes for customers;
- Additional wastewater treatment measures are required (organic complexing agents and stabilisers necessary for trivalent chromium electroplating);
- Higher chemical costs;
- Higher analytical efforts (maintaining trivalent chromium bath quality takes about 14 hours per week, compared to 2 hours per week for the chromium trioxide bath);
- Additional process equipment is required for cooling of the trivalent chromium bath. (This contradicts a statement from (Interview 4)).

Generally, it can be distinguished between different kinds of cost issues.

Costs of chemicals

From the perspective of an electroplating company (Interview 28) the costs of trivalent chromium electrolyte processes are estimated to be up to 10 times higher than chromium trioxide processes due to higher chemical costs (gloss additives, boric acid, chromium sulphate etc.), as well as more and complex measurements to control the process. However, chromium coating would be only one step out of 20 to 30 steps, so the overall coating costs usually would only be 5 to 10 % higher than for hexavalent chromium, depending on the kind of coated products.

From the perspective of a provider of plating chemicals (Interview 29) the chemical costs for trivalent chromium electrolytes would be 1.5 to 2 times higher than chromium trioxide electrolytes with chemical costs amounting to about 10 – 20% of total coatings costs. Meanwhile, about the same productivity and coating time as for chromium trioxide processes can be achieved.

Costs for process control

Chromium (III) electrolytes contain more than twice as many ingredients, which significantly increases the analysis effort. In practice it turns out that fully automatic dosing is currently not possible, in particular because some additives cannot be correctly analysed (WOMAG 2017). In (Interview 4) it was stated that there are no additional efforts regarding process control.

Costs for modification of production lines

According to the analysis of alternatives from the application for authorisation of chromium trioxide by the FGK consortium the required investments refer to the project planning, official permissions, reconstruction work, process changes as well as qualification of components. The actual costs would depend on the size of the company and the respective throughput. The provided cost would not include additional labour, quality control and scrap costs. Modifications of serial production lines, especially for processing of large parts, is a very costly process. In particular, the need for additional baths is a significant drawback. Several companies stated during the consultation that the building conditions do not allow the installation of further baths. The companies carrying out these operations explained that new buildings would have to be constructed. Consequently, even higher investment cost than outlined here would have to be taken into account for structural measures. A comparison of production costs between chromium trioxide and trivalent chromium processes reveals that costs for trivalent chromium are 20 to 30 % higher compared to chromium trioxide and is expected to decrease to a level equal to the chromium trioxide process over the years. Taking all these costs into account it can be stated that trivalent chromium electrolytes are more expensive than chromium trioxide-based treatments. Higher costs and shorter time intervals for maintenance are expected, since the whole process technology is more complex (more baths required, ion exchangers, prone electrodes, sensitive process parameters). In addition, analytical tests are getting more complicated and thus might not be performed in-house anymore. Further investments have to be considered for (re-)training of workers, due to additional process steps, such as manual regulation of additive additions not required for chromium trioxide electrolytes. Another important aspect is the need for more frequent daily quality tests, leading to increased personnel costs. With regard to the currently applied chromium trioxide passivation on trivalent chromium coatings, this process based on two separate steps is less economically feasible compared to the chromium trioxide-based process. Trivalent chromium electroplating is the alternative to PoPAA main-treatment favoured by the automotive industry. Despite of significant efforts achieved over the last years, the overall maturity of the alternative to eliminate chromium trioxide from the plating process depends on the availability of a chromium trioxide-free etching pre-treatment. From an economic perspective the implementation of an entirely chromium trioxide-free plating-process would be more reasonable than the stepwise replacement of the main-treatment and subsequently of the pre-treatment. A stepwise introduction is accompanied by full re-qualification of the coating at the OEMs, once when introducing the main-treatment and again when introducing the pre-treatment. From the economic perspective it is advisable to further develop the entire trivalent chromium electroplating process until it is completely chromium trioxide-free, avoiding partial substitution (FGK 2015). In (Interview 4) it was stated that nowadays process costs are comparable.

Some of the chemical providers claim to have already existing products for combined chromium trioxide-free pre-treatment and plating solutions, which are used in industry (Interview 29, Interview 30). The acceptance of these products would be better outside of Germany. From perspective of the plating industries in Germany, chromium trioxide-free etching systems would be far from market readiness and would not be compatible with their processes ((Interview 28), WOMAG 2019). It seems that further research and testing efforts are necessary to qualify these solutions for industrial practise.

From the perspective of an electroplating company (Interview 4) a bigger problem in Germany would be that facility modifications need a permission, which can take up to one year. Additional costs arise from necessary qualification/certification processes for customers. Costs for modification are estimated up to 2.5 m € per company, if costs for recertification is included up to 5.5 m €. Due to a full utilisation of existing facilities, for many companies there is no scope for a parallel operation of alternatives. For new facilities, which are built mainly outside of Germany because of cost reasons, the switch to trivalent chromium-based processes can be achieved at much lower costs. This could lead to a weakening of the German industry, which to date hold ca. 60 % of the automotive plastic plating market with Italy and Spain also being important players. One of the interviewed companies operates new plants in Slovakia and China. All other products except plastics for automotive application will be manufactured in China using chromium trioxide electrolytes.

From the assessment of a provider of plating chemicals (Interview 29) the additional costs for ion exchange system and equipment for passivation are estimated to about 20,000 to 50,000 €. Another provider claims that the change from chromium trioxide to trivalent chromium requires investments between 100,000 to 300,000 €. Investments for new plants are comparable for both processes (Interview 4).

Costs for R&D

In order to further improve technically feasibility and for further development or adaptation of trivalent chromium solutions to meet the minimum requirements, investment in research and development activities are necessary in the coming years, which are estimated to exceed 0.15 m € per company (FGK 2015). In a recent publication the company Sedus Stoll AG reported that a switch from chromium trioxide to trivalent chromium was possible within the existing production facility at conversion costs in total of 250.000 €. The modifications of the production line could be carried out within eleven working days. (BOHNET 2019).

Costs for protective and environmental measures (in production)

There is no significant difference, but there are additional costs for waste water treatment (de-complexing, evaporation), because of complexing agents in trivalent chromium electrolytes (Interview 28).

Costs for Energy

From a perspective of an electroplating company (Interview 4) energy consumption is considered to be higher due to higher current density and higher voltage. According to estimates, 20–30% more energy is consumed depending on the component, due to higher process temperatures and energy needed for cooling efforts to avoid additional heating during operation. Contradicting this, the company Surtec claims that their trivalent chromium-process needs less energy due to lower current density (LIEBERT 2019).

5.2.6 Risk characterisation

Even if Cr(III) electrolytes are used for plating, chromium trioxide baths are currently still needed for plastics pre-treatment (etching), so the requirements for occupational safety and health are more or less the same. Exhaustion is needed not only due to chromium trioxide but also due to the strong acid used in the electrolytes. For exhaust air total chromium measurements and chromium trioxide measurements are required. Exhaust air has to be treated with air scrubbers. Plastic electroplating facilities for automotive application usually have modern equipment and are fully automated with high capital expenditure. Systems dimensions are 50 to 100 m in length. Hydrogen generation is an issue for both processes (Interview 4).

Besides chromic acid there are several other hazardous chemicals used in electrolytic bathes of plating processes, which are mainly still present in trivalent chromium electrolytes e.g. boric acid as buffer.

For some galvanic processes there are already solutions to eliminate boric acid (e.g. trivalent hard chromium processes). With trivalent decorative chromium plating, this step is still pending. Here a chemical supplier argues, that in the critical time of imminent chromic acid prohibition, the company wanted to deliver the technically and visually best possible process for trivalent chromium electrolytes. This is mainly for time and resource planning, as the company assesses the likelihood of early authorisation of boric acid as rather low compared to other substances identified as SVHC under REACH (Interview 29).

One substantial advantage of trivalent chromium electrolytes is that no per- or polyfluorinated surfactants are needed to control aerosol formation. For chromic acid baths it is very difficult to find alternatives for the toxic perfluorinated octylsulfonate (PFOS), because very oxidation stable substances must be used, which on the other hand usually are also very persistent in the environment (JORDAN 2013, UBA 2017). PFOS-free chromium trioxide-based processes are dependent on high addition rates of non-fluorinated wetting agents, as these break down very quickly and also produce a large amount of degradation products. On the other hand, several interview partners stated that they do not use fluorinated surfactants, neither in chromium trioxide baths nor in trivalent chromium baths (Interviews 3, 6, 7, 8 and 11).

For all weakly acidic baths (such as for chrome plating with trivalent chromium, nickel plating etc.) wetting agents such as sodium lauryl sulphate are used more for technical reasons to improve the coating result (Interview 29).

For trivalent chromium the following additional environmental and occupational health aspects have to be considered:

- Boric acid is used in the electrolytes as buffering system. At present there are no alternatives available. Boric acid has been identified as SVHC (Repr. 1B, H 360FD) included on the candidate list and currently on the 6th recommendation for inclusion in Annex XIV.
- In some cases, trivalent chromium chloride is used, which has a classification as Skin Irrit. 2, Eye Irrit. 2, Acute Tox. In general, the trivalent electroplating processes are less toxic than chromium trioxide plating due to the oxidation state of the chromium. Trivalent chromium solutions do not pose serious air emission issues, but still pose the problems of disposal of stripping solutions (depending on the type

of stripping solution) and exposure of staff to chrome dust during grinding.(FGK 2015)
- Another aspect to be mentioned is the significantly increased aerosol-formation during the trivalent chromium process due to the inferior current yield compared to the chromium trioxide process (FGK 2015). Otherwise, less toxic surfactants can be used for aerosol suppression in trivalent chromium electrolytes, due to less oxidative conditions.
- Trivalent chromium-electrolytes contain complexing agents, which have to be broken up during waste water treatment. Usually precipitating reagents are used, so the complexing agents could reach the waste water and can cause further problems due to mobilising of heavy metals. To avoid this, evaporators have to be used, which are quite cost intensive. One company reported that it uses a trivalent chromium-based process, which did not utilise complexing agents (Bohnet 2019). However, an interviewee stated, that only Cr(III) electrolytes with complexing agents have a sufficient performance (Interview 29).

5.2.7 Conclusions

From the "Analysis of Alternatives" of the application for authorisation of chromium trioxide (CrO_3) by the FGK consortium it was concluded that at the development stage of the year 2015, trivalent chromium-based electroplating could not be seen as a general alternative to chromium trioxide electroplating due to some economic and technical limitations.

The current situation as derived from the interviews and the literature analysis can be assessed as follows:

- Cr(III) electrolytes can now be described as industrially mature. Meanwhile trivalent chromium fulfils the technical requirements for plating of plastic for automotive applications to a large extent and is an industrially mature process. Trivalent chromium has been used in series production in the automotive industry for several years. However, there is still potential for further improvements and the process is considered to be more complex and difficult to care for than chromium trioxide plating. Further process improvements, such as electrolytic composition, passivation, or anode materials, are continuously underway.
- From an economic perspective, trivalent chromium-based processes are in principal competitive, especially for new plants. Concerning the process conditions and the costs, the statements of the stakeholders differ to some extent. But there is a consensus that a shift from chromium trioxide to trivalent chromium will not have a big influence on the costs of the whole coating process and the applications. From the point of view of existing production lines, however, there are significant barriers for substitution, such as restrictions on production during conversion, plant approval and recertification costs or no space for additional galvanic baths in existing facilities. Furthermore, the acceptance of the customer and supply liabilities for long periods of time are still key issues, although a shift of industries to more willingness to use chromium trioxide alternatives can be observed. Nevertheless, a rash substitution of chromium trioxide with trivalent chromium could weaken the strong German position in the automotive supplier chain and encourages the building of new facilities in regions with lower costs. From an economic perspective the implementation of an entirely chromium trioxide-free plating-process seems to be more reasonable than the stepwise replacement of the main-treatment and subsequently of

the pre-treatment. As claimed by some chemical providers, there are already existing products for combined chromium trioxide free pre-treatment and plating solutions. Further research and testing efforts are necessary to qualify these solutions for industrial practise.

- From an environmental and occupational health perspective the substitution of only the plating step while still using chromium trioxide for pre-treatment is no significant advantage. There are still other critical chemicals used in the trivalent chromium-plating process like boric acid identified as SVHC under REACH. One advantage of trivalent chromium electrolytes is that no per- or poly-fluorinated surfactants are needed to control aerosol formation. For chromic acid baths it is more difficult to find alternatives for the toxic perfluorinated octylsulfonate (PFOS), although several users of chromium trioxide stated that they do not use polyfluorinated surfactants. However, the issue of waste water is even more costly for trivalent chromium electrolytes due to the necessary removal of complexing agents. From the statements of the interviews and the publications there is no clear picture, to what extent harmful substances such as boric acids or complexing agents can be removed from trivalent chromium-based processes by means of further research and development.

According to FGK individual member companies have already implemented trivalent chromium processes in series or have testing procedures installed. FGK expects that until 2024 German plating on plastics companies will have switched to trivalent chromium-based processes. Meanwhile also some of the OEMs in the automotive sector have already implemented requirements for a change to the trivalent chrome plating (FGK 2019).

5.3 Chromium trioxide free etching for plating of plastics

5.3.1 Overview

Etching of plastics with chromium trioxide is a pre-treatment step integrated in the whole plating process and is mainly used for ABS (Acrylonitrile-Butadiene-Styrene) and ABS-Blends. It creates a rough surface in order to prepare the metallisation of the plastic. The stain used for this purpose consists of equal parts (each approximately 375 g/l) of chromium trioxide and concentrated sulphuric acid (LAKE, 2009, p.45). During the etching process, a specific amount of butadiene 1,3 (elementary component of ABS) is removed selectively from the surface, creating caverns that act as contact points (anchor points) for the subsequent metal layers. Besides creating caverns on the plastic surface, the surface of the substrate is cleaned simultaneously from minor impurities (FGK, 2015, p.19).

The following Table 5.4 gives an overview of potential alternatives as were analysed in the AoA documents. The order implies no ranking. A detailed list with attribution to the respective application can be found in the appendix.

Tab. 5.4 Potential alternatives for chromium trioxide-based etching of plastic substrates

Identification in the AoA	**Description**
Conductive lacquer coating /lacquer/painting	A conductive lacquer is used as the basis for the subsequent layers.
Direct metallisation of different polymers	Combination of copper immersion and autocatalytic Cu(I)-oxide deposition in the activator bath.
Ionic liquids	Salts in the liquid state.
Mineral acid-based etching solutions	Different mineral acids (the most promising is sulphuric acid) can be used as substitute for chromium trioxide etching solutions. Wet-in-wet process. The overall technique is comparable to the chromium trioxide-based process.
Plasma coating	A plasma coating is used as the basis for the subsequent layers.
Plasma etching with oxygen or ozone	No water basis. The basic idea is to use a strong oxidising species to crack the smoother parts of the ABS.
Polyamide (alternative substrate)	Self-explanatory
Polymers with conductive filling (alternative substrate)	Polymers containing Cu- or steel-fibres.
Potassium permanganate-based etching solution	Wet-in-wet process. The overall technique is comparable to the chromium trioxide-based process.

In several Analysis of Alternatives (e.g. FGK 2015, GROHE 2015 and KEUCO 2018) etching with potassium permanganate is treated as a promising alternative. Additional information on potassium permanganate-based etching was gained in interviews with experts, which is described in the following sections.

5.3.2 Process overview

Instead of chromium trioxide and concentrated sulphuric acid in this case the etching agent includes an aqueous solution containing potassium permanganate. FGK (2015) describes the process as follows: Potassium permanganate ($KMnO_4$) is a strong oxidising agent with manganese in the oxidation state of VII. It is widely used for water disinfection. Acidic permanganate solutions are reduced to Mn^{2+} (MnO) giving the solution a pink colour. Under neutral conditions, permanganate is reduced to Mn^{4+} (MnO_2), exhibiting a brownish colour to all materials that are in contact with the solution. In alkaline solutions, potassium permanganate (Mn(VII)) is spontaneously reduced to Mn(VI) (K_2MnO_4), having a green colour.

The following details were given by one supplier of plating chemicals (Interview 30) explained about its trial results that they show applicability for several branches (automotive – interior and exterior, sanitary and others). Products to be treated are all plated plastic parts, such as front grille, decorative trims, door handles, shower heads, consumer goods.

5.3.3 Technical Requirements and Limitations

Major technical requirement is good adhesion of the coating.

Tab. 5.5 Technical requirements for etching of plastics

Property	**Target value**	**Achieved value (with permanganate)**	
Adhesion (peel strength)	> 1 N/mm^2 for ABS	> 1 N/mm^2 for ABS	√
	> 0.5 N/mm^2 for ABS/PC	> 0.5 N/mm^2 for ABS/PC	√
Thermocyclic tests (multiple tests, OEM/customer dependant)		pass	√
Appearance		pass	√

+: exceeding √: comparable –: constraints/not meeting criteria
0: not comparable

5.3.4 Legal or normative requirementsy

There are neither product specific legal requirements nor normative restrictions.

5.3.5 Design requirements

There are no product specific design requirements or restrictions.

5.3.6 Risk characterisation

Exposure conditions are comparable to the chromium trioxide-based process but the classification differs as the alternative substance ($KMnO_4$) is classified as Acute Tox. 4, H302, Aquatic Chronic 1, H410, Aquatic Acute 1, H400, Repr. 2, H361d, Ox. Sol. 2, H272).

5.3.7 Economic and cost issues

Overall the process costs are estimated to be higher, because for each parameter (performance, labour, energy, process, investment) costs are equal or higher.

Besides costs major obstacles for implementation are larger required space and missing customer specifications. Also noted was the workload of existing equipment and therefore missing leeway for parallel operation of alternatives. This poses a general obstacle for all innovation processes.

5.3.8 Additional findings

Another supplier of plating and etching solutions (Interview 29) stated that outside Europe chromium trioxide free etching of plastics is already ready for the market. A permanganate stain is established, which is technically similar to the chromium trioxide-based method as well as with similar etching time. Different plastics can be etched with the process (ABS, polyamide, ABS-PC). An important application is high-quality packaging based on solvent-resistant polypropylene (for example, caps of perfume bottles, especially in France).

Reject rates are approximately 1%, which is similar to that of chromium trioxide-based processes. As an additional investment, a reoxidation cell for regeneration of the etching solution is necessary. Additional process steps are required so that 2 to 3 additional baths are needed for new plants.

A third supplier (Interview 4) who is also developing a permanganate stain pointed to additional fire hazards during dry running. Also, it was pointed out that as a consequence of the higher aggressiveness of MnO_4, PVDF coated pumps have to be used and service life of bath components is expected to be lower. Finally, the low selectivity of the etching process was seen as a major problem as it is not applicable for complex multicomponent systems.

Lehmann et al. state that to date no substitute procedure has prevailed, which can compete either in quality or costs (LEHMAN et al., 2018, p. 44), but they do not mention Mn based processes in their paper.

KÄSINGER (2019, p. 486) reports on a series of tests on chromium trioxide-free pre-treated plastic parts that were performed by FGK. Participating companies pre-treated and coated selected parts. These parts were subjected to different stresses like climate cycling tests, warm storage etc. Test results showed large differences and revealed that none of the treatments could pass all tests.

In a research project, Fraunhofer Institute for Silicate Research ISC has collaborated with an industrial company to produce a coating consisting of a new conductive inorganic-organic hybrid polymer that generates a platable surface on polyamide (ROSE and MEINHARDT 2017). A single immersion bath for the polymer coating could, therefore, be used not only to pickle with chromium trioxide but also to replace several further process steps (including activation and acceleration). This simplifies the overall process and saves process chemicals.

5.3.9 Conclusions

As of today, there are several manganese-based stains on the market, with more being tested. As compared to the situation a few years ago significant progress seems to have been made, but on the other hand users still report of relevant drawbacks.

Additionally, there is quite some research going on with focus on different technologies e.g. conductive inorganic-organic hybrid polymers.

5.4 Decorative plating on steel with trivalent chromium

Today practically all chemical suppliers for the coating industry also offer chromium (III) sulphate-based coating solutions for decorative chrome plating.

Chrome plating of steel is applied on top of a Nickel or Copper-Nickel undercoat, which can be bright or matte finished ("pearl nickel"). Depending on the type of Nickel layer the final surface either takes a shiny or matte look. Thus, chrome plating is part of a multi-step process with pre- and post-treatments like cleaning, degreasing, etc.

Therefore, this alternative is very close to the original chromium trioxide-based process and can in principal be considered as drop-in replacement. The major differences are described in the process overview.

5.4.1 Process Overview

In the described use case steel parts for store fixtures were chrome coated with the specific baths for the trivalent chromium-based process being integrated into a fully automated bath line with other plating processes (nickel plating as well as chromium trioxide-based plating). (Interview 3)

Major differences to the chromium trioxide-based plating process are:

- Plating bath uses chrome (III) sulphate instead of chromium trioxide.
- Boric acid (H_3BO_3), which is included in the candidate list for authorisation, is used as a buffer in this process not just for the nickel-plating step but also for chrome plating, and in a higher concentration (80 g/l as compared to 40 g/l for nickel plating).
- Bath preparation takes place at about 70°C due to the low solubility of chromium compound and buffer (H_3BO_3).
- There are up to two additional electrolytic passivation baths, which are not needed in a chromium trioxide bath (due to "auto-passivation").
- There is no need for a reductive flush, which is necessary in a chromium trioxide process.
- Flushing temperatures are higher than for chromium trioxide due to the low solubility of H_3BO_3 (buffer).
- Lead anodes are not usable. MMO anodes are needed.
- Two ion exchangers are needed in order to control concentrations of iron and nickel ions.
- Trivalent chromium-based coating takes longer than chromium trioxide-based coating for the same layer thickness.

5.4.2 Technical Requirements

Technical requirements are highly dependent on the respective use case. The following evaluation is based on an interview with one producer of store fixtures, furniture fittings and metal parts for automotive (Interview 3). The use focusses on store fixtures.

Tab. 5.6 Summary of technical properties of trivalent chrome coating of steel for shop fixtures

Property	Description/ test methods	Evaluation	
Corrosion resistance	Common tests: 96 h CASS EN ISO 9227	Not met, but results acceptable for specific use case	–
Chemical resistance	Chemical resistance refers to the sensitivity of optical properties of the coating when contacted with chemicals (e.g. fatty acids from fingerprints, skin creams etc.). It is usually tested according to drop tests (OEM specification)	Not relevant for specific use case, but e.g. for furniture parts fingerprint stains would not be acceptable	–

Property	**Description/ test methods**	**Evaluation**	
Wear resistance	Wear resistance of chromium coating is important because wear adversely affects the optical properties (scratches etc.), corrosion resistance as well as nickel-leaching. There are different types of wear mechanisms and test methods thereof e.g. touching (ABREX-Test), Wiping or polishing (Taber Abraser-Test) Brushing, (Amtec Kistler Test), Scratching (Scratch Tester). There is no existing standard for Cr-plated surfaces. Wear is also depending on thickness, grain structure. Most test show similar results.	Not met, but results acceptable for specific use case. In case of moving furniture parts (height adjustable tables, kitchen furniture poll-outs) wear resistance is too low.	–
Adhesion of the coating		Same as with chromium trioxide	√
Hardness	chromium trioxide: ~1,100 HV	~850 HV, sufficient for purpose	–
UV/Light resistance	No difference over time	darkens over time	–
Temperature resistance	chromium trioxide: 450°C	380 °C, not relevant for specific use case	√
Coating thickness	0,3 µm	OK	√
Nickel leaching	Depends on porosity and thickness of the layer. Abrasion and leaching test according to EN 12472 and EN 1811:2011	Not met but not relevant for specific use case. Not acceptable for products with food contact.	–

+: exceeding √: comparable –: constraints/not meeting criteria
0: not comparable

5.4.3 Design Requirements

In order to warrant colour consistency high levels of prudence have to be maintained with regard to bath conditions as already described in section 5.2.3. It is possible – with Cobalt additives – to achieve dark shaded coatings, which are sought after, e.g. for furniture fittings. The lack of fingerprint resistance is an important issue for the application of this process for furniture fittings (Interview 3).

5.4.4 Legal or normative requirements

Most important problem is the failure of Nickel leaching tests. Therefore, an application under food regulations is not possible (Interview 3).

5.4.5 Economic and Cost Issues

The issues as described in section 5.2.5 for chromium plating on plastics hold for the coating of steel as well. From the perspective of the user of this process the following elaborations were given (Interview 3).

The trivalent chromium process takes 7 minutes to reach the necessary layer thickness of 0,3 µm, which is about twice as much as the chromium trioxide based process (3 – 4 minutes) a second chromium trioxide bath had to be integrated into the bath line in order to maintain throughput performance (given cycle time was 4 minutes).

In case of a complete change to trivalent chromium, three chromium baths would not suffice to maintain the overall process rate therefore one additional bath would have to be integrated.

The trivalent chromium process has a higher scrap rate of about 10% as compared to nearly 0 with chromium trioxide. This is caused by discolouration, especially in case of parts with a complex geometry or tubes. The reason is that chromium is not deposited as a pure metal but as an Cr-Fe alloy of variable composition. Obviously, the iron content of the deposited layer varies especially in zones of low current (in corners or undercuts). As described, control of the amount of Ni and Fe ions is crucial, but at the same time it is inevitable that both metals are brought into the system. While scrap from the chromium trioxide-based process can be refurbished by polishing, rejects from the trivalent chromium-based process have to be dechromed and rechromed again, because the deposited chrome layer cannot be refurbished by polishing due to the lower wear resistance.

Bath chemicals are more costly for the trivalent chromium-based process.

Working costs are clearly higher due to the higher amount of bath control, the higher efforts for bath preparation and because of the described scrap rates.

Investment costs are higher due to the necessity of ion exchangers and the use of MMO anodes, which are more than three times as costly than the usual lead anodes. The higher bath sensitivity combined with the higher sensitivity of the MMO anodes also requires their more frequent exchange.

Waste water treatment is more expensive as a complexing agent has to be utilised in order to reach the necessary coating rates. This complexing agent hinders the slurry sedimentation and therefore has to be eliminated beforehand.

Overall the user estimates the process costs to be about eight times higher than the comparable chromium trioxide-based process, not accounting for anodes and waste water treatment.

5.4.6 Risk Characterisation

As of now there are still chromium trioxide baths in the production line. Therefore, exposure time and frequency are higher than with a pure chromium trioxide process, because of the higher control and maintenance requirements of the trivalent chromium bath, which furthermore contains 80 g/l boric acid as compared to 40 g/l in the nickel bath.

Additional exposure results from the fact that the chromium trioxide baths can be dosed from pumps while the trivalent chromium bath has to be prepared from solids at 70° water temperature.

In the whole process fluorine free surfactants are used so there is no risk reduction in this field as well.

5.4.7 Additional findings

BOHNET (2019) reports on the successful migration to a trivalent chrome coating process at an office furniture manufacturer. The process is described to be stable and to offer sufficient colour stability and scratch resistance to be applied for quality office furniture with warranted service times of up to ten years. Major constraints like no use complex forming agents, short migration time frame (10 workdays) and conforming with the space confinements of the existing bath line could be met.

Relevant activities during the implementation process were (BOHNET, 2019):

- Alteration of production process
- Modification of exhaust air system
- Adaptation of cycle times
- Exchange of chrome baths
- Anode conversion to titan mixed metal oxide anodes
- Installation of filtration system for the chrome electrolyte
- Disposal of hexavalent chromium electrolyte and stained parts
- New piping of rinsing system
- Evaluation of the new plant in cooperation with the local authorities.

Investment costs are reported to be € 250,000. The line is in production since January 2019 without any problems. There was positive customer feedback. The process is less sensitive for changes in current density, therefore there are less burns or stains at the parts. But it is also stated that process handling is more challenging. Bath chemistry has to be stabilised by an automatic dosage system, because deviations of electrolyte concentration or pH as well as contaminations lead to quality discrepancies.

One interviewee (Interview 8) points out that for musical instruments trivalent chromium processes are no alternative as customers expect the bluish tint of decorative chromium. Also, sufficient colour stability could not be achieved.

5.4.8 Conclusions

Trivalent chromium-based steel coating has developed towards a suitable and marketable alternative, although there are some drawbacks with regard to process stability, which can lead to quality loss. Maintenance is more costly as process conditions have to be observed (and if necessary: corrected) frequently. One interview partner applied the process only for products with relatively low endurance requirements (for shop fitting) while still running hexavalent chrome baths. But there is at least one furniture manufacturer of office products who substituted chromium trioxide completely.

This method is also being tested for car exhaust trims, although automotive OEM require a whole spectrum of products, most of them chromium trioxide coated. In one case passivation by chromium trioxide is explicitly required.

5.5 Nickel free decorative plating on brass for sanitary applications with trivalent chromium

Brass cast faucets, fittings etc. usually are coated by successive layers of nickel and chromium. The German Environment Agency maintains a list of substrates and materials (drinking water hygienic suitable metallic materials) which, following an approved testing method, meet the binding requirements for hygiene and are therefore allowed to be used in contact with drinking water (UBA, 2018). For nickel and chromium, the German drinking water ordinance (TRINKWASSERVERORDNUNG 2001) defines binding threshold values of 20 µg/l and 50 µg/l, respectively . For metals in contact with drinking water there is a so-called "positive list" maintained by the German Environment Agency. Regarding chromium coats of outer surfaces, it defines additional testing requirements. Furthermore, it states (UBA, 2018) that certification of nickel compliance requires (manual) plugging of parts before coating and conformity with a standard test method (DIN EN 16058).

One German producer of chromium/nickel plated brass cast sanitary armatures is currently implementing a trivalent chromium-based nickel-free process. The process is supposed to be fully implemented and marketable by the end of 2020. (Interview 1)

5.5.1 Process overview

In principal, the process is identical to chromium trioxide-based chromium/nickel plating, but instead of the primary nickel coating a white bronze coating is applied and chrome plating is carried out with chromium sulphate instead of chromium trioxide.

Process parameters for the chrome plating step differ slightly, e.g. a higher bath temperature (50°C instead of 40°C), while pre- and post-treatments are virtually identical, but the trivalent chromium-based process is slightly slower.

Bath temperature is lower for white bronze coating (30°C instead of 60°C) than for Nickel, current is lower (~1 A instead of 4 to 6 A), and especially the manual activity of parts plugging can be dispensed with, which improves process speed remarkably.

5.5.2 Technical Requirements

The following evaluation is based on the interview with the process user. (Interview 1)

Tab. 5.7 Summary of technical properties for trivalent chrome plating of brass on white bronze

Property	Evaluation	
Corrosion resistance	as defined by EN 248 (method: EN 9227) met by 90%	–
Chemical resistance	fulfilled	✓
Wear resistance	fulfilled	✓
Adhesion of coating	fulfilled	✓

Hardness	fulfilled	✓
UV/Light resistance	met by 90%	–
Temperature resistance	fulfilled	✓
Coating thickness	fulfilled	✓
Nickel leaching	fulfilled, no Nickel	+
Geometry	no restriction	✓
Process temperature	no restriction	✓

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

5.5.3 Legal or normative requirements

Mostly relevant is the requirement from the German drinking water ordinance as described above. This was the main reason for the undertaken efforts to change the coating. Due to the exemption of nickel, compliance with food or medical law is expected to be easier as well.

5.5.4 Design requirements

The company's objective was to achieve the same look with the trivalent chromium/white bronze layer system as the chromium/nickel coating. According to the interview partner this objective is nearly fulfilled.

5.5.5 Risk characterisation

Exposure conditions are identical to the chromium trioxide-based process with nickel. Differences result from different use of chemicals. While waiving chromium trioxide and nickel, the following hazardous substances are used in the process:

Tab. 5.8 Hazard classifications of bath components for white bronze/trivalent chrome process

Substance	CAS-No.	Risk	Process
Boric acid	10043-35-3	Repr. 1B (H360FD)	Cr (III)
Dichromium tris(sulphate)	10101-53-8	Acute Tox. 4 (H302), Skin Irrit. 2 (H315), Skin Sens. 1 (H317), Eye Irrit. 2 (H319), Acute Tox. 4 (H332)	
Dicopper oxide	1317-39-1	Acute Tox. 4 (H302), Eye Dam. 1 (H318), Acute Tox. 4 (H332), Aquatic Acute 1 (H400), Aquatic Chronic 1 (H410)	White bronze
Tin methane sulfonic acid	53408-94-9	Acute Tox. 4 (H302), Skin Corr. 1B (H314), Skin Sens. 1 (H317), Aquatic Chronic 2 (H411)	

The described white bronze coating is – in contrast to the “classic” process – free of cyanides, which posed a main obstacle to this Ni alternative. Usage of boric acid poses no additional risk as this substance is in use in the Cr(VI)/Ni process as well.
The process is automated with the baths in a separate hall. Two workers are potentially exposed during maintenance and repair works. Two other workers responsible for fitting the racks are not exposed to the process.
Exposure times are estimated as follows:

- one worker four times a week, 1 h each
- one worker once a week, 4 - 5 h

Protection measures are as follows:

- exhaust ventilation at bath line
- spatial separation of bath line and rack fitting/manual plugging
- personal protective equipment of maintenance workers (masks, eye protection, protective clothing).

5.5.6 Economic and cost issues

In the following some expected costs are summarised (**Tab. 5.9**). All data are relative to the chromium trioxide-based process with regard to chrome plating only, unless stated otherwise.

Tab. 5.9 Summary of expected costs for nickel-free trivalent chrome coating

Cost type	Comparison	Remarks
Performance	+ 10 %	
Process quality/ scrap rate	not yet known	serial suitability end of 2020
Material cost	+ 20 %	analysis instruments
Labour cost	+ 5 %	bath maintenance
Energy cost	+ 5 %	higher temperature
Process cost	+ 20 %	chemicals
Investments	250,000-300,000 €	additional baths (absolute values)
Others	process quality and experience not yet on the same level as for Cr(VI)/Ni	

Costs for ESH, OSH and waste disposal are potentially lower, but as the protection level will be upheld there is no change.

Further aspects which will have an impact on the economic assessment of the alternative were mentioned in the interviews: Service life of products is comparable to chromium trioxide coated products., and the availability of materials is comparable to the Cr(VI)/Ni based process.

Main obstacles for implementation are:

- Larger required space (in implementation phase both processes are run in parallel)
- Missing essential knowledge for process conversion
- Missing customer/OEM specifications
- Competitive disadvantage as long as chromium trioxide process are still authorised

5.5.7 Additional findings

One producer of sanitary products (Interview 2) reports that they are testing the substitution of chromium trioxide by trivalent chromium, but that product quality as well as process stability are far from sufficient. The process is less stable with a higher scrap rate and higher costs both for the process components as well as for maintenance leading to 20 – 30 % higher costs for the total process (including nickel sub coating). The more expensive process on the other hand leads to lower product quality especially with regard to colour stability and corrosion resistance. The latter reduces product life time considerably, especially for professional end users like e.g. hotels where bath cleaning processes occur more often and are more intense than in private homes. Also, they see a problem regarding nickel leaching, which is regulated for products in contact with drinking water as described above.

5.5.8 Conclusion

In the case described in detail the main advantage results from the combined substitution of chromium trioxide and nickel by a trivalent chromium salt and a cyanide-free white bronze. Economic and technical drawbacks of the new process are seen as of lower importance, because they are compensated by the impacts of the resulting nickel free production and a higher over-all efficiency (no more manual plugging). From a health and safety point of view it has to be pointed out that boric acid, which was in use for the nickel plating still remains in the system.

5.6 Physical Vapour Deposition on plastics

PVD was already described in general in section 4.8 as a potential alternative for hard chrome plating in certain fields. In the case of decorative coatings, PVD in general is used in combination with one or more lacquer coatings.

Two systems have been established predominantly in the market, which were considered in this project:

- Lacquer + PVD + lacquer: three-layer system with an initial lacquer applied on the substrate, a subsequent PVD layer and a, typically clear, topcoat,
- Lacquer + PVD: two-layer system with an initial lacquer followed by a PVD layer.

The two systems are not fundamentally different. The following explanations apply to the three-layer system (Interview 31). In section “Additional findings” the main differences of the two-layer system are described (Interview 33).

5.6.1 Process overview

The described coating consists of three layers: one lacquer base coat, one decorative metallic coat and one protective lacquer top coat. The base coat equalises irregularities of the injection moulded plastic substrate. A thin metallic film is deposited using PVD vacuum sputter technology. On top another lacquer coating is applied, which is durable, stable and protective.

Conditions for paintworks are 23°C, 60 rel.% humidity. Process time is about 50 min. Clock rate is 70-90 seconds per rack, resulting in an annually throughput of >200,000 m^2. Temperature is maintained below 80° C for all process steps.

The process poses an alternative for all decorative galvanic coatings on plastics (mostly in chrome optics). Branches are automotive, sanitary armatures, household goods and aerospace. Products are car interiors as well as exterior attachments, shower head, casings for razors, toothbrushes, or plane interiors.

5.6.2 Technical Requirements

The process has approvals of several major automotive OEMs, the tests for which exceed the requirements listed here.

Tab. 5.10 Summary of technical properties of PVD plastic coating process

Property	**Objective**	**Evaluation**	
Corrosion resistance	Depends on use case	All kinds of corrosion tests in the automotive industry have successfully passed (depending on the metals used in the PVD process). However, with a highly corrosion-resistant surface, the brightness is lower by about 2 to 4 points.	✓
Chemical resistance	Granted approval of automotive industry	System has passed OEM approvals for the automotive sector.	✓
Wear resistance	Wear resistance as such is less important than micro scratch resistance	Wear resistance has been approved for the automotive interior, exterior and sanitary industry.	✓
Adhesion of coating	Higher adhesion than galvanic coatings	OK	✓
Hardness	No requirement		
UV/Light resistance	Prevents the system from long-term degradation or yellow-ng	OEM requirements met (Florida, Arizona, and Kalahari exterior test)	✓
Temperature resistance	Depends on plastic substrate	Highly resistant to temperature changes from -40°C to +80°C.	✓
Coating thickness	PVD layer: 0.2 µm		✓
Nickel leaching	No requirement		
Geometry	3D-Coating	In principle: Part size restricted by size of vacuum chamber.	-

+: exceeding ✓: comparable –: constraints/not meeting criteria
0: not comparable

5.6.3 Design Requirements

All relevant requirements, esp. the metallic look are met. Also, matte chrome look as well as darker shades is possible with the process. Lacking “cool touch”, which has long been seen as a major drawback of lacquer coatings is no longer a requirement according to the interview partner. One advantage of the process is the ability to create radar and light transparent surfaces, which can also act as capacitive sensors ("capsense") as well as other sensor types.

5.6.4 Legal or normative requirements

There are applications for plastics parts in permanent skin contact e.g. hearing aids. Tests regarding food regulations have not been done. End-of-life vehicle directive regarding recycling is fulfilled (thin metal coat).

5.6.5 Economic and Cost Issues

Throughput is described as being less than one hour with less than 15% scrap rate. Regarding work costs as well as material costs the process is described to be neutral to chrome plating (PVD layer cheaper, UV lacquers more expensive). Energy costs are lower than in galvanic processes. Investment costs are higher than for a galvanic plant due to the novelty of the process, but degressive effects are expected for the future. The anticipated timeline to install the process is estimated to be 18 months for machine assembling, installation and ramp-up.

Costs for protection measures are lower (closed system). The coating line needs exhaustion and emission control. There are no toxic wastes to dispose of.

General economic aspects like market availability and competition are given as there are several similar processes on the market, although at least for today there is only one process with two lacquer layers.

5.6.6 Risk Characterisation

Exposure during the process is no issue due to closed systems. The only relevant exposure is given during maintenance and on coupling of pipes between, e.g. intermediate bulk containers (IBC) and the plant.

5.6.7 Additional findings

One supplier of a two-layer PVD lacquer system points to the following important aspects (Interview 33):

- Chemicals used are solvent-free UV lacquer, hexamethyldisiloxane (HMDSO) and “REACH compliant metals”; acetone is used as cleaner for the spraying gear
- A two-layer system (base coat + metal layer) fulfils relevant automotive norms regarding corrosion, chemical resistance, wear resistance etc.
- Process time is less than 10 minutes
- Possible size of the coated parts: height < 1.5 m, width < 1.2 m, depth < 0.22 m
- Optic and haptic properties are customer accepted (metallic shine, cool touch)

- Exposure is only relevant for one person during change of tanks (lacquer, acetone, HMDSO), which would be about once a week (lacquer) and about monthly (acetone, HMDSO) for 15 – 30 minutes.
- Performance is 25 m^2/h with a scrap rate below 15%.
- Material and energy costs are below 500 € /h.
- Investment costs for a new plant are about 8,5 m €.
- Annual OSH and environmental costs are < 3,000 € for PPE and below 40,000 € for waste disposal (mixture of lacquer and acetone).
- The plant can be run in three shifts for about 300 days per year with standard maintenance once a week and two major maintenance dates per year (five days each).
- There are two plants in operation. Current production capacity is two plants per year.
- Important implementation aspects are
    - capacity building for change process
    - missing OEM specifications, which take technological differences into account

5.6.8 Conclusions

PVD with its diverse coating materials (e.g. metals or carbon as DLC) can be applied as a substitute for decorative chrome coating where restrictions regarding geometry, material properties or corrosion resistance do not apply. The automotive sector has certified the process for several applications, especially for interior plastic parts. The multiplicity of available materials and colourings in combination with some “new” surface properties like, e.g. radar and light transparency makes the process an interesting alternative.

5.7 Varnishes and films in chrome optics

5.7.1 Process overview

Varnishes

For varnishes in chrome optics, a special paint system is on the market since a few years, which usually consists of three layers. A primer is applied to compensate for unevenness and to improve adhesion (ca. 15 microns). Subsequently, a colour layer is applied in which PVD pigments are dissolved. This layer must have a thickness of 1 µm after drying. The pigments are uniformly aligned and thus give a mirror-like effect by reflection. Finally, a clear varnish is applied as a topcoat, with which the roughness and the degree of matting can be adjusted. Finishes are matte as a high-gloss chrome effects with paint cannot compete in appearance with electroplated surfaces. OEM colours such as Silver Shadow can be realised. The varnish allows transilluminating systems and laser engraving. The paint system consists of metallic PVD pigments and solvent-based PUR coatings, which are sprayed and thermally cured (usually about 30 min drying at 80 °C). UV curing is under development to increase chemical resistance.

In-mould decoration (IMD)

In-mould decoration (IMD) is a technique where a polyester film usually carries a printed image, which is used for the actual decoration of injection-moulded parts. First, the film is guided by a film feeding device between the two tool halves, positioned and fixed with a clamping frame. Subsequently, during closing of the tool the film adapts to the cavity shape. Analogous to the IML technique (see below), under pressure and temperature the plastic melt forms a solid bond with the detaching paint layers. Foil packages with up to 10 coats of paint can be transferred in one process. After cooling the melt and opening the tool, the finished decorated part can be removed, the decoration being automatically peeled off from the backing sheet. Now the feed unit brings the carrier film in position for the next injection cycle. IMD technology is currently used to decorate components made of various plastics such as PP, ABS, PC, ABS/ PC, ASA, SAN, PMMA and PBT.

In-mould-labelling (IML)

For in-mould labelling (IML) printed, formed and cut plastic sheets, so-called labels, are inserted into the cavity of an injection mould by means of a handling device. By applying a vacuum or static charge, the labels are fixed and then back-injected with plastic. By means of heat and pressure, the foils, which are precisely matched to the plastic, weld in the filling and holding pressure phase with the introduced melt to form an end product. The film has a sandwich construction in which a PVD layer lies between two transparent film elements. In the raw state, the film is almost transparent. Only after backprinting of the film a mirrored appearance is obtained. If the black colour is left out in some places, these remain translucent. The process produces gloss and matte chrome colour effects. The surfaces have chrome optics in daylight and are translucent in the dark.

Decorative lacquers and foils in chrome look are used for various applications such as e.g. in the consumer, sanitary and automotive sectors. In 2016 the first varnish systems in chrome look came onto the market. In automotive interiors, the first series applications for new platforms are currently being launched (for example painted air vents in A-Class Daimler, but also at VW, Volvo, Porsche) (Interview 22).

It has to be noted that this technique is applicable only if just visual functionality is required (e.g. small-scale applications) and a lack of cool touch as well as lower resistance are not significant.

5.7.2 Technical requirements

Varnishes and films cannot generally be regarded as substitute for chrome plated plastic surfaces but rather as supplement for specific applications. Main drawbacks are the missing cool touch. Therefore, customers' expectations regarding the haptic impression of metallic surfaces are not met. Also, resistance to wear, scratch and chemicals is lower. Optical properties are good for small painted components, in particular curved components.

The technological properties and their evaluation derived from interviews and literature analysis are summarised in the following table (Interview 22, KOB 2017).

Tab. 5.11 Summary of technical properties of chrome optics varnishes and films

Property	**Evaluation (Interview 1 LF)**		
	Varnish system	**Film**	
Corrosion resistance Chemical resistance Wear resistance Adhesion of coating Hardness	Significantly lower than chrome plated surfaces. Automotive OEM requirements apply to painted surfaces for interior applications e.g. Delivery specification DBL 7384 from Daimler-Benz, TL 226 from VW AG, or Opel standard GMW 14797. Requirements for painted surfaces are met. Releases available.		–
UV-/light resistance	Lower than chrome plated surfaces. Requirements to painted surfaces for interior applications met.		–
Layer thickness	Few µm		√
Nickel leaching	There is no nickel used.		+
Optical properties	High variety of shades possible, matte chrome look can be displayed, but no glossy finish	Cr is transferred to film, high gloss and matt chrome look can be displayed.	√
Haptics	No cool-touch		–
Other properties	Transilluminable, laser marking, capacitive surfaces (no conductivity of the pigments)	Transilluminable, capacitive surfaces	+
Substrates	Conventional plastics can be painted, and a wide range of possible substrates can be used.	IMD: Many substrates suitable. IML: Must be exactly matched to the component.	+
Geometry	Geometry of the components Limits set, pronounced 3D geometries only limited paintability, undercuts, turbulence	3D limitations; works for flat parts, slightly formed parts or parts with large radii.	–
Durability	Paint surface lasts 7-10 years, if not scratched by metal surfaces, UV protection ensures colour resistance in the interior area.		–

+: exceeding √: comparable –: constraints/not meeting criteria
0: not comparable

5.7.3 Design requirements

The strengths of varnishes and films are a high colour variety and integrable special effects such as transmittance or touch functionality. With films both high gloss and matt chrome look can be displayed. However, there are some 3D limitations. The processes are most suitable for flat parts, slightly curved parts or parts with large radii.

5.7.4 Legal or normative requirements

There are no specific legal requirements for the use of varnishes or films for coating processes. The matching of OEM specifications for the coating systems is most relevant e.g. specifications for painted surfaces for interior applications in the automotive industries (e.g. DBL 7384 from Daimler-Benz, TL 226 from VW AG, or Opel standard GMW 14797).

5.7.5 Economic and cost issues

Varnishes
1-component lacquered plastic parts are generally more costly compared to decorative chrome plated parts. However, a 2-3 K component in decorative chrome plating can be replaced by a painted 1K-component, so that the overall costs are comparable. The costs are high due to three subsequent coating operations including drying. The PVD pigments are expensive also. Thermal curing results in high energy consumption. The investment required for a painting line with the same parts throughput is approximately 50% of the capital expenditure compared to a galvanic plant. The reject rates are 20 – 40%, due to the product requirements, which are comparable to a high-gloss finish, where defects and pits in the coating can be seen easily (Interviews 22 and 28). The rejects are not equivalent recyclable but can be fed to a lower value recovery.

Decorative films
With decorative films percentages of production rejects are low and comparable to those in chromium trioxide-based processes. IMD is a mass process which can be cost competitive to chrome plated parts. IML is relatively expensive due to the high costs of film substrates and economically viable only for applications with special requirements (e.g. translucency, touch switches etc.).

5.7.6 Risk characterisation

Varnishes
Multi-component varnishes in chrome optics contain acrylic/polyurethane resin-based binders as well as finely divided metallic reflective pigments (mainly aluminium). Lacquering processes are usually solvent based requiring the respective measures for safety and worker protection. VOC emission levels to the environment shall be controlled and exhaust must be post-treated e.g. by post-combustion of the solvents. In the equipping zone, there are no requirements for respiratory protection, here protective clothing is worn to avoid contamination of components. Lacquering production lines are automated and consist of inlet zone, paint booth and oven for drying/curing. From the finished product no health impairments are to be expected.
In comparison to electroplating lacquering processes use much less toxic chemicals.

Decorative films
Film systems work solvent-free, so special occupational safety measures are not required.

5.7.7 Conclusions

Varnishes and films cannot generally be regarded as substitute for chrome plated plastic surfaces but rather as supplement for specific applications. The use of lacquers and foiling is a complementary process to produce plastic surfaces in metal optics e.g. in car interiors that are not subject to mechanical stress. With regard to feel (cool-touch) and durability, lacquered and coated plastics are clearly inferior to electroplated chromium coatings. Strengths of the processes are high colour variety and integrable special effects such as transmittance or touch functionality. Therefore, a growing demand of such systems can be seen on the market. Some limitations regarding component geometries have to be taken into account e.g. pronounced 3D geometries are not suitable. Varnishes and especially films are generally more expensive than electroplated chromium coatings. However, for certain applications in the automotive sector the processes are already used in series production e.g. air vents of Daimler Benz A-class (Interview 22).

6 Summarising discussion

Plating metals or plastics with chromium trioxide is a technically stable, well established and optimised economic process that can create surfaces displaying a variety of different properties which can fulfil multiple technical and aesthetical requirements at the same time.

In this survey, information was to be gathered regarding the technical and economic feasibility of alternatives to the use of chromium trioxide for functional and decorative chrome plating in order to be able to determine their potential to substitute chromium trioxide and to assess their technical or economic limitations in the respective application areas. As an extension to the initial project scope alternatives to chromium trioxide-based etching of plastics were analysed as well. The analysis of the socioeconomic impact of using alternatives to chromium trioxide-based processes, however, was not within the scope of the study.

Based on results of published “analyses of alternatives” from REACH authorisation applications, current literature and the outcomes of a workshop on the substitution of chrome trioxide (organised by BAuA) several promising alternative processes could be identified, which were evaluated in more detail based on expert interviews.

Functional chrome plating

One important outcome was that until today no one-to-one replacement to chromium trioxide has been discovered for functional chrome plating, which meets all requirements. However, the identified alternatives are technically and economically feasible sometimes in one or few uses only, but sometimes even in larger areas of application. The results are summarised and discussed in the following.

Although a variety of possible alternatives are described in the literature and AoA of applications for authorisation under REACH, only a limited number of methods are of practical importance from an industry perspective. The present report focuses on alternatives to which empirical values from industrial practice could be collected in interviews with experts in the field and practical users.

These identified potential alternatives for hard chrome plating with chromium trioxide are:

- Laser cladding (extreme high-speed laser material deposition)
- Case hardening processes like nitriding and nitrocarburising
- Thermal spraying and HVOF
- Physical vapour deposition
- Trivalent chromium based hard chrome plating

Some of the alternatives are long-established methods with known strengths and weaknesses. However, there are developments in these processes that expand the fields of application and specifications.

Extreme Highspeed Laser Deposition (EHLA) is a special variant of laser cladding. It has been in industrial use since 2017 in the field of hydraulic cylinders for offshore applications, where hard chrome coatings are not a viable alternative.

The process is restricted to rotational symmetric components. It extends the application possibilities of laser cladding to large parts with small layer thicknesses and also overcomes the problem of cracks in the coatings due to thermal stress. The reworking effort is lower due to the precisely controllable layer thickness. The strengths of the process are highly adhesive coatings through a metallurgical bond to the base material and optimised wear and corrosion protection through dense coatings as well as targeted selection of the coating alloys. Another advantage is the integrability in production lines due to the relatively low space requirements. Just like conventional laser cladding EHLA can be used as repair technology for worn out components. Investment costs are comparable to those of thermal spraying. From a health and safety point of view it is a benefit that no processing chemicals or solvents are used. Only the coating material is applied as powder and is physically treated by laser radiation. However, the resulting welding fumes, which contain inhalable dusts and toxic substances, must be taken into account. The composition of the welding fume corresponds approximately to the chemical components of the filler material. Protection measures are comparable to conventional laser cladding. Currently, the process is being investigated for other applications, in which rotationally symmetric components with high wear and corrosion protection requirements have to be sealed by thin protective layers e.g. for paper or printing rolls, possibly also brake discs in the car. EHLA is no one-to-one replacement for chromium trioxide-based coatings, but serves as an alternative for applications where special property profiles are required.

Case hardening processes like salt bath nitriding, salt-bath nitro-carburising or plasma nitriding are no coating processes but heat treatments that diffuse nitrogen (or nitrogen and carbon in the case of nitro-carburising) into the surface of a ferrous metal. Products are e.g. piston rods, engine valves (non-automotive) or hydraulic manifolds. The processes have been marketable for many years. Their major strength is the high and durable wear resistance resulting in relatively long service times, which can counter higher process costs as described exemplarily for a plasma-nitriding application. Higher corrosion resistance can be achieved by an additional oxidation step (e.g. “oxi-nitro-carburising”), but which may also not be sufficient for some applications. Additional PVD or DLC coating is another option, but which adds significantly to the costs. Investment costs were described to be comparable to new chrome lines, but it has to be taken into account that this technology differs significantly from hard chrome galvanising so that existing lines cannot be reused. The processes are restricted to nitrable ferrous base materials. Due to the relatively high processing temperatures they are also restricted to substrates of sufficient thermal resistance. Health and safety issues resulting from high process temperatures and the applied chemicals have to be taken into account. Toxic cyanides are used or formed intermediately.

Thermal spraying describes a bundle of coating techniques where melted materials are sprayed onto a surface. Two varieties have been inspected: high velocity oxy-fuel (HVOF) and thermal spraying with inductive coating. They have in common that they operate along line of sight only and that they are restricted to rotationally symmetric geometries. Internal machining is restricted as well. In general, hardness and wear resistance are higher than for hard chrome surfaces, but very high hardness can pose a problem for post-processing. Costs are described to be several times higher than comparable hard chrome coatings, but this can be countered by longer service times of the coated products.

While it is possible to reduce surface roughness by inductive surface melting, necessary smoothness ($R_{max} \leq 0.025$) for e.g. printing presses or high-quality plastic films, is still not achieved. Coated products are mostly piston rods for hydraulic cylinders or other uses.

Vacuum technologies like PVD are applied where very high hardness (up to 4,000 HV) and high wear resistance but no corrosion resistance is required. PVD is a mature technology for the production of e.g. machine parts, cutting tools or forming dies with thin but wear resistant surfaces with low friction coefficients. Post-treatments can be avoided as the deposited layers follow the part geometry very closely. Process temperature is higher than for chrome coating, which reduces the base material variety. The low layer thickness poses high demands on the base material as it is not self-supporting. Furthermore, the process offers no repairing options with geometric restoration as excess coating with subsequent machining is not possible. The applicability is also restricted by the size of the vacuum chambers. Therefore, very large parts cannot be treated. Investment costs have been described as higher (20 – 30%) than for a comparable hard chrome line, but it has to be taken into account that PVD is a completely different technology and a reuse of existing plants is not possible.

Compared to other alternative processes, substitution of chromium trioxide with a trivalent chromium electrolyte comes closest to a drop-in replacement. But in detail the process differs significantly. The identified trivalent chromium-based processes rely on a nickel sub coating in order to achieve better corrosion protection. In cases where better hardness is needed an additional heat treatment step has to be included. Also, the bath chemistry is more complex as, due to the different chemical deposition mechanism, complexing agents and buffer substances (in one case boric acid) have to be used. As the deposition is cationic, ion exchangers have to be utilised in order to minimise concentrations of foreign metal cations and therefore co-deposition of these metals. This also requires more expensive anode materials as mixed metal oxide anodes have to be used. Interview partners reported of supply problems for these anodes. Although the processes were described in some cases to be in industrial use (e.g. by a hydraulic cylinder manufacturer), some interview partners reported of inadequate test results, describing the processes as not yet marketable. No regular user of at least one of the trivalent chromium based hard chrome processes could be identified and interviewed. This would be necessary in order to reach a final conclusion. One process supplier emphasised that applications had to be implemented on a case-by-case basis in order to find optimal process conditions and outcomes. Technical problems were seen especially because of the additional heat treatment, which leads to temperatures that can be detrimental for coated parts, especially if size accuracy is a relevant feature. From a health and safety point of view at least one of the described trivalent chrome processes introduces another hazardous component into the bath chemistry e.g. boric acid, identified as SVHC under REACH, is used as a buffer. But it has to be mentioned that the process suppliers is preparing a new variant with a different buffer substance. A further obstacle results from the presence of complex forming agents within the bath chemistry, because this leads to higher demands on waste water treatment. On the one hand due to water protection requirements these complex agents must be removed from the waste water stream, on the other hand the necessary precipitation of metal ions is impeded by complex forming substances. Economically the above-mentioned aspects are also seen to add up to higher process costs. Relevant investments result from additional or even new tanks, different anodes, necessity of ion exchangers and additional waste water treatment facilities. Alternatively, process steps and facilities needed only for the processing of chromium trioxide e.g. Cr(VI) reduction in waste water, occupational safety measures, could be dispensed with. But this is not seen to be compensating. Especially as there are still some hazardous chemicals like nickel or boric acid in the process, a significant reduction regarding OSH measures or an improvement in occupational health for the workers is not seen by current users of chromium trioxide. As these obstacles were seen combined with higher overall costs, especially because of higher requirements regarding bath sensitivity and therefore maintenance, all interviewed users of chromium trioxide stated that the solutions are not yet as technically and economically feasible for their purposes.

Decorative chrome plating

Although the deposition of thinner chromium surfaces on metals or plastics from chromium trioxide is generally referred to as “decorative chrome plating” it has to be appreciated that these surfaces in most cases serve important additional functions besides purely aesthetic aspects e.g. wear resistance.

The identified potential alternatives for these processes are:
- Decorative plating on plastics with trivalent chromium
- Chromium trioxide free etching for plating of plastic
- Decorative plating on steel with trivalent chromium
- Nickel free decorative plating on brass for sanitary applications with trivalent chromium
- Physical Vapour Deposition on plastics
- Varnishes and films in chrome optics

The most general applicable alternative for decorative chrome plating on plastic with chromium trioxide is the use of trivalent chromium electrolytes. Trivalent chrome plating can be described as industrially mature process which fulfils the requirements for almost all known applications to a great extent, including decorative plating on plastics for the automotive industry. However, the alternative still uses hazardous chemicals, like boric acid, identified as SVHC under REACH. Furthermore, decorative plating on plastics requires an etching process, which usually uses chromic acid (derived from chromium trioxide). Alternatives for chromium trioxide in etching processes are not as mature as the trivalent plating electrolytes. Further research and development efforts are required to adapt hexavalent chromium-free solutions for existing plating production lines. Therefore, with respect to environmental, health and safety aspects, the application of trivalent chromium as an alternative is not yet a substantial progress at the present stage, but ongoing work and efforts in this field could pave the way for plating solutions completely avoiding hazardous chemicals in the future. It also has to be emphasised that substitution of chromium trioxide is connected with some financial and administrative burdens for the affected companies. The extent of efforts for investments, adaptations of process lines and administration for official permissions depends on individual conditions of the respective production facility. From an economic perspective, processes using trivalent chromium are in principal competitive, especially for new plants. There is a consensus within the branch of industry that a shift from chromium trioxide to trivalent chromium will not have a big influence on the costs of the whole coating process and the applications.

According to a statement of ZVO most of the involved companies will transit to trivalent plating processes within the next four years.

There are other alternatives for decorative plating on plastics like PVD coatings, varnishes as well as foils in chrome optics. These alternatives are also industrially mature but cannot be regarded as one to one substitutes for chrome platings. Each alternative has advantages and shortcomings with regard to technical properties, geometrical prerequisites and costs. The technical and economic feasibility of the alternatives has to be evaluated on a case-by-case basis for the relevant applications, depending on the required properties and performance of the coatings.

Decorative chrome plating on steel in general is also possible with trivalent chromium electrolytes. But the obstacles as described for trivalent hard chrome plating are relevant for this application as well. Even where the decorative properties are in the foreground some technical properties like wear resistance are essential. In one case a trivalent chrome coating was not sufficiently wear resistant for moving chrome coated parts of high-quality furniture fittings (e.g. adjustable tables or chairs, kitchen cabinet drawers). But there is also at least one furniture manufacturer who has completely abandoned chromium trioxide-based plating for his office products. The process therefore in general can be evaluated as technically and economically feasible, but each substitution process still has to be evaluated on a case-by-case basis. Another aspect of this process is, that the different bath chemistry opens up the application of a new colour spectrum due to the variety of (mostly darker) colour shades that can be produced by modified bath mixtures.

Regarding the application of trivalent chrome coats for sanitary applications with brass as base material, diverging information was found. One interview partner who was actively testing a trivalent chromium process for high-end sanitary products stressed quality problems especially regarding colour stability, corrosion protection, product lifetime and possible higher nickel leaching. It was also pointed to the lower process stability with significantly higher costs (including for maintenance and additional materials and installations e.g. ion exchangers). Another company, likewise in the process of substituting chromium trioxide, attempts to replace simultaneously the underlying nickel coating for a cyanide free white bronze subcoating. This combination was making the substitution profitable as nickel is regulated by the drinking water ordinance and high efforts (with corresponding work costs) have to be made to conform with the legal nickel regulation. Although most of the implementation obstacles were confirmed as well, the opportunities opened by dispensing with both nickel and chromium trioxide clearly stood in the foreground.

These findings can be summarised as follows:

- As surfaces deposited from chromium trioxide electrolytes serve multiple purposes in the product, it is challenging to find a one-to-one replacement or single alternative technology which can fulfil all requirements in different areas of application at once. This can pose a relevant economic problem for small or medium sized electroplating subcontractors, who cannot afford to provide several different alternative processes, but would have to in order to serve their diverse clients' needs. In the scope of this survey – without claiming completeness – several applications were identified where currently none of the discussed alternatives are technically feasible.

- The plating process from chromium trioxide is well understood, robust and inexpensive in contrast to plating with the most promising potential drop-in replacement: trivalent chromium plating. Major drawbacks of this alternative are lower bath stabilitiy (leading to stricter process monitoring requirements), the use of other SVHCs or hazardous substances (which bears potential to be REACH-regulated as well), challenging wastewater management and related higher costs. Especially for functional chrome plating serious optimisation is still necessary. However, for decorative chrome plating, progress has been made to stably and competitively apply trivalent chromium.
- A fundamental obstacle for the implementation of alternative processes is the workload of existing equipment and therefore no leeway for parallel operation of alternatives.
- Substitution activities that are part of a larger innovation strategy regarding the overall processes (or products) are more promising than activities that only deal with the replacement of one hazardous chemical.
- However, there is a growing number of successful substitution activities. Also, providers of alternative processes are intensifying their efforts to increase their market shares.

7 Outlook

In summary, the development of alternatives for hexavalent chromium plating has made significant progress in recent years and significant market share in the area of decorative chrome plating has been gained. However, the user industry has still pointed out technical deficiencies of alternative methods especially regarding functional chrome plating, which are unacceptable for the respective applications. The practicability of a switch to alternatives depends on the respective requirements of the industrial applications, which have to be checked on a case-by-case basis.

Within the scope of this project it became obvious that in general there are no one-to-one replacements that can substitute all intended properties of a chromium surface deposited from chromium trioxide. Therefore, substitution is often driven by overarching innovation objectives where a combination of effects, e.g. increased safety at work, resource-saving production, improvement of product properties etc., is targeted.

Looking ahead it has to be noted that the revision process of the BAT document “Surface Treatment of Metals and Plastics” (European Commission 2006) regarding Directive 2010/75/EU on industrial emissions (integrated pollution prevention and control) will start in 2020. It is to be expected that developments regarding the substitution of chromium trioxide will also be considered.

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Conducted Interviews

Tab. 8.1 Overview on conducted interviews

No.	Alternative(s)	Institution
1	Cr(III) based decorative coating	Manufacturer of sanitary equipment
2	Cr(III) based decorative coating	Manufacturer of sanitary equipment
3	Cr(III) based decorative coating	Manufacturer of store fixtures, furniture fittings and other steel parts products

No.	Alternative(s)	Institution
4	Cr(III) based decorative plating on plastics, Cr(VI) free etching, Cr(III) based functional chrome plating	Provider of plating chemicals, the company offers trivalent chromium electrolytes for functional and decorative plating
5	Cr(III) based functional chrome plating	Provider for functional Cr(III) based plating
6	Diverse alternatives for hard chrome plating	Contract coating company (hard chrome plating)
7	Diverse alternatives for hard chrome plating	Pressure casting and surface coating company (decorative chrome plating)
8	Diverse alternatives for hard chrome plating	Metal finishing company (hard and decorative chrome plating)
9	Diverse alternatives for decorative chrome plating	Tool producers
10	Diverse alternatives for hard chrome plating	Manufacturer of textured press plates for furniture and flooring industries
11	Diverse alternatives for hard chrome plating	Contract coating company (hard chrome plating)
12	Diverse alternatives for hard chrome plating	Contract coating company (hard chrome plating)
13	EHLA	Research institution that invented the EHLA process. The institute has cooperation projects with companies to implement EHLA for industrial processes
14	EHLA	Manufacturer of hydraulic cylinders, the company has implemented the EHLA process in their production line since 2017
15	EHLA	Manufacturer of lasers and turn key systems for EHLA, the company runs an application centre for the EHLA process
16	EHLA	Surface technology company with a wide range of applications
17	Thermal spraying	Thermal spraying company
18	EHLA	Mechanical and plant engineering company
19	Thermal spraying	Mechanical and plant engineering company
20	Thermal spraying	Manufacturer of aircraft landing gear
21	Thermal spraying	Surface technology company with a wide range of applications
22	Varnishes and films in chrome optics	Producer of plastic components and finishes, the company applies varnishes and films for decoration of plastic
23	Salt bath nitriding	Surface Hardening Company
24	Plasma nitriding	Plant engineering and surface treatment company
25	Nitriding	Surface hardening company
26	Salt bath nitrocarburising	Provider of nitriding and other surface treatment processes

No.	Alternative(s)	Institution
27	DLC/Nitriding	Provider of Heat Treatment Technology as well as Plasma and PVD coating equipment
28	Decorative Plating on Plastics	Plating company, the company focuses on plating of plastics for the automotive industry
29	Cr(III) based decorative plating on plastics, Cr(VI) free etching, Cr(III) based functional chrome plating	Provider of plating chemicals, the company offers trivalent chromium electrolytes for functional and decorative plating as well as chromium trioxide free etching solutions for pre-treatment of plastics
30	Cr(III) based decorative plating on plastics, Cr(VI) free etching, Cr(III) based functional chrome plating	Provider of plating chemicals, the company offers trivalent chromium electrolytes for functional and decorative plating as well as chromium trioxide free etching solutions for pre-treatment of plastic
31	PVD	Plant engineering and surface treatment company
32	PVD	Provider of PVD and other surface treatment processes
33	PVD	PVD/ lacquer application plants and services
34	PVD	Surface treatment with PVD

List of Tables

List of Abbreviations

AoA	Analysis of Alternatives
BAT	Best Available Technique
BAuA	German Federal Institute for Occupational Safety and Health
CVD	Chemical Vapour Deposition
DLC	Diamond-like Carbon
EASA	European Union Aviation Safety Agency
ECHA	European Chemicals Agency
EHS	Environmental Health and Safety
HRC	Rockwell Hardness C (force: 1,372.931 N)
HV	Vickers Hardness
IBC	Intermediate Bulk Container
IMDS	International Material Data System
IML	In-mould-labelling
m €	Million Euros
MMO	Mixed Metal Oxides
NSST	Neutral Salt Spray Test
PVD	Physical Vapour Deposition
REACH	European Union Regulation 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals
RTCA	Radio Technical Commission for Aeronautics
SAM	Self Assembled Monolayer
SVHC	Substance of Very High Concern
TRL	Technical Readiness Level

Appendix

Sectors and product categories of functional chrome plating

Tab. A.1 Sectors and product categories of functional chrome plating as described in the applications for authorisation

Consultation No.	Sector/product category
0032-02	Aerospace
	Automotive
	General Engineering
	Steel
	Manufacture of Printing Equipment
	Metal Precision Parts
0127-01	Engine Valves for Automotive Applications
0033-01	Heavy industrial Items (of paper machines, vehicles, marine equipment, textile machines etc.) e.g. valves, riddle drums
0050-01	piston rings for two-stroke and four-stroke large bore engines as applied in the industrial sectors Construction & Industry, Power Generation, Railway and Maritime
0051-01	valves for the use in petrol and diesel engines for light- and heavy duty vehicles
0052-01	piston rings for automotive engines as applied in the segments light vehicle petrol, light vehicle diesel, middle range diesel and heavy duty.
0055-01	Aerospace
	Automotive
	General Engineering
	Steel
	Manufacture of Printing Equipment
	Metal Precision Parts
0057-01	military armament steels parts which are thermomechanically stressed and in contact with oxidising gas at high temperature, so as to ensure a thermal barrier with high melting point, resistance to wear and oxidation associated with weapons as well as resistance to impact and atmospheric corrosion.
0057-02	military armament parts in order to ensure surface hardness, resistance to atmospheric corrosion, abrasive wear resistance and friction coefficient for parts in relative movement.
0057-03	steel weapon barrel designed for military use, to ensure, during the whole gun barrel service life, stealth, erosion, corrosion and high temperature resistances in the condition of uses.
0064-02	only general applications named
0064-03	only general applications named
0064-04	only general applications named
0066-01	aerospace applications for civil and military uses, comprising coating of new components for aircraft engines as well as

Consultation No.	Sector/product category
	maintenance, repair and overhaul work on aircraft engine components
0067-01	mechanical and electromechanical cylinders, cam- and padlocks, electromechanical lock cases and architectural hardware
0068-01	work rolls used in the steel and aluminium industry
0069-01	Filament guiding parts, special work pieces (e.g. automotive, textile and carbon processing industry)
	Feed rolls (e.g. sheet metal industry) Rolls (e.g. sheet metal, steel and foil industry) Rolls and rollers (e.g. printing industry)
	Coating of injection moulding tools (e.g. plastic industry) Coating for extrusion tools
	Interior and exterior coating of highly strained parts Interior coating of transport pipes (e.g. oil, petroleum, chemicals industry.)
	Interior coating of continuous casting moulds Coating of forming tools
0070-01	military small- and medium-calibre firearms barrel bores and auxiliary parts subject to thermal, mechanical and chemical stresses, in order to provide hardness, heat resistance and thermal barrier properties, as well as corrosion resistance, adhesion and low friction properties.
0070-02	civilian firearms barrel bores and auxiliary parts subject to thermal, mechanical and chemical stresses, in order to provide a low friction coefficient as well as heat, corrosion and wear resistance properties.
0092-01	only general applications named
0095-02	Aerospace
	Automotive
	General Engineering
	Steel
	Manufacture of Printing Equipment
	Metal Precision Parts
0100-01	Aerospace
	Automotive
	General Engineering
	Steel
	Manufacture of Printing Equipment
	Metal Precision Parts
0119-01	piston rods for automotive and rail applications

Sectors and product categories of decorative chrome plating

Tab. A.2 Sectors and product categories of decorative chrome plating as described in the applications for authorisation

Consultation No.	Sector/product category
0032-03	Automotive Sector Interior
	Automotive Sector Exterior
	Cosmetic Sector
	Furniture
	General Engineering
	Store Construction
	White Goods Sector
0034-01	Sanitary Products
0071-01	Plastics for Automotive Applications
0095-03	Sanitary Sector
	Automotive Sector
0114-01	Sanitary Products

Potential alternatives for functional chrome plating

The following Table A.3 gives an overview of potential alternatives as were analysed in the AoA documents with attribution to the respective application für authorisation.

Tab. A.3 Potential Alternatives for functional chrome plating with attribution to applications for authorisation

Consultation No.	Identification in the AoA
0032-02	Electroless nickel plating
	Nickel electroplating
	Case hardening (carburising, carbonitriding, cyaniding, nitriding, boronising)
	Thin and thick chemical vapour deposition (CVD)
	Nanocrystalline cobalt phosphorus alloy coating
	High velocity thermal process
	Trivalent hard chromium
	Physical vapour deposition
	Plasma spraying
	General laser and weld coating technology
	Stainless steel
	Thermal spray coatings
0127-01	XXXX electroplating[3]
	Nitriding
	No Coating

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[3] "XXXX" stands for blanked out text.

Consultation No.	**Identification in the AoA**
	High Velocity Oxygen Fuel spraying
	Chemical Vapour Deposition
	Physical Vapour Deposition
	Trivalent Hard Chrome
0033-01	Trivalent chromium based functional plating
	Thermal sprays
	Electroless plating
	Vapour deposition methods
0050-01	High velocity oxygen fuel spraying (HVOF)
	Physical vapour deposition (PVD) – CrN-based
	Hydrogen-free thick DLC coatings
	Thermal spraying: Plasma
	Case hardening: nitriding/nitrocarburising
	Wire flame spraying
	Chemical vapour deposition (CVD) – thin DLC coatings
	Trivalent hard chromium deposition
0051-01	Nitriding (bath, plasma and gas nitriding)
	Plain valves
	Electroless plating
	Nickel electroplating
	Case hardening: carburising, cyaniding, boronising
	Chemical vapour deposition (CVD)
	High velocity thermal process
	Trivalent hard chromium
	Physical vapour deposition (PVD)
	Plasma spraying
	Thermal spray coatings
	Nanocrystalline cobalt phosphorus alloy coating
0052-01	Case hardening: nitriding/nitrocarburising
	High velocity oxygen fuel spraying (HVOF)
	Physical vapour deposition (PVD) – CrN-based
	Hydrogen-free thick DLC coatings
	Chemical vapour deposition (CVD) – thin DLC coatings
	Wire flame spraying
	Plasma spraying
	Trivalent hard chromium deposition
0055-01	Electroless nickel plating
	Nickel electroplating
	Case hardening (carburising, carbonitriding, cyaniding, nitriding, boronising)
	Thin and thick chemical vapour deposition (CVD)
	Nanocrystalline cobalt phosphorus alloy coating
	High velocity thermal process
	Trivalent hard chromium
	Physical vapour deposition
	Plasma spraying

Consultation No.	Identification in the AoA
	General laser and weld coating technology
	Stainless steel
	Thermal spray coatings
0057-01	Nickel electroless plating
	Nickel electroless plating with Poly Tetra Fluoro Ethylene (PTFE)
	Atmospheric Plasma Spraying - MCrAlY // Refractory oxides
	Nitrocarburation with post oxidation
	Physical Vapour Deposition (PVD)
	Hard Chrome by Trivalent Chromium
0057-02	High phosphorus electroless nickel
	Atmospheric Plasma Spraying: MCrAlY // refractory oxides
	High phosphorus electroless nickel + PTFE
	Nitrocarburising with post-oxidation treatment
	Physical Vapour Deposition (PVD)
0057-03	Black nickel electroless plating
	Electrolytic black zinc nickel
0064-02	Cr(III) based plating
	Thermal spraying
	DLC coatings
	Heat treatment/hardening
	Laser methods and build-up welding techniques
	Currentless nickel plating
0064-03	Cr(III) based plating
	Thermal spraying
	DLC coatings
	Heat treatment/hardening
	Laser methods and build-up welding techniques
	Currentless nickel plating
0064-04	Cr(III) based plating
	Thermal spraying
	DLC coatings
	Heat treatment/hardening
	Laser methods and build-up welding techniques
	Currentless nickel plating
0066-01	Thermal spray coatings
	Nickel and nickel alloy electroplating
	Thick chemical vapour deposition (CVD)
	Nanocrystalline cobalt phosphorus alloy coating
	Electroless nickel plating
	Case hardening: carburising, carbonitriding, cyaniding, nitriding, boronising
	Trivalent hard chromium
	Physical vapour deposition
	General laser and weld coating technology
0067-01	trivalent chromium electroplating
	Nickel based electroplating

Consultation No.	Identification in the AoA
	Cobalt based electroplating
	Electroless plating
	Thermal spraying
	Physical vapour deposition
	Chemical vapour deposition
0068-01	Forged steel work roll grades (without chromium coating)
	Chrome coating based on a chromium trioxide free deposition process
	Electroless plating
	Nickel and nickel alloy plating
	Nano-crystalline cobalt phosphorous alloy coating
	High velocity thermal process
	Electro-Discharge Coating (EDC)
0069-01	Trivalent hard chromium
	Nickel electroplating
	Alternative texturing methods
	Nanocrystalline cobalt phosphorus alloy coating
	High velocity thermal process
	Plasma spraying
	General laser and weld coating technology
	Stainless steel
	Thermal spray coatings
	Copper electroplating
	Electroless Plating
	Case hardening: carburising, carbonitriding, cyaniding, nitriding, boronising
	Chemical vapour deposition (CVD)
	Physical vapour deposition (PVD)
	Ion Implantation
	Iron-phosphor coating
	Plastic coating
	Chromium III ionic liquids
	Cobalt-tin plating
	Zinc-based materials (zinc, zinc-tin, zinc-aluminium, zinc-nickel based passivation, non-electrolytic zinc plating)
0070-01	High Velocity Oxygen Fuel
	Thermochemical surface modification (Nitriding)
	Ni and Ni alloy coatings (Ni-B, Ni-P; Ni-W)
	deposition of chromium from trivalent chromium electrolyte
	Physical/Chemical Vapour Deposition
0070-02	Thermochemical surface modification (Nitriding)
	deposition of chromium from trivalent chromium electrolyte
	Physical/Chemical Vapour Deposition
0095-02	Electroless nickel plating
	Nickel electroplating
	Case hardening (carburising, carbonitriding, cyaniding, nitriding, boronising)

Consultation No.	Identification in the AoA
	Thin and thick chemical vapour deposition (CVD)
	Nanocrystalline cobalt phosphorus alloy coating
	High velocity thermal process
	Trivalent hard chromium
	Physical vapour deposition
	Plasma spraying
	General laser and weld coating technology
	Stainless steel
	Thermal spray coatings
0100-01	Electroless nickel plating
	Nickel electroplating
	Case hardening (carburising, carbonitriding, cyaniding, nitriding, boronising)
	Thin and thick chemical vapour deposition (CVD)
	Nanocrystalline cobalt phosphorus alloy coating
	High velocity thermal process
	Trivalent hard chromium
	Physical vapour deposition
	Plasma spraying
	General laser and weld coating technology
	Stainless steel
	Thermal spray coatings
0119-01	Case Hardening Process (Nitrocarburisation)
	Physical Vapour Deposition (PVD) Process
	Chemical Vapour Deposition (CVD) Process
	Trivalent Hard Chrome Plating Process
	High Velocity Oxygen Fuel (HVOF) Spraying Process
	Chemical Coating Process
	Chemical Coating Process
	Powder Coating Process
	Sol-Gel Process
	Lubricant Varnish Coating Process
	Galvanic Coating Process
	Synthetic Material-Teflon-Coating Process
	Zinc - Diffusion Process with Passivation
	Change of base material (stainless steel)

Potential Alternatives for decorative chrome plating

The following Table A.4 gives an overview of potential alternatives as were analysed in the AoA documents with attribution to the respective application für authorisation.

Tab. A.4 Potential Alternatives for decorative chrome plating with attribution to applications for authorisation

Consultation No.	Identification in the AoA
0032-03	Trivalent chromium plating
	PVD based processes: Lacquer + PVD + Lacquer and PVD metal
	Satin & black anodised aluminium
	Chromium free electroplating: multi-component coating systems (Cu, Sn, Zn, Ni, Co), gold and platinum electroplating, zinc electroplating
	Wet lacquering
	CVD: Chemical Vapour Deposition
	DLC: Diamond Like Carbon
	Electroless Nickel plating
	Powder Coating
	Stainless steel (alternative substrate)
0034-03	Trivalent chromium plating
	PVD based processes: Lacquer + PVD + Lacquer and PVD metal
	Satin & black anodised aluminium
	Wet lacquering
	CVD: Chemical Vapour Deposition
	DLC: Diamond Like Carbon
	Stainless steel (alternative substrate)
0064-02	trivalent chromium based coating
	PVD Cr
	Painting
	Currentless nickel plating
0064-03	trivalent chromium based coating
	PVD Cr
	Painting
	Currentless nickel plating
0064-04	trivalent chromium based coating
	PVD Cr
	Painting
	Currentless nickel plating
0071-01	Trivalent chromium plating (+ a chromium trioxide free etching pre-treatment)
	PVD-based processes
	Wet lacquering
	Electroless Nickel plating
0092-01	trivalent chromium based coating
	PVD Cr
	CVD

Consultation No.	Identification in the AoA
	Painting
0093-01	trivalent chromium based coating
	Wet lacquering
0095-03	Trivalent chromium electroplating
	PVD based processes: Lacquer + PVD + Lacquer and PVD metal
	Satin & black anodised aluminium
	Chromium free electroplating (zinc electroplating, multi-component coating system of copper, tin, zinc, nickel, cobalt; gold and platinum electroplating)
	Wet lacquering/colour painting
	CVD: Chemical Vapour Deposition
	DLC: Diamond Like Carbon
	Electroless nickel plating
	Powder coating
	Stainless steel (alternative substrate)
0114-01	Trivalent chromium electroplating
	PVD Chrome
	Lacquer + PVD Metal – (Lacquer)
	Satin & black anodised aluminium
	Wet lacquering/colour painting
	CVD: Chemical Vapour Deposition
	DLC: Diamond Like Carbon
	Stainless steel (alternative substrate)
0114-02	Trivalent chromium electroplating
	PVD Chrome
	Lacquer + PVD Metal – (Lacquer)
	Satin & black anodised aluminium
	Wet lacquering/colour painting
	CVD: Chemical Vapour Deposition
	DLC: Diamond Like Carbon
	Stainless steel (alternative substrate)