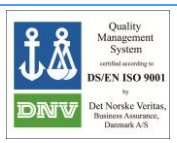
Analysis of alternatives to nickel plating in decorative coatings

In cooperation with Jean-Jacques Duprat

Nickel Institute
Final Report, February 2013

This report has been prepared under the DHI Business Management System certified by DNV
Quality Management ISO 9001


Approved by
21-02-2013 X  Approved by Signed by: Jens Tørsløv

Analysis of alternatives to nickel plating in decorative coatings

Prepared for **Nickel Institute**

Represented by **Ms France Capon**

Illustration text

Project No	11809838
Classification	Confidential

Authors	Jens Tørsløv
	Jean-Jacques Duprat
	Peter Kortegaard

Contents

1 Summary 1

2 Introduction 2

3 Objectives 3

4 Methods and approach 3

5 Nickel used in decorative coatings 4

5.1 Technical functions and requirements 4
5.1.1 Various types of nickel and nickel alloy layers of the decorative industry 5
5.1.1.1 Nickel prior chromium plating 5
5.1.1.2 Nickel prior to last metallic finish 5
5.1.1.3 Other alloys as an alternative to the nickel substrate 5
5.1.1.4 Nickel as sole coating 5
5.1.1.5 Electroless nickel for plating on plastic (POP) 5
5.1.2 Corrosion resistance 6
5.1.2.1 Sweat Corrosion testing ISO 3160-2 7
5.1.2.2 Corrodkote corrosion test ISO 4541 (CORR) 7
5.1.2.3 Neutral salt spray test ISO 9227 (NSST) 7
5.1.2.4 Copper-accelerated acetic acid salt spray test ISO 9227 (CASS) 7
5.1.2.5 ASTM G85-11 Modified salt spray (fog) testing 7
5.1.2.6 Russian mud testing 7
5.1.2.7 Various tests for precious metals 8
5.1.3 Hardness and wear resistance 8
5.1.4 Colour and appearance 9
5.1.4.1 Metallic colours 9
5.1.4.2 Appearance - brightness 9
5.1.4.3 Appearance - nickel satin appearance 9
5.1.5 Usage of nickel according to selection of substrates 9
5.2 Alternatives to nickel used in decorative industry 12
5.2.1 Alternative to bright and levelled nickel by considering the type of substrate 12
5.2.1.1 Steel 12
5.2.1.2 Copper alloys 12
5.2.1.3 Plating on plastics (POP), zinc die cast (Zamak) and aluminium 13
5.2.2 Alternatives to bright and levelled nickel prior to last metallic finish: Bright acid copper plus a barrier diffusion 13
5.2.2.1 White bronze description 14
5.2.2.2 Palladium or palladium alloys description 14
5.2.3 Alternatives to bright and levelled nickel in case of further deposits as top-coating or last passivation 14
5.2.3.1 Paint or lacquer 14
5.2.3.2 PVD/CVD 15
5.2.3.3 Antique finishes 15
5.2.3.4 Zinc 16
5.2.3.5 Tin-cobalt 16
5.2.4 Alternatives to bright nickel as used as last finish 16
5.2.5 Alternatives to various nickel alloys 17
5.3 Technical evaluation of alternatives 17
5.3.1 Alternative to bright and levelled nickel by considering the type of substrate 17
5.3.1.1 Base material, steel 17
5.3.1.2 Base material, copper alloys 18
5.3.1.3 Base material, plastics 18
5.3.1.4 Base material, zinc and tin cast alloys 19

5.3.2 Alternative to bright and levelled nickel prior to last metallic finish: bright acid copper plus a barrier diffusion 19
5.3.2.1 Bright acid copper 19
5.3.2.2 White bronze 20
5.3.2.3 Palladium or palladium alloys 20
5.3.3 Alternatives to bright and levelled nickel in case of further deposits as top-coating or last passivation 20
5.3.3.1 Paint 20
5.3.3.2 Transparent cataphoretic lacquers 20
5.3.3.3 PVD/CVD 21
5.3.3.4 Antique finishes 21
5.3.3.5 Zinc 21
5.3.3.6 Tin-cobalt 21
5.3.3.7 Alternatives to black nickel 21
5.3.4 Alternatives to bright nickel when used as last finish 22
5.3.4.1 White bronze 22
5.3.5 Summary of technical evaluation of alternatives to nickel plating in decorative coatings 22
5.4 Evaluation of the potential of the alternatives to reduce risks 25
5.4.1 Exposure scenarios for formulation and coating processes 25
5.4.2 Hazard and risks of the alternatives 27
5.5 Cost-related aspects of alternatives 32
5.5.1 Nickel plating 33
5.5.2 White bronze plating 33
5.5.3 Palladium plating 34
5.5.4 Zinc plating 34
5.5.5 Copper plating 35

6 Conclusions 36

1 Summary

The aim of the current project is to provide the nickel plating industry with a support document that identifies and analyses potential alternatives to nickel used in decorative plating. The scope of the work has been specifically on decorative uses of nickel plating alone or in combination with other coatings, e.g. bright chromium. Alternatives to nickel used in technical/ mechanical plating have not been considered here, but are covered in other reports exemplified by the automotive and aerospace industry.

The specific objective is to identify potential alternatives to current uses of nickel in plating techniques and to evaluate their suitability in terms of reduction of the overall risk, their technical performance and the economic feasibility of a substitution.

Alternatives include substances and techniques that provide the same or similar properties to the plated item. We have focused only on techniques that are currently available for industrial scale production. Furthermore the design and appearance is regarded as very important and only alternatives that meet the market requirements of a metal like glossy (or satin) appearance has been regarded as acceptable from a design point of view.

For some applications alternatives to nickel based plating have been identified (please refer to the main text for the other of alternatives considered):

- White bronze seems a potential alternative for some uses, but the process involves use of highly poisonous cyanide-containing baths. Development of cyanide free solutions for industrial scale production may take years. White bronze is suitable and already used for plated articles intended for contact with human skin. , e.g. watches, eye-wear and jewellery, although the plating costs are 2.5 times the price of nickel plating. White bronze has not, however, the same resistance as nickel to wear and corrosion, which is required for a number of well-known uses, e.g. for sanitary fittings in bathrooms.

- Zinc plating on steel with trivalent chromium, a cobalt-free passivation layer plus additional topcoat can be a convenient solution for fasteners, supermarket trolleys and windows frame mechanisms. This solution has outstanding corrosion resistance and a convenient friction coefficient but as zinc is supposed to be corroded over time, it does not, however, preserve the same bright appearance as a nickel + bright chromium (VI) coating.

- It is very difficult to replace nickel plating as sub-coat for chromium (VI) plating on furniture. Copper cannot be used instead because it does not apply to steel pipes and tubes. No alternative has been identified for industrial scale production.

Ultimately a potential alternative to nickel needs to be evaluated against the specific requirements that in every case are defined by the actual use of the coated item, e.g. technical qualities as hardness and resistance to corrosion and wear, in addition to the design and appearance.

2 Introduction

The current report covers the assessment of alternatives to nickel substances used for decorative coatings.

Nickel chemicals are used widely in industry, one of the main applications being in the coating industry. Nickel metal has unique properties and is used to protect parts against wear and corrosion in e.g. automobiles and airplanes. However, nickel is also widely used in decorative coatings on metal or plastic, often as sub-coat for subsequent coating with e.g. bright chromium.

Nickel is normally applied to the base material in an electrochemical process or deposited chemically. In both cases, nickel salts are used as raw material and during the process the ionic nickel is transformed into metallic nickel. Therefore, the final coating does not contain nickel salts.

A number of the most frequently used nickel salts are classified as hazardous and may cause cancer by inhalation as an aqueous mist. Due to these properties, these nickel salts may or may not be identified as so-called: "substances of very high concern (SVHC)" under the REACH legislation, which may eventually be included in REACH Annex XIV on substances that require an authorisation before use.

The overall aim of the REACH authorisation provisions is the substitution of SVHC substances with suitable alternatives. Therefore, an application for authorisation requires that alternatives are identified and evaluated. Authorisation shall be granted if adequate control can be demonstrated but if a suitable alternative do exist, a substitution plan must be included in the application. In case adequate control cannot be demonstrated, e.g. for non-threshold carcinogens and PBT substances, the applicant must document that no alternatives are available and the socio-economic benefits of using the substance out-weight the risks to humans and the environment.

The analysis of alternatives thus plays a key role in the authorisation process.

In order for an alternative to be regarded as suitable, the REACH legislation requires that it reduces the overall risks to humans and the environment. It should be noted that substituting one SVHC substance by another with a similar or equivalent hazard profile is not regarded an option. Secondly, the alternative should fulfil the same technical function whether it is an alternative substance providing the same function or it is a different technique that eventually will provide a product fulfilling the technical requirements. And thirdly, an alternative should be feasible from an economic point of view.

The aim of the current project is to provide the nickel plating industry with a support document that identifies and analyses potential alternatives to nickel used specifically in decorative plating. Nickel used in technical coating represented by the two selected sectors of automotive and aerospace is covered by another report submitted to the Nickel Institute in April 2012.

The current identification of alternatives was focused primarily on techniques that are already available on the market for industrial scale application and less on techniques for niche production. Techniques that require further development were considered if they seem to provide viable alternative solutions in the near future. It should, however, be noted that applicants for authorisation need also to consider alternatives under development.

The work was carried out by DHI in a close cooperation with Mr. Jean-Jacques Duprat who has extensive practical experience from a long career within industrial and decorative coatings.

The project was followed by a group of industrial experts representing the decorative plating industry:

Lorenzo dalla Torre, Industria Galvanica Dalla Torre Ermanno & Figli S.p.A.
Dr Paul Lansdell C Eng FIOM3 FIMF B.Sc., Operations Director Hart Materials Ltd
Berthold Sessler, CETS, Chairman of the Plating Section
Dave Elliott, Surface Engineering Association, Chief Executive Officer
Denis Théry, UITS France, Délégué Général
Henk de Man, Brandsma Metaalveredeling B.V.
Herbert Breidenbach, ZVO Head of Environment Department
Prof. Dr. Andreas Moebius, Enthone R&D Fellow, Enthone GmbH

3 Objectives

The objectives of the current project were:

- To identify potential alternatives to nickel used in decorative plating
- To analyse the suitability of the identified alternatives, including:
    - The potential to reduce risk to humans and the environment
    - Ability to provide a technically suitable alternative to nickel-based coating
    - Identify and observe economic issues related to the substitution

4 Methods and approach

According to REACH and the ECHA guidance, an alternative may be any substance or technique that can replace the substance of concern and is technically and economically viable.

When assessing whether suitable alternative substances or technologies are available, all relevant aspects should be taken into account including (REACH Article 60, 5):

- Whether the transfer to alternatives would result in reduced overall risks to human health and the environment, taking into account the appropriateness and effectiveness of risk management measures
- The technical and economic feasibility of alternatives for the applicant

In the current report, the scope was potential substitutes for nickel used in decorative coatings, mainly electroplated nickel used as sub-coat for further plating with bright chromium/precious metals or electroplated nickel as sole coating.

Focus was on alternatives that may replace the use of nickel in such coatings and fulfil the requirements regarding technical properties as well as to the metallic appearance. This means that we have not included techniques and substances that may be used as coating purely from a technical point of view but accepted that there is a market demand for a bright metallic finish. For example, a painted, plastic-coated or stainless steel tap may technically fulfil the function but will from a marketing or consumer point of view not be suitable.

The first step was the identification of potential alternatives. The identified alternatives were then evaluated against the requirements of technical properties and appearance that different applications may have and where a nickel-based coating is used today.

The risk reduction requirement was assessed for each of the identified alternatives by addressing the hazard (e.g. classification and DNEL values) of the applied substances as well as the potential exposure during the formulation and plating processes, i.e. preparation of chemical baths and their application in the plating industry. The exposure scenarios developed for the plating industry in the registration dossier for nickel and nickel compounds were used as a reference for the exposure of workers in the plating industry in general and the water environment. The exposure in the formulation steps was estimated by use of Tier 1 tools. It was assumed that the substances applied in the coating are transformed in the process, e.g. a metal salt is transformed into a metal coating, and that the exposure to the metal salts is not relevant further down in the supply chain.

The risk to humans and the environment is indicated, on the one hand, by the classification and derived DNEL values of the applied substances and, on the other, by the estimated exposure values for workers and the water environment.

The assessment of costs focusses on estimating the overall costs of a coating compared with an equivalent nickel coating. This includes prices of the alternative raw materials, altered production capacity, e.g. due to lower efficiency, and costs of other chemicals. The current report does not intend to provide a quantitative analysis of the costs of substitution but highlights only issues that could be considered in a more elaborated socio-economic assessment.

5 Nickel used in decorative coatings

5.1 Technical functions and requirements

In the decorative industry, electroplated nickel aims to cover the base material, the so-called substrate, by a bright and well-levelled deposit. The plated parts receive a perfect shiny surface, which is enhanced by bright nickel. The electroplating industry applies two types of processes:

- **Rack plating**: Parts are hooked and unhooked from jigs manually. This operation provides a material without scratches and damages
- **Bulk plating**: In barrels for electroplating and in baskets by dip-spin applications for various inorganic or organic coatings

The rack plating is obviously dominant in the decorative segment.

The discovery of the bright and high-levelled electroplated nickel in the late 60s was highly appreciated by the users as it reduced the costs of polishing, which remains manual although many automatic plants exist for polishing both simple and complex shape parts. The term 'Bright Nickel' includes the satin/dull finishes as well. These deposits are made by either an emulsion of organic compounds in the solution or inorganic particles in suspension in a bright nickel electrolyte. The co-deposited particles are entrapped within the metallic structure and create a roughness at the surface, which diffuses the reflection of the light. The emulsion produces artificial roughness lower

than 1 micrometer. The measure of the brightness and the measure of the roughness calibrate the type of satin effect that can vary up to total anti-reflective effect.

5.1.1 Various types of nickel and nickel alloy layers of the decorative industry

5.1.1.1 Nickel prior chromium plating

This type of application is made by rack plating. The Nickel can be plated usually as mono layer on 5 to 20 µm or as double layer (so-called bi-nickel or duplex nickel) on 10 to 40 µm or even as tri-nickel with a2-µm interlayer of high sulphur-containing nickel between semibright and bright nickel. Because of requirements for severe corrosion testing, 2-µm microdiscontinuous layers of nickel can be plated over bright nickel prior to chromium plating.

5.1.1.2 Nickel prior to last metallic finish

The final deposit can be gold, silver, palladium or palladium alloys, ruthenium, rhodium, platinum or white bronze over a single bright nickel layer as support for brightness, wear resistance and barrier to copper diffusion. In case of higher corrosion requirements, a bi-nickel layer can be applied.

5.1.1.3 Other alloys as an alternative to the nickel substrate

Tin-nickel 65/35 can be used for replacing nickel +chromium layers in acidic and fluoride electrolyte. The deposit has a whitish pink colour and offers good chemical resistance and good anti-tarnish properties. But the brittle deposit does not allow thick deposits over 3 µm. Only few applications are still using this type of plating. Various other tin-nickel processes exist but usually prior to transparent paint or lacquer:

- Grey-black at pH 4.5
- Fluoride-free grey-black at neutral pH for thin flash deposits
- Cyanide grey-black nickel

Nickel-iron alloy is an economical solution for reducing the nickel costs. The properties of Nickel-Iron alloy are very close to pure Nickel and similar to Bright Nickel, although the corrosion resistance is much lower.

Black nickel is made of nickel-zinc, sulphur-containing nickel or cyanide nickel. The colour varies from dark grey to dark blue.

Palladium-nickel 80/20 is appreciated in the decorative industry for replacing one part of a thick gold deposit. Even cheaper than 18 carat gold alloys, it offers a similar corrosion protection at the same thickness. Its white appearance can be covered by 0.5 µm of yellow gold alloy and the final colour will be the same as a thicker gold alloy.

5.1.1.4 Nickel as sole coating

Chromium plating in barrel or in bulk is extremely difficult and costly. Consequently, many small parts for furniture and home appliances receive a single nickel layer without other finish, e.g. fasteners and hinges, which are usually plated by barrel plating with a thin 5-µm layer of bright nickel.

5.1.1.5 Electroless nickel for plating on plastic (POP)

A very thin layer of 0.06 to 0.2 µm of nickel phosphorous is coated by reduction on top of the plastic prior to electroplating. Electroless nickel leads to electrical conductivity,

which is enhanced by a 2-µm strike of nickel or copper. Electroless nickel has excellent functional properties with respect to corrosion protection and wear resistance, but is far more expensive than electroplating and for this reason seldom used for purely decorative purpose. For Plating on Plastic (POP) it can be replaced by electroless copper.

5.1.2 Corrosion resistance

The corrosion is more or less the simple oxidation of metals but the users must take into consideration all kinds of exposure and must select the preferred anode under many various environmental conditions:

- Humidity
- Temperature
- pH value
- Aggressiveness of the gas/liquid/solid in contact with the parts
- Role of the wear

In some instances with decorative applications, the cosmetic appearance is more important than the functional properties. The evolution of the appearance will depend on the first oxidation of the surface and on the ranking of the unavoidable damages.

The substrate plays a major role in the selection of the requirements. For instance, the red rust of the steel substrate is a major consideration. On plastic, corrosion creates unacceptable surface damages such as greenish nickel salts. And on zinc die cast, the corrosion of zinc produces voluminous white rust on shiny chromium-plated parts.

Therefore, the choice must depend on the projected life of the parts and be in accordance with the desired specifications of the end-user.

The most severe exposure is certainly the situation of a vehicle that is supposed be present in all atmospheric conditions of the world and from the coldest to the hottest climate as well. The conditions can be industrial close to the factories or salty close to the sea border or both. The car industry normally does not consider any of the existing standards relevant for reproducing the life of a vehicle. They have developed life tests, in which cars are driven on various roads, are submitted to various projections of corrosive liquids and are stored during the night in a corrosive atmosphere. All car makers have developed their own life tests in combination with the feed-back and the experience of their business partners all over the world. The standards are mainly used for Quality Control of the production and they reproduce partially the ability of the plated layers to resist to the corrosion.

Another example is the conditions of corrosion within a bathroom with hot humidity and severe abrasion due to the use of cleaning products. It is common to see the colour of the nickel at the angles of a tap due to wear of the chromium layer. Then, the colour of the base material succeeds rapidly after due to wear of the nickel layer. The wear combined with the corrosion provokes a worn appearance, which is unacceptable to the tap manufacturers. Therefore, the crystalline and consistent chromium (VI) layer is recommended for these uses. However there are also non pure chromium deposits being produced using trivalent chromium salts with co-deposited elements present, which provide lower wear resistance than chromium (VI) deposited finishes.

Furniture or wire goods that are exposed to outdoor or humid conditions in non-ventilated room require a double nickel layer of bi-nickel and/or microdiscontinuous structures in order to resist corrosion. The benefit of the bi-nickel layer is not limited to

chromium-plated coatings and more or less all metallic finishes can be corrosion protected by bi-nickel layers.

The third example is corrosion resulting from sweat. Human sweat is slightly acidic and made of lactic acid, urea and minerals. This solution is very aggressive for most metals and various tests exist for reproducing the corrosion in contact with human skin:

5.1.2.1 Sweat Corrosion testing ISO 3160-2

ISO 3160-2 addresses the various conditions of corrosion of a watch. For all of them, the sweat test is made with an acidic solution of sodium chloride, ammonium chloride, urea, acetic acid and lactic acid at pH 4.7.

The European Standard NF EN 1811 describes the nickel leaching test with sodium chloride, DL lactic acid, urea, ammonia solution and nitric acid at pH 6.5.

5.1.2.2 Corrodkote corrosion test ISO 4541 (CORR)

The CORR test was first used for vehicles, motorcycles, bicycles and furniture for measuring the penetration of the corrosion down to the steel substrate. The bi-nickel layer is of particular relevance for this test. The combination is made of 2/3 of semibright nickel and 1/3 of bright nickel. As the bright nickel contains more than 0.04% of sulphur and the semibright nickel less than 0.005%, the potential electrochemical difference between the two layers is equal to or higher than 100 mV according the VW standard TL 528 (issue 2008-6).

5.1.2.3 Neutral salt spray test ISO 9227 (NSST)

The NSST is applied for many applications on various steel-plated parts such as furniture and wire goods. It shows the eventual porosity of the nickel layers and the benefit of an alkaline copper underlayer for covering defects in the substrate (solders on grills, cavities in wrought or cast iron). NSST can be applied for all types of substrate. For testing zinc containing deposits, the NSST is of particular relevance.

5.1.2.4 Copper-accelerated acetic acid salt spray test ISO 9227 (CASS)

The CASS test is a variant of the NSST with a more aggressive copper acetic acid containing solution. The test is intended for multilayer of nickel followed by microdiscontinuous deposits. Many car makers include the CASS test in the specifications for plated plastics and zinc die cast.

Another variant, the AASS, exists with acetic acid but without copper. It can be used for sanitary fittings. AASS is more representative of single layer or duplex layers of nickel while CASS is intended for microdiscontinuous layers.

5.1.2.5 ASTM G85-11 Modified salt spray (fog) testing

Another variant, the G85 AASS, exists with acetic acid but without copper. It can be used for sanitary fittings. AASS is more often used for decorative applications of single layer or duplex layers of nickel while CASS is intended for microdiscontinuous layers.

The standard is applied in the US and Canada for testing of water fittings used in bathrooms etc. It is also accepted on the European market where a number of the larger US manufacturers of water fittings are established.

5.1.2.6 Russian mud testing

In order to reduce the global quantity of sodium chloride spread on roads in the winter time, the coldest countries usually mix calcium chloride in the sodium chloride. This

combination is highly detrimental for Ni-Cr plated parts and, more and more, car makers are including a "Russian mud test" in their specifications (e.g. VW PV 1067 or Nissan NES M 4063).

5.1.2.7 Various tests for precious metals

The ISO 3160-2 addresses various additional tests used in case of gold-plated parts such as thioacetamid, sodium metabisulfite or diluted acetic acid. Specifications may require these tests.

5.1.3 Hardness and wear resistance

The electroplated nickel is hard (over 400 HV) with good wear resistance for a long working life of plated parts. Due to its wear resistance, electroplated nickel is used for application in machined parts. It is important that the friction does not remove the nickel deposit, which has a consistent whitish colour in comparison with the substrate (often pink-red copper or grey steel that are both very sensitive to tarnishing and will corrode).

By considering the various conditions of wear depending of material in friction, the users selected different dedicated tests for measuring the wear. These tests are often followed by corrosion testing:

- For fashion or jewellery, the parts in friction with clothes or leather are tested in wood or plastic barrels in rotation with dedicated chips. For this area, wear resistance is tested in an empirical way and varies from one manufacturer to another.
- For sanitary taps, the wear is provoked by the household detergents used for cleaning and by the corrosion of the various layers in humid atmosphere. For most of the taps, the final chromium layer is the wear barrier against the attack on the nickel underlayer from corrosive and abrasive cleaning.
- For automotive industry, the front grills are submitted to the wear of the stone or other flying objects and can be submitted to stone chip test. Carwash brush test is another option. This type of test usually applied on paints can serve also for metallic coatings.

The watch industry normally defines precisely the wear resistance, the scratch resistance and the impact resistance. The standard ISO 23160 defines different testing procedures for

- Wear resistance using moving ceramic chips or balls
- Wear resistance in friction against a textile belt
- Wear resistance by reciprocating movement against an abrasive surface
- Scratch resistance by transport, handling or rubbing on lightly abrasive surface such as clothes or furniture
- Impact resistance in case of accidental friction with rough, hard and abrasive surfaces.

This standard is applicable for many plated parts and simulates the life of many objects that we are using every day.

For all applications with organic finishes, e.g. transparent cataphoretic lacquer on top of electroplated metal, the paint industry refers to the hardness pencil test ISO 15184.

The method is used for determining the film hardness by pushing pencils of known hardness "HB" over the film.

5.1.4 Colour and appearance

5.1.4.1 Metallic colours

The colour of a coated item is usually measured by colourimeter. Gold alloys colours are classified by the ISO 8654 or compared with the Swiss Standard NIHS. The colour is measured with 3 parameters called L, a, b (CIE 1976, Minolta Spectrophotometer) or Q, x, y (ISO 8654) depending on the units.

Most of the potential electroplated metals are easily deposited on top of nickel and are used depending on fashion, engineering requirements and colour requests:

- Without lacquering: Gold alloys, white bronze, pure palladium or palladium alloys, ruthenium and rhodium and silver
- With lacquering: Silver (to avoid yellowing or blackening), brass, yellow bronze and black nickel

The replacement of a bright nickel underlayer by a thin palladium layer can be convenient if the affinity for hydrogen of the palladium is under control (e.g. by plating dedicated acidic pre-gold layer). This alternative leads to additional costs, which only thick precious metals layers can amortize. It is not competitive for most of the thin last finishes with precious metals or chromium finishes.

5.1.4.2 Appearance - brightness

The brightness of electroplated metals is given by the grain refiners, so-called brighteners. The most efficient brighteners reduce the grain size down to the nm size and are consumed by breakdown and co-deposition within the metallic matrix and by breakdown at the anode. Bright nickel is one of the most applied processes for brightening surfaces. However, many processes of metal electro-deposition are able to compete with bright nickel. Both white bronze and palladium alternatives can give bright deposits within the limit of the thickness of the deposit. For a very thin palladium or palladium alloy layer, the thickness of 0.1 µm = 100 nm does not make an important difference in term of brightness.

5.1.4.3 Appearance - nickel satin appearance

On top of a well-levelled and bright deposit, it is possible to plate nickel composite deposits made of organic or inorganic inclusions. The roughness increases and the light reflexion is diffused. Depending on amplitude and frequency of the roughness, the deposits can be anti-reflective and have various degrees of satin intensity. Normally, we consider roughness between 40 nm to 1 µm for organic inclusions and up to some µm for inorganic particles.

Acid copper satin represents an alternative to satin nickel and is based on copper crystallization with larger grain size (up to some µm) or organic emulsions as for satin nickel coating. However, the copper satin layer also needs an anti-diffusion barrier such as bronze or palladium or palladium alloys.

5.1.5 Usage of nickel according to selection of substrates

In most of cases, nickel is electroplated on steel, on electroplated copper or on copper alloys. All alloys of tin, zinc and aluminium and non-metallic substrates receive a cop-

per underlayer prior to nickel plating. Brass and bronze can be directly nickel-plated or after a pre-copper treatment depending on the composition of the substrate (contents of traces of heavy metals). Consequently, the same plating sequence on copper will be found for all applications, except for steel.

Steel

Steel offers outstanding mechanical properties. The metal is convenient for manufacturing processes and remains relatively cheap. Steel is protected by electroplating of nobler metals on the surface. Many applications are still using steel base material, for instance:

- Indoor trolleys: Ni + Cr
- Baby buggies: Ni + Cr
- Furniture: Ni + Cr but various metals can be plated as well with or without transparent lacquer
- Lighting: Ni + various metals + often a cataphoretic lacquer
- Household appliances: Ni +Cr

Copper alloys

Copper alloys are certainly the noblest substrates and they are called brass or bronzes. The costs are relatively high and the specific gravity of the alloys is required for producing gold-plated parts with the similar appearance to solid gold. Typical examples are bracelets and earrings. Most of the solid gold bracelets and earrings are hollow. The production can be made by electroforming around a shell. The gold-plated bronze is given similar appearance and weight.

For the water taps, the solid brass gives sustainable resistance to the flow of hot and cold water.

Please note that the metal alpaca, an alloy of Ni/Cu plus occasionally Sn or Zn is mainly used for eye wear and concerns more the parts in contact with human skin.

The area is dominated by cast or forged alloys for high quality sanitary fittings such as water taps. The component is well polished and a perfect mirror aspect is required. Usually, a single layer of bright nickel, followed by a 0.25- 0.6 µm thick chromium layer can guaranty the sustainability for the long term despite high friction due to cleaning with aggressive hard powder detergents.

Others decorative items can be made of laminated copper alloys but most of them are used for jewellery, eye wear, watches, buckles and medals in contact with the skin.

Plastics

Most of the plastics used for decorative applications are made of ABS (acrylonitril-butadiene-styren), ABS-PC (blend of acrylonitrile-butadiene-styrene and polycarbonate), PP (polypropylene) and, more recently, PA (polyamide). Decorative coated plastic is used in cars, sanitary fittings, perfume caps, electric or electronic equipment (razors, telephones, cameras and writing pens) and furniture. The automotive industry requires often multilayers of Ni prior to microdiscontinuous chromium whereas bright or satin chromium appearances are used in other areas. The perfume industry requires various precious metal deposits.

By plating on plastics, the electrolytic sequence starts with a 2-µm pre-copper strike or pre-nickel strike on the initial 0.2 µm thin electroless nickel or electroless copper. A

possible alternative is a layer of electroless special copper layers made by so-called direct metallisation.

1. Then the main appearance is achieved with a thick acid copper layer between 10 and 40 µm for a good ductility and the highest levelling

2. The bright nickel layer brings an additional brightness and prevents copper migration. Or multi-layers of nickel are used for fulfilling the CASS test, the neutral salt spray test, the ASTM G85 or the Russian mud corrosion standards depending on requirements but always with a chromium finish.

3. On top of nickel

    a. Chromium for vehicles on grills, emblems, buttons and handles, and for sanitary fittings and furniture

    b. Gold, white bronze, palladium alloys and ruthenium for perfume caps

Zinc die cast and tin alloys casting

Although both types of metallic casts are suitable for casting complicated parts, zinc die cast, the so-called Zamak, is very popular and has a competitive price.

This material is particularly porous under the surface skin. Zamak is sensitive to temperature as well due to the risk of gasing and deterioration of the plated layers. The plating sequence can be compared to the POP plated with the mandatory pre-cyanide copper.

The Zamak compete with the plastics on the same markets and must meet the same requirements.

The plating sequence on all casts need to plate first a pre-cyanide copper prior to further deposits similar to the POP. Nickel on top of copper gives a hard and thick protection to wear and corrosion.

Zamak is widely used in all industries and is submitted to the full range of specifications depending on applications (automotive industry, furniture, locks, sanitary fittings and bicycles).

Tin cast alloys are less frequent and are applied more in the jewellery and fashion industries.

Aluminium alloys

Plating of aluminium is less popular in Europe compared with the US market where the chromium-plated aluminium wheels are very successful. In Europe, the trend is that an increasing number of parts are plated aluminium die cast, e.g. for motorbikes, in bathroom, cars, furniture and door handles.

The plating sequence on aluminium is similar to that on plastics or on Zamak, i.e. a 2-µm pre-cyanide copper is plated on the initial 0.2 µm zincate for adhesion.

The function of nickel is similar to the use on copper alloys where nickel is the hard and noble layer resistant to wear and corrosion.

5.2 Alternatives to nickel used in decorative industry

5.2.1 Alternative to bright and levelled nickel by considering the type of substrate

5.2.1.1 Steel

Steel is very sensitive to the humid corrosion and nickel makes the surface noble by plating a more cathodic deposit. The nickel plated steel will be corroded superficially by nickel oxidation or directly in red rust through the pores in the deposits. Depending on the steel quality and the metal forming (e.g. after stamping, soldering, brazing or for sintered steel), the nickel deposits cannot be consistent and many porosities go down to the substrate. Pre-cyanide copper helps to reduce the tendency to porosities as the cyanide electrolyte helps to plate on surfaces difficult to prepare.

In case of zinc plating, the zinc is supposed to corrode instead of the steel, generating white rust. White rust is made of voluminous hydroxyl-carbonate of zinc and, sometimes, black non-stoichiometric oxides of zinc can appear as well. Zinc is the most popular anode for protecting steel against corrosion but the discovery of bright acid chloride zinc made the process popular for decorative plating, especially with a very nice blue conversion coating on top. Recently, new developments in term of chromium (VI) free passivation and inorganic and organic topcoats delay the modification of the cosmetic appearance and the apparition of rust. Due to the topcoat, the colour becomes less iridescent and a stainless look can be achieved. E.g., supermarket trolleys and window/door mechanisms use this technology for outdoor parts.

For many items, the mechanical properties of steel are required and nickel serves to protect the surface against corrosion. On a base of nickel-plated steel, it is possible to add many other metallic finishes.

Because of immediate exchange of Fe-Cu in acidic sulphate solution, it is not possible to plate a layer of bright acid copper directly on steel but only after a pre-layer of nickel or alkaline (cyanide) copper. Nickel can be applied as electroless plating inside tubes and pipes but the costs and the complicated plating sequence make the solution non-competitive. Copper can be plated either by using an electroless copper solution or by using cyanide-containing electrolytes or better from alkaline cyanide-free electrolytes. However, these cyanide or alkaline solutions are not suitable for plating on the interior surfaces of tubes or pipes.

Often corrosion resistance is required in order to avoid generation of brownish iron oxides. An advantage of the alkaline copper underlayer prior to nickel is that it reduces the porosities of the nickel deposit by plugging the micro-caverns on the steel surface

Currently, the only alternative remains the highly sophisticated zinc + chromium (VI) and cobalt-free passivation + organic-inorganic topcoat. This solution is acceptable for many exterior items but cannot be accepted where a durable and shiny metallic aspect is required.

5.2.1.2 Copper alloys

Due to the risk of nickel release for parts that come in contact with the skin, an alternative with copper + bronze is applicable despite a lower wear resistance due to the thinner deposit.

5.2.1.3 Plating on plastics (POP), zinc die cast (Zamak) and aluminium

Plastics, which need to be coated for decorative reasons, are sensitive to temperature and use of paint or lacquer that need to be cured and are thus not applicable. Therefore, in order to substitute nickel, e.g. in parts that come in contact with the skin, white bronze is an alternative.

There are nickel-free processes that allow an electroless metallization on plastic materials. This is called direct metallization and uses a technique, in which tin deposits applied at an earlier step are exchanged with a metalizing layer of 0.2 µm of pre-copper layer prior to an electroplating sequence where the topcoat is added.

5.2.2 Alternatives to bright and levelled nickel prior to last metallic finish: Bright acid copper plus a barrier diffusion

Electroplated nickel can reduce the surface roughness of a component by controlled deposition. . This is a property in electroplating that only bright acid copper deposits can achieve as well. The levellers are organic compounds that act as adsorbed dipole on the top of the peaks that restricts the rate of deposition and increases the rate of growth of the metallic layer in the valleys. It is known that a valley of 5 µm can be levelled by a deposit of 10 µm. The bright acid copper solutions achieve a similar rate of levelling as nickel solutions.

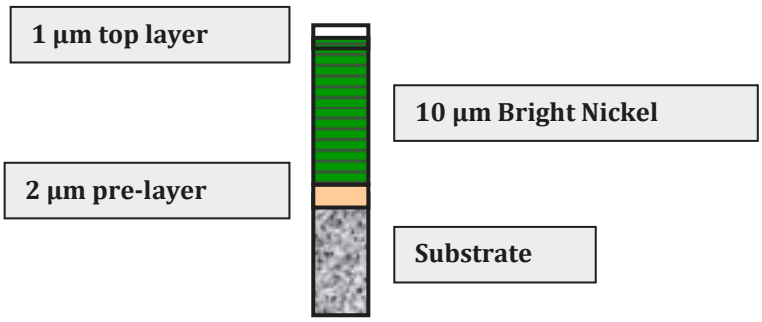


Figure 5. Structure of a bright nickel layer on e.g. pre-layer, depending on substrate. The top layer can be Cr/Au/Ag/Rh/Ru/Pt/Pd/bronze

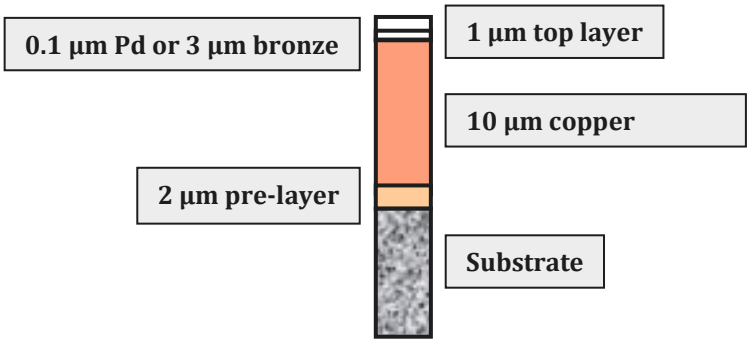


Figure 5. Structure of a nickel-free combination with bright acid copper + palladium or bronze in replacement of nickel

If replacing nickel, the copper alternative must be covered by a 3-µm white bronze layer or a 0.1-µm palladium or palladium-alloy to prevent copper diffusion by aging. However the colour and reflectivity of the alternative coating will be different and the corrosion resistance of the whole deposit will be significantly reduced.

Semibright nickel has also an important capacity for levelling. It can also be replaced by bright acid copper.

For very few applications where the quality of the substrate is perfectly mirror bright with a roughness much lower than 100 nm, the levelling effect is not so critical and many bright electroplated metals can be plated directly onto the polished surface. Depending on other specifications: white bronze, pure palladium or palladium alloys can be deposited onto copper-based materials. Or onto a pre-copper plated substrate such as plastics, zinc die cast and aluminium alloys. Here also the colour and corrosion resistance will be altered with the substitution of the nickel for copper and other layers.

5.2.2.1 White bronze description

The white bronze is appreciated for its white colour and good anti-tarnish properties. It can be made of copper/tin (55/45) or more frequently copper/zinc/tin (55/30/15). It has a good wear resistance but the layer thickness is usually under 5 µm because of brittleness.

The process is now widely used to replace nickel for all applications where contact with skin is foreseen. But for many applications, it cannot fulfil specifications in terms of corrosion and wear resistance where thick bright nickel will pass.

White bronze is on its own used as a bright and white end layer. It is not, however, suitable for further chromium (VI) plating but plating with chromium (III) as topcoat is used in some cases.

Many patents have been issued for various cyanide-free white bronzes, from acidic and alkaline electrolytes. However, real industrialization will take some more years.

5.2.2.2 Palladium or palladium alloys description

Palladium is an excellent barrier to the copper diffusion from the lowest thickness. It has a nice white colour, slightly darker but less yellow than nickel. Palladium is very noble and will not be oxidized. The convenient thickness to plate on copper is at least 0.1 µm in order to avoid copper diffusion even after 24h of curing at 180°C.

However, the palladium electrolyte is very sensitive to copper contamination, and the alkaline ammonia-containing electrolyte limits usage of Pd solutions to well-equipped plants with sophisticated maintenance and internal process product cleaning facilities so as to not poison the palladium solution.

5.2.3 Alternatives to bright and levelled nickel in case of further deposits as top-coating or last passivation

5.2.3.1 Paint or lacquer

In some cases, with a substrate that can be heated, the nickel-plated parts are receiving a top layer of paint or lacquer. The parts are cured and the last appearance becomes bright coloured paint or transparent lacquer over a metallic appearance.

Various water-based or solvent-containing paints can be coated from 5 to 80 µm by spraying or dipping prior to curing. The coated parts look “organic painted” regardless of the under layers that serve mainly as support for corrosion protection or wear resistance.

Transparent lacquers are more efficient for preserving a metallic appearance and only a specialist can recognize the presence of a lacquer on the surface. In order to prevent

drop effect and to plate on the same line, water-based cataphoretic lacquer that gives 10 µm of protection is applied.

The fresh plated cataphoretic lacquer is cured on line at 160°C. With reference to ISO 15184, the relative hardness of a pen 5H reduces the risks of scratches. The cataphoretic lacquer improves the durability of the parts and prevents tarnishing of sensitive metals: e.g. silver, brass, black nickel and yellow bronze. There are many automatic plating lines in Europe using this technique for lighting, furniture, home appliances, locks and leisure equipment.

The above applications are base materials that are resistant to temperature curing, e.g. steel or copper alloys.

Please note that the only combination of paints + phosphatizing as applied on a car body is due to design requirements not accepted for certain applications despite similar performances to Ni-Cr plated parts.

5.2.3.2 PVD/CVD

Physical vapour deposition (PVD) or chemical vapour deposition (CVD) provides a thin and very hard deposit of inorganic coatings. The material is vaporized at very low pressure close to vacuum and condensed on the substrate. The thickness can be between few up to 100 nm. For use on electroplated metals, these applications are mainly limited to three types of coatings:

- The yellowish titanium nitride (TiN) that has a golden colour and is currently used on top of gold deposits for a new design and a better wear resistance.
- The blacken tungsten carbide (WC) that gives a new design in black colour and a better wear resistance. Its brittleness limits the thickness and the application.
- Zirconium derivatives that contains materials for various colours.

PVD layers are coated at high temperatures, which limit the potential substrate mainly to steel and brass. Under these conditions, an alternative with white bronze is unlikely.

However, the plasma-arc process can be carried out at lower temperatures and this allows coating on top of chromium- or nickel-electroplated substrates including zinc die castings and plastics. A wide range of colours can be achieved by varying the chamber conditions during the coating process.

New types of coatings have been introduced using PVD/CVD based on deposition of oxides, ceramics or pigments aiming to give shiny chromium appearance. The thickness of the coating can reach several µm but there is currently no experience with industrial scale production.

Thin PVD/CVD coatings cannot protect against corrosion and must be considered an additional toplayer for increasing wear resistance and for achieving new colours by many combinations of deposits.

5.2.3.3 Antique finishes

Most of these coloured appearances are made by oxidizing the last copper layer by sulphur or selenium. The colours can be black, brown or green with many variants. Here, the use of a bright acid copper instead of a nickel underlayer is an obvious alternative.

5.2.3.4 Zinc

Zinc electroplating covers a range of processes including alkaline cyanide and acid cyanide-free processes. To increase corrosion resistance, zinc can be alloyed with nickel, cobalt, iron or manganese. Zinc and zinc alloy coatings are always coated with chromium-containing conversion layer as finishing layer or prior to an organic-inorganic topcoat. The coating becomes non-metallic with blue, clear iridescent, yellow, green or black colours.

In some cases, a bright zinc layer with a "chrome-like" look can replace nickel-chromium plating. The deposit is made of an initial well levelled chloride acid zinc layer of 5 to 10 µm. The blue finish with a "chrome" look is made from a chromium and cobalt conversion finish. Today this is used in cars and electronic equipment, which are regulated under the EU ELV and WEEE Directives[1]. An alternative coating based on chromium (III) is available but contains relatively high amount of cobalt in order to provide a bluish colour (0.5 mg Co/dm^2).

If accepted by designers and consumers, other colours are available using cobalt-free passivation on top of highly corrosion-resistant zinc (preferably alkaline).

Zinc coating with a stainless steel or other appearance can be obtained by an inorganic-organic topcoat, which increases the corrosion protection and wear resistance significantly and gives a more uniform appearance. Moreover, a clear conversion coating can give a stainless or satin-like appearance. Because of the drop effect, rack application is difficult for these processes and dip-spin application is preferred, where possible.

In general, zinc-based coatings offer a range of alternatives but cannot give the bright metallic and sustainable nickel-chromium (VI) coating.

5.2.3.5 Tin-cobalt

Tin-cobalt coatings can be applied by two types of processes, which are both candidates for replacing nickel–chromium plating:

- Tin/cobalt at a ratio of 75/25 applied at pH 8.5. The colour deposit is grey-black
- Tin/cobalt at a ratio of 78/22 applied at neutral pH. The colour is slightly white-blue

In general, tin-cobalt alloys do not have good corrosion and wear resistance. Moreover, the coating does not allow further plating with a chromium layer.

5.2.4 Alternatives to bright nickel as used as last finish

Bright chromium (VI) plating requires advanced and costly equipment. Consequently, nickel is used as top finish for many indoor applications where tarnishing is accepted for hidden parts, e.g. fasteners, parts for locks, plugs, kitchenware or furniture.

However, white bronze plating provides an alternative resistant to tarnishing but at much higher costs and a reduced overall corrosion resistance.

In addition, zinc plating can be used but with the limitations described in the section above. A possible replacement for nickel barrel plating could be plating with zinc and chromium (VI) followed by a thick cobalt-free passivation layer applied in a basket pro-

[1] DIRECTIVE 2000/53/EC of 18 September2000, on end-of life vehicles; DIRECTIVE 2012/19/EU of 4 July 2012 on waste electrical and electronic equipment (WEEE)

cess and finishing with a topcoat applied by dip-spin. The corrosion and wear resistance of the basic zinc layer will be increased at a competitive cost. It should be noted that this process is mainly for coating of relative small objects where the appearance often is less important.

5.2.5 Alternatives to various nickel alloys

- No alternatives are available for white pink tin-nickel 65/35. Only the costly palladium or palladium alloys over white bronze can be used in this case.
- Alternatives to the grey-black tin-nickel (applied at pH 4.5) and fluoride-free grey-black tin-nickel (at neutral pH) used for thin flash deposits and cyanide-based grey-black nickel can be replaced by cobalt alloys. However ,several cobalt salts have been identified as Substances of Very High Concern according to REACH Title VII.
- Nickel-iron coatings can be applied in the same way as bright nickel plating and have the same alternatives.
- The alternative to black nickel is black ruthenium over white bronze. this solution is not suitable from an economic viewpoint because of the high costs.
- Black chromium (III) plating on top of acid copper + white bronze is a suitable alternative to black nickel. However, black trivalent chromium (III) does not give the same intense black colour as black nickel but it does not require additional lacquer to provide anti-tarnishing properties.
- Black coatings on a zinc-plated layer can be a suitable alternative but the slightly different appearance has to be accepted.
- A possible alternative to palladium-nickel 80/20 could be nickel-free palladium alloys but most of them are under development for the decorative market: Pd-Ag, Pd-Cu, Pd-In or Pd-Fe. Palladium–cobalt is also a suitable candidate from a technical point of view but not suggested as alternative here because of the hazardous properties of cobalt salts. However, these alloys do not allow bright plated deposits above 2 µm in industrial scale production.

5.3 Technical evaluation of alternatives

5.3.1 Alternative to bright and levelled nickel by considering the type of substrate

5.3.1.1 Base material, steel

The quality of nickel plated on steel depends on the quality of the substrate and on the quality of the plating sequence.

- Mild steel (plain carbon steel): On single mild steel, the corrosion resistance can be improved by multilayers of nickel with or without copper as underlayer, used on car bumpers in the 70ies. Even the most severe conditions do not affect the elaborated multilayer of microdiscontinuous nickel-chromium (VI) plating. The nickel-chromium combination for outdoor and corrosive environments cannot be replaced with known alternatives.

  However, for parts where the anti-corrosion requirements are low, cyanide pre-copper + acid copper + white bronze provides an alternative if the slightly different colour can be accepted. The colour of white bronze is white or darker if an additional coating with trivalent chromium is plated on top. Palladium is rejected as alternative on steel because of the high price.

- Hard steel, sintered steel, stamped steel, cast iron, soldered steel: The complexity of the substrate makes the quality of nickel plating very difficult without a pre-cyanide copper layer that covers all defects of the surface. For these applications, the use of cyanide is already managed and a transition to white bronze, which also involves use of cyanide-containing baths, is therefore easier.

The limitations of white bronze is the colour, which is different from the traditional bright chromium, the lower wear resistance but also the temperature resistance, e.g. for uses in ovens.

Zinc plating is less sensitive than white bronze to the quality of the substrate and offers many advantages despite the lack of the bright look that characterizes bright chromium. By comparison, zinc plating is very cost effective compared to nickel plating and can be used in combination with other coatings to improve the quality in term of friction and anti-corrosion, e.g. zinc + conversion coating + topcoat. Zinc offers an additional advantage via the possibility of re-plating the used articles, e.g. steel wire goods exposed to outdoor conditions. Thus from a lifecycle perspective, zinc coating may outweigh the nickel chromium because of this re-plating possibility.

For passivationd zinc-plated fasteners, the control of the coefficient of friction can be provided by an organic–inorganic topcoat combining good economy in term of worker costs and corrosion resistance. The benefit is by easy unscrewing during repair operations.

For fasteners used under interior conditions, white bronze by barrel plating can be used as well. The deposit will have a longer lasting brighter appearance compared with a zinc coating.

5.3.1.2 Base material, copper alloys

The segment is more or less dominated by the plating on taps and sanitary fittings. This industry is already suffering under the restriction of usage of hexavalent chromium. A chromium layer of minimum 0.25 µm is required over 10 µm of nickel plating is required to adequately resisting the wear of the cleaning detergents and provide corrosion resistance.

Modern trivalent chromium plating solutions will not deposit a layer much thicker than 0.3 µm, but unlike early deposits it is no longer microporous and has a colour much closer to hexavalent chromium deposits. The deposit has very little in the way of co-deposited elements or compounds in it and gives corrosion resistance results similar to hexavalent deposits when tested with the ASTMS G 85 acetic acid salt spray test

The alternative of white bronze does not provide the required resistance to wear and cannot compete with Ni-Cr on taps.

For other parts not in contact with human skin, such as jewellery, medals, buttons, non-chromium plated beer draft serving systems, lighting, leisure equipment, white bronze can be used if no special demands for corrosion or wear resistance are requested.

5.3.1.3 Base material, plastics

Alternatives based on white bronze will fail the specifications for corrosion in the automobile industry.

This is also the case for uses of white bronze as coating of sanitary fitting where the coating cannot fulfil the corrosion and wear resistance requirements, e.g. due to the frequent use of abrasive detergents.

However, for perfume caps, white bronze can be a convenient technical alternative and the process is already applied as top finish on top of nickel. The lower wear resistance may be seen as wear of the coating on the corner of the caps.

For various electronic items, e.g. telephone and cameras, the limitation of white bronze is only due to the lack of possibility to add a further toplayer based on chromium (VI).

On plastic, 0.2 µm of electroless copper can be used instead of 0.2 µm electroless nickel applied as subcoat before further coating, e.g. with acid copper + white bronze.

5.3.1.4 Base material, zinc and tin cast alloys

These porous metals limit the possibility of coatings due to the emission of gasses at high temperatures. Thus, paint, lacquers and CVD/PVD are not suitable on these base materials.

Tin cast alloys are mainly used in the fashion industry and for souvenirs, ornaments and trinkets. Here, white bronze provides a convenient alternative because most of the plating shops already use cyanide-containing electrolytes. Furthermore, these items often have to comply with the restriction on release of nickel if used in contact with skin.

For Zamak, the coating possibilities are comparable with those for plating on plastic and with the same conclusions as for decorative plated parts used in automotive industry, sanitary fittings, perfume caps and electronic items.

Only for parts used for furniture, in locks and window mechanisms may zinc + chromium (III) passivation + topcoat as described previously for steel, be considered an alternative to nickel plating.

5.3.2 Alternative to bright and levelled nickel prior to last metallic finish: bright acid copper plus a barrier diffusion

5.3.2.1 Bright acid copper

If copper could have a white appearance with consistent anti-tarnish behaviour, it would be ideal for replacing nickel on its own. Copper is cheaper, is an excellent electrical conductor and has antibacterial properties. Its capacity of levelling and brightening a surface is equal or better than bright nickel.

However, copper turns brown rapidly and, unlike nickel, it creates corrosive deposits. Furthermore, copper must be 1.5 times thicker than nickel in order to give the same corrosion protection.

The copper diffusion is a disadvantage for all decorative applications because the surface layer becomes brown rapidly. Only few metals can prevent copper from diffusing through the top layer. It is possible to measure the capacity of electroplated layers to block copper diffusion by baking the plated parts at 180°C for 48h and measure the colour change with a spectro-colorimeter. Only few metals, e.g. rhodium effectively blocs copper diffusion but is not feasible because of the extremely high costs of the metal. Also cobalt prevents copper diffusion but may not be suitable from a health point of view. Palladium cannot be used alone on top of copper but 0.1 µm palladium or palladium alloy is a possible, but expensive, diffusion barrier, which however reduces the corrosion resistance unless further plated in trivalent chromium solutions.

5.3.2.2 White bronze

The most common cyanide-based white bronze coating is Cu/Sn/Zn 55/30/15. The technique was developed more than 20 years ago and is now applied as underlayer instead of nickel on items intended for use in contact with human skin. The white bronze remains an acceptable alternative for a range of purposes and has a relative good performance:

- It prevents copper diffusion
- It protects against corrosion initiated by sweat
- It complies with wear resistance according to the ISO 23160 test

However, white bronze lack temperature resistance above 400°C which can be critical for some applications.

5.3.2.3 Palladium or palladium alloys

Pure palladium or iron or indium palladium alloy at 20% maximum of the alloyed metal is a good alternative that makes an efficient barrier against copper diffusion from a 0.1-µm layer. However, the resistance to corrosion and wear is not increased significantly. Palladium-nickel and palladium-cobalt alloys are not considered suitable alternatives due to the hazard profiles of nickel and cobalt.

Nevertheless, palladium coating can be used prior to thick precious metal plating and as part of plating systems for precious metals where a palladium interlayer between copper and gold is highly beneficial.

5.3.3 Alternatives to bright and levelled nickel in case of further deposits as top-coating or last passivation

5.3.3.1 Paint

Most of the paints applied on nickel plating are transparent and coated by electrostatic spraying. The paint aims to avoid tarnishing of the last metallic layer (nickel alone or with a topcoat of a metal sensitive to tarnishing such as silver, yellow bronze, brass and black nickel). For most of these applications, the appearance is of importance and the nickel underlayer is appreciated for its brightness and its levelling ability. An alternative with copper + white bronze is acceptable, especially in plating lines where cyanide is already used and handled safely. Applications for fashion industry or for souvenirs, ornaments, trinkets, leather goods and buckles can use acid copper + white bronze without technical advantage but also without drawback, except for higher costs.

5.3.3.2 Transparent cataphoretic lacquers

Cataphoretic lacquers efficiently preserve a metallic look by a 10-µm protective layer without drops. It is possible to integrate the cataphoretic lacquer in a plating process line. The productivity is high and the quality can be controlled with automatic equipment. The only limitation is that the base material should be able to resist a curing temperature up to 180°C.

The lacquer layer is quite difficult to identify and does not have any significant impact on the colour. Only the reflectivity is slightly lower.

A thin cataphoretic film does not provide a significant advantage in terms of in anti-corrosion and hardness.

Thus, for uses where specific corrosion or wear protection is not needed, e.g. indoor lamps and furniture, white bronze can be applied as an alternative to nickel.

5.3.3.3 PVD/CVD

As PVD/CVD coating are usually made at high temperatures, it can only be applied on some base materials. Considering the high costs of this type of coating, the uses are limited to the luxury industry and fashion. CVD/PVD can provide many colours and provides an opportunity for designers. In the case of PVD/CVD on plastic, an electroplated underlayer of e.g. nickel or nickel and chromium is needed.

Some deposits are extremely hard and used as toplayer on tools (drills). However, the wear resistance is limited due to the low thickness of the coated layer.

The corrosion resistance is practically not modified by a thin PVD/CVD coating.

5.3.3.4 Antique finishes

The appearance of an antique look can be obtained by oxidation of the last copper layer by sulphur or selenium.

For plating antique finishes, a single acid copper layer is enough without white bronze or palladium layer. Antique finishes will be much more productive without nickel but with an acid copper over the usual cyanide copper.

5.3.3.5 Zinc

Zinc is a serious candidate for replacing nickel on steel and zinc die cast, but only in combination with new techniques in terms of corrosion protection, wear and shock resistance. This includes zinc (or zinc alloy) combined with a cobalt-free chromium (III) passivation plus a topcoat. The benefit of the quality and productivity of the plating technique can outweigh the lack of a metallic shiny deposit.

Zinc has to be considered an alternative with the right combination as described in the section above. The weakness in terms of appearance is compensated by outstanding increase of corrosion protection and wear and shock resistance. The process is also cost efficient.

For all mechanical parts in movement, the wax and silica-containing topcoat protects also against shock and friction (e.g. for all window frame mechanisms).

5.3.3.6 Tin-cobalt

Tin-cobalt aims to replace bright chromium but gives a darker and bluish appearance. However, the hardness and corrosion resistance is lower than bright chromium. It is plated on top of nickel and cannot be considered a nickel alternative.

5.3.3.7 Alternatives to black nickel

Tin-cobalt is mainly used as black top finish applied at pH 8.5 and with a lacquer finish.

Trivalent black chromium has the same low thickness as conventional trivalent chromium but it does not require a lacquer finish. Apart the thin layer, black chromium can be considered a good candidate for replacing black nickel but only on white bronze.

5.3.4 Alternatives to bright nickel when used as last finish

5.3.4.1 White bronze

White bronze is offering a convenient alternative, which will be resistant to tarnishing, but at much higher costs. The coating has a white colour with good resistance to tarnishing. It offers good resistance to sweat but is not suitable for outdoor conditions. The hardness is high and the coating offers a relatively good wear resistance, which is, however, limited by its low thickness.

5.3.5 Summary of technical evaluation of alternatives to nickel plating in decorative coatings

The table below aims to summarize the above discussion of the technical suitability of the identified alternatives. In the table, corrosion resistance and hardness are focussed even though related issues like wear resistance and longevity as an integrated measure of various properties are discussed and may be of importance. The column on 'Uses' indicates the main uses that the types of plating are used for where it currently is regarded as a suitable surface treatment.

Table 5. Summary of the technical evaluation of alternatives to use of nickel in decorative coatings

	Colour and appearance	Corrosion	Hardness	Uses
Nickel subcoat under bright chromium (VI)	White blue	High resistance with multilayers of nickel	High hardness	Wide application Not suitable on white bronze
Nickel subcoat under chromium (III)	Slightly darker than bright chromium (VI)	Poor corrosion resistance to all salt spray tests	Deposit non crystalline and thus lees hard than bright chromium (VI)	Only for decorative purposes
Nickel subcoat as subcoat under precious metal	All combination of existing yellow, white and dark precious metal colours	Depending on thickness but dedicated for sweat testing	Depending on precious metal	Jewellery, eye wear, watch, luxury goods, souvenirs, sanitary fittings, fashion industry, buckles, locks
Black nickel + lacquer on bright nickel or on copper	Intense dark appearance	Very low but depends on underlayers	Low	Fashion industry, luxury goods, souvenirs, locks
Base material, steel				
Bright acid copper White bronze	Whiter than nickel	Passes sweat test but fails external accelerated tests	Good hardness but due to low thickness, the wear resistance is low compared with nickel	Not suitable on tubes and pipes
Zinc + clear chromium (III) passivation	White blue but slightly iridescent but without shiny metallic appearance	Medium corrosion protection	Low hardness but good wear resistance by use of appropriated silica containing passivation	Fasteners
Zinc + chromium (III) passivation + topcoat	White blue but could be stainless like but without shiny metallic aspect	Outstanding corrosion protection	Low hardness but outstanding wear resistance with self-healing effect	Supermarket trolleys, window frame mechanisms, fasteners, hinges, small parts by bulk plating
Black chromium (III) layer over copper + white bronze	From “smoke” to black	Passes sweat test but fails external accelerated tests	Good hardness but due to low thickness, the wear resistance is low compared with nickel	Not suitable on tubes and pipes but can be an alternative to black nickel + lacquer
Base material, copper alloys				
Bright acid copper white bronze	Whiter than nickel	Low corrosion resistance but sufficiently corrosion resistance to sweat	Low wear but passes ISO 23160	Jewellery medals, buttons, eye wear, watches, lighting
Copper + palladium or palladium alloys	Nice white colour slightly darker than white bronze	Low corrosion resistance because of very thin layer but good in combination with further top precious metal layers	Good hardness but low wear resistance because of very thin layer	Jewellery, luxury items, watches, eye wear, medals

	Colour and appearance	Corrosion	Hardness	Uses
Base material, zinc and aluminium				
Cyanide copper, acid copper, white bronze	Whiter than nickel	Passes sweat test but fails external accelerated tests	Good hardness but due to low thickness, the wear resistance compared with nickel	Indoor door handles, locks, fashion goods, trinkets, souvenirs
Plastics (POP)				
Copper and white bronze	Whiter than nickel	Passes sweat test but fails external accelerated tests	Good hardness but due to low thickness, the wear resistance is low compared with nickel	Perfume caps, electronic equipment (razors, telephones, cameras), writing pens
Nickel prior to last metallic finish				
Bright acid copper + white bronze	Whiter than nickel	Topcoating by precious metals provides excellent corrosion resistance	Toplayer is often soft and/or the layer is thin and gives little wear resistance. Can, however, fulfil ISO 23160	Gold-plated parts, writing goods, jewellery, fashion industry, watches, luxury items
Bright acid copper + palladium or palladium alloys as undercoat to precious metal layer	Whiter than nickel	Topcoating by precious metals provides excellent corrosion resistance	Toplayer is often soft and/or the layer is thin and gives little wear resistance. Can, however, fulfil ISO 23160	Small market segment: 3-µm gold - plated items (plaqué or).
Nickel in case of further deposits as top-coating or last passivation				
Acid copper + white bronze prior to cataphoretic lacquer or end finish paint	Whiter than nickel	Low, only applicable for indoor uses	Low, only applicable without friction	Lightings (except pipes and tubes)/ furniture, eye wear
Acid copper+ palladium + PVD/CVD	A range of colours are possible	Corrosion protection is low and used only on indoor parts	Hardness of the top layer and palladium is high but limited by the low thickness of the layer	Jewellery, luxury items, watches, eye wear
Acid copper + Antique finishes + potential lacquer	Green, brown black	Low	Low	Trinkets, souvenirs, medals
Bright nickel when used as last finish				
Alternatives to bright nickel when used as last finish				Fasteners, small items, hinges, tools
White bronze	Whiter than nickel	Passes sweat test but fails external accelerated tests	Good hardness but due to low thickness, the wear resistance is low compared with nickel	Fasteners, small items, hinges, tools

	Colour and appearance	Corrosion	Hardness	Uses
Zinc + chromium (III) passivation	Clear iridescent	Medium corrosion protection	Low hardness and poor wear resistance	Fasteners, small items, hinges, tools
Zinc + chromium (III) passivation + silica and wax containing topcoat	Clear colour or stainless-like	High corrosion protection	High wear resistance and constant coefficient of friction	Fasteners, small items, hinges, tools

5.4 Evaluation of the potential of the alternatives to reduce risks

The current assessment of the reduction potential of the identified alternatives includes the two lifecycle steps formulation of the preparations used in coating processes (electroplating) and the actual coating process itself.

In all the identified alternatives, the applied substances are transformed into another substance or integrated into a coating e.g. from a metal salt in a solution to a metal or an alloy coating. In general, the exposure to the substances in the coating matrix is much lower than during the formulation and use of the substances in the production process.

5.4.1 Exposure scenarios for formulation and coating processes

In the assessment of the exposures of the alternatives as well as in the base scenario, it is assumed that solution rather than dry salts are used for make-up and maintenance of the electrolytic baths. Often, maintenance includes use of metal pellets. It is assumed that these are non-dusting and that the main exposure to the metals arises from handling and use of metals in solution.

By far the most critical exposure route for exposure of workers is by inhalation. Oral exposure is considered minimal in an industrial setting and use of protective gloves and clothing is assumed to be a general standard. The most critical environmental exposure is release to the water environment via waste water, which is normally treated on-site and/or in a public sewage treatment plant (STP). Waste will normally be treated as hazardous waste or collected for re-cycling by authorized companies.

The exposure estimates for the formulation steps are based on the 'MEASE' and ECETOC TRA tools. For the coating processes, the GES for nickel plating is used under the assumption that the exposure via inhalation is due to aerosol formation and that the exposure to other components is proportionate to their concentration in the electrolytic baths. Furthermore, it is assumed that Local Exhaust Ventilation (LEV) is applied in all cases and that suitable protective gloves and clothing are used. It needs to be mentioned that where the calculation are based on Tier 1 tools (MEASE, ECETOC TRA), the estimates tend to be very conservative. Refined calculations and measurements are likely to show lower exposure levels but this is outside the scope of the current report.

The exposure of workers and the environment during formulation of solutions of substances used in coating is summarized in Table 5..

Table 5. Exposure of workers via inhalation to substances during formulation of chemicals used in electrochemical coating processes

Process	Most critical exposure, conditions and risk management
Transfer to/from vessel or large container (PROC 8A)	0.008 mg/m³ (estimated by MEASE tool[1])
Mixing or blending in batch processes for formulation (PROC 5)	0.008 mg/m³ (estimated by MEASE tool[1])
Formulation of metal compounds in solutions	6.9 µg/L (freshwater) 0.69 µg/L (marine water) Estimated by EUSES[2]

1) Assuming use of LEV and protective gloves.
2) The calculation is based on release of 0.05% of the amount of substances handled in the formulation step and efficient pre-treatment of waste water on-site before discharge to a municipal STP.

The exposure to nickel during the electrochemical coating processes is summarized in the table below based on the GES for the use of nickel sulphate, nickel chloride and nickel sulphamate. The GES indicates that the exposure to workers via inhalation, which is the most critical exposure route, lies in the range of 0.001-0.02 mg Ni/m³. The estimates assume that LEV is applied or integrated into the production equipment and that RPE (P2, corresponding to 20 times reduction of particles and aerosols) is applied during maintenance and cleaning operations. The most critical environmental exposure is to the freshwater environment and is estimated at 3.22-3.36 µg Ni/L. This estimate assumes pre-treatment of wastewater by advanced techniques, e.g. effective chemical precipitation and/or ion-exchange followed by treatment at a municipal sewage treatment plant (STP). It should be noted that all estimated releases to the water environment is subject to modification and scaling to local conditions. Regarding air emissions, it is assumed that all emissions pass bag filters or wet scrubbers. Finally, it is assumed that all waste generated from the processes is treated as hazardous waste or collected for re-cycling by authorized companies.

The assessment of the exposure to the substances used in the identified alternative processes is based on the nickel GES. The exposure in the work environment is assumed to be proportionate to the concentration of the substances in the electrolytic baths. The reasoning behind this assumption is that the exposure is by inhalation of aerosols formed by agitation or mechanical blending of the baths rather than inhalation of vapours. For example, the concentration of nickel salts in a Watt's bath is assumed to be approx. 250 g/L nickel sulphate and 60 g/L nickel chloride, corresponding to a nickel ion concentration in the bath at approx. 120 g/L. The corresponding (worst case) exposure (long-term inhalation) in the work environment is estimated in the nickel GES for electroplating at 0.02 mg Ni/m³. For the alternative coatings, the exposure concentration of the individual substance used is calculated as:

$$[\text{substance}]\text{ihl, workers} = 0.02\,\frac{\text{mg}}{\text{m3}} \times \frac{\text{subst. conc}}{\text{nickel ion conc}}$$

It is assumed that the substances are handled and added as solutions and that the most critical exposure is by inhalation. The same approach is followed for environmental exposure: the release from the site is assumed to be the same as for nickel but corrected for the relative concentration of the ion compared with nickel salts in the applied electrolytic bath.

Table 5. Summary of generic exposure scenarios for the use of nickel sulphate, nickel chloride and nickel sulphamate in electroplating processes. It is assumed that the substances are applied as solutions of metal salts and not as powder.

Name of GES	Critical exposure route and DNEL/PNEC	Most critical exposure, conditions and risk management
End use – DU of Ni sulphate: Metal surface treatment – nickel electroplating, nickel electroforming and electroless nickel plating Operations with salt solutions	Workers: DNEL = 0.05 mg Ni/m³ (long-term inhalation)	Exposure estimate: 0.02 mg Ni/m³ (long-term inhalation, estimated value) Assuming LEV for non-closed manual operation steps and use of suitable gloves. RPE (P2) used during maintenance and cleaning.
	Environment: PNEC: 3.55 µg Ni/L (fresh water)	3.04-3.34 µg Ni/L Onsite treatment by chemical precipitation, sedimentation, filtration or a combination. Air: bag filters and wet scrubbers.
Intermediate use of $NiCl_2$ Metal surface treatment – nickel electroplating, nickel electroforming and electroless nickel plating	Workers: DNEL = 0.05 mg Ni/m³ (long-term inhalation)	Exposure estimate: 0.02 mg Ni/m3 (long-term inhalation, estimated value) Assuming LEV for non-closed manual operation steps and use of suitable gloves. RPE (P2) used during maintenance and cleaning.
	Environment: PNEC: 3.55 µg Ni/L (fresh water)	3.04-3.34 µg Ni/L (fresh water) Onsite treatment by chemical precipitation, sedimentation, filtration or a combination. Air: bag filters and wet scrubbers.
End use of nickel sulphamate, $Ni(SO_3NH_2)2 \times H_2O$: Metal surface treatment – nickel electroplating, nickel electroforming and electroless nickel plating Operations with salt solutions	Workers: DNEL = 0.05 mg Ni/m³ (long-term inhalation)	Exposure estimate: 0.02 mg Ni/m³ (long-term inhalation, estimated value) Assuming LEV for non-closed manual operation steps and use of suitable gloves. RPE (P2) used by maintenance and cleaning.
	Environment: PNEC: 3.55 µg Ni/L (fresh water)	3.04-3.34 µg Ni/L (fresh water) Onsite treatment by chemical precipitation, sedimentation, filtration or a combination. Air: bag filters and wet scrubbers.
End use – DU of Ni metal Metal surface treatment – nickel electroplating and nickel electroforming	Workers: DNEL = 0.05 mg Ni/m³ (long-term inhalation)	Exposure estimate: 0.001-0.002 mg Ni/m³ (long-term inhalation, estimated value) Assuming LEV and RPE (P2) for all non-closed manual operation and cleaning and maintenance. Assumed use of suitable gloves.
	Environment: PNEC: 3.55 µg Ni/L (fresh water)	3.04-3.34 µg Ni/L (fresh water) On site treatment by chemical precipitation, sedimentation, filtration or a combination. Air: bag filters and wet scrubbers.

5.4.2 Hazard and risks of the alternatives

In the following section, the hazards of the substances applied as well as the potential risk in standard scenarios have been calculated. It should be noted, however, that the assessment of the potential risk is a Tier 1 assessment and that further refinement is

needed in order to assess the potential risk at individual production sites. For the purpose of the current assessment, it may, however, be useful when comparing the potential risk of the identified alternatives.

It should be noted that REACH Title VII on authorisation includes the use of substances on Annex XII applied in mixtures in concentrations under 0.1% or below the lowest of the concentration limits specified in Directive 1999/45/EC or in Part 3 of Annex VI to Regulation (EC) No 1272/2008, which result in the classification of the mixture as dangerous. For the substances assessed in this report the relevant concentration is 0.1%. The revision of the CLP regulation by 2015 may change some thresholds. However, it seems unlikely that changes will dramatically increase this threshold to a level that will have an impact on the current assessment. The relevant substances evaluated here are contained in much higher concentrations in the range of >25 g/L with one exception of cobalt nitrate being used in chromium (III) passivation coating at 3 g/L (i.e. 0.3%).

The identified hazards of the raw materials are summarized in Appendix A and show the substance classification, preferably the harmonized classification according the CLP, Annex VI, or if not available, the reported classification in the ECHA C&L inventory data base.

It need be noted that only the main substance components are included and it is assumed that they are also the main contributors to the risk to humans and the environment. Only where specific hazardous additives have been identified, these have been included as well.

In order to get an indication of the potential risk, OEL values from EU member states[2] or, alternatively, derived DN(M)EL and PNEC values for long-term exposure have been extracted from registration dossiers or from available databases.

The potential risk of the alternatives is calculated by comparing the exposure to workers (long-term inhalation) and the water environment as indicated in Section 4.4.2 with the corresponding OEL, DNEL and PNEC values (Appendix B). The resulting risk characterization ratios (RCR) indicate the potential risk of the individual substances, i.e. a high RCR close to or above 1 indicates a risk.

$$RCR = \text{estimated exposure level/OEL or DNEL}$$

2: The Social and Economic Council of the Netherlands (SER), http://www.ser.nl/

Table 5. shows the RCR values of the most critical components applied in the alternatives coating techniques.

Table 5. Preliminary risk assessment of alternatives

Process	Substance	RCR, long-term inhalation	RCR, water environment	Comments relevant to SVHC status
Bright, semi-bright and satin nickel	Nickel sulphate $NiSO_4$ 250 g/L	0.400	0.928	Classified as Carc. 1A. (CLP, ATP VI)
	Nickel chloride $NiCl_2$ 60 g/L			
	Boric acid H_3BO_3 45 g/L	0.015	0.001	Classified as Repr. 1B (CLP, Annex VI)
Bright chromium (VI)	Chromic acid $Cr0_3$ 250 g/L	4.098	2.013	Classified as Carc. 1A. (CLP, ATP VI)
	Sulphuric acid H_2SO_4 1,5 g/L	0.005	0.164	
Chromium (III)	Chromium (III) sulphate $Cr_4(SO_4)_5(OH)_2$ 125 g/L	0.023	0.728	
	Potassium bromide KBr 35 g/L			
	Boric acid H_3BO_3 45 g/L	0.015	0.001	Classified as Repr. 1B (CLP, Annex VI)
Alternative coating processes				
Base material, steel				
Alkaline cyanide-free copper (pre-layer)	Copper hydroxide $Cu(OH)_2$ 20 g/L	0.002	0.046	
	1-hydroxyethylidene-1,1,-diphosphonic acid HEDP 180 g/L	-	0.036	
Bright acid copper	Copper sulphate $CuSO_4$, 5 H_2O 220 g/L sulphuric acid	0.036	1.158	
White bronze	Copper cyanide CuCN 11 g/L	0.100	0.017	Cyanides are highly acute
	Potassium stannate K_2Sn0_3 86 g/L	0.007	n.a.	
	Zinc cyanide $Zn(CN)_2$ 1.8 g/L	0.000	0.002	
	Potassium cyanide KCN 45 g/L	0.003	0.493	

Process	Substance	RCR, long-term inhalation	RCR, water environment	Comments relevant to SVHC status
Zinc + chromium (III) passivation + topcoat	Zinc chloride $ZnCl_2$ 65 g/L	0.011	0.292	
	Potassium chloride KCl 220 g/L	0.000	0.060	
	Boric acid H_3BO_3 25 g/L	0.008	0.001	Classified as Repr. 1B (CLP, Annex VI)
Chromium (III) passivation	Chromium (III) chloride $CrCl_3$ 50 g/L	0.044	0.113	
	Sodium nitrate $NaNO_3$ 100 g/L	na	na	
	Cobalt nitrate $Co(NO_3)_3$ 3 g/L	0.004	0.016	Classified as Carc 1B and Repr 1B (CLP, Annex VI)
Base material, copper alloys				
Alkaline cyanide-free copper (pre-layer)	See above under Base material, steel	0.002	0.046	
Bright acid copper	See above under Base material, steel	0.036	1.158	
White bronze	See above under Base material, steel	0.100	0.017	
Bright acid copper + palladium or palladium alloys	Palladium tetramino chloride $Pd(NH_3)_4Cl_2$ 4,5 g/L	n.a.	n.a.	
	Ammonium chloride NH_4Cl 50 g/L	0.001	n.a.	
	Di potassium phosphate K_2HPO_4 35 g/L	0.001	n.a.	
Base material, zinc and aluminium				
Alkaline cyanide copper (pre-layer)	Copper cyanide CuCN 30 g/L	0.005	0.158	
	Potassium cyanide KCN 55 g/L	0.004	0.602	
	Potassium hydroxide	n.a.	n.a.	
Bright acid copper	See above under Base material, zinc and aluminium	0.036	1.158	
White bronze	See above under Base material, zinc and aluminium	0.100	0.017	
Plastics (POP)				
Alkaline cyanide copper (pre-layer)	See above under Base material, zinc and aluminium	0.005	0.602	
Bright acid copper	See above under Base material, zinc and aluminium	0.036	1.158	
White bronze	See above under Base material, zinc and aluminium	0.100	0.017	

Process	Substance	RCR, long-term inhalation	RCR, water environment	Comments relevant to SVHC status
Nickel prior to last metallic finish				
Alkaline cyanide copper (pre-layer)	See above under Base material, zinc and aluminium	0.005	0.602	
Bright acid copper	See above under Base material zinc and aluminium	0.036	1.158	
White bronze	See above under Base material zinc and aluminium	0.100	0.017	
Bright acid copper + palladium or palladium alloys	See above under 'Base material copper alloys'	n.a.	0.000	
Nickel in case of further deposits as top-coating or last passivation				
Acid copper + white bronze prior to cataphoretic lacquer or top finish paint	Pre-layer, acid copper and white bronze as above	0.036	1.158	
White bronze		0.100	0.017	
	Colloidal Silica at 44% SiO_2 90 g/L	n.a.	n.a.	
	Wax copolymer acrylic polyethylene 120 g/L	n.a.	n.a.	
Acid copper+ palladium + PVD/CVD	Pre-layer and acid copper as above	0.036	1.158	
	PVD/CVD could include a range of different metals (in their metallic form)	na.	na.	
Acid copper + antique finishes + potential lacquer	Pre-layer of alkaline cyanide copper + bright acid copper as above	0.036	1.158	
Zinc	Zinc chloride	0.011	0.292	
	Potassium chloride	0.000	0.060	
	Boric acid	0.008	0.001	Classified as Repr. 1B (CLP, Annex VI)
Chromium (III) passivation	Chromium (III) chloride	0.044	0.113	
Bright nickel when used as last finish				
Bright acid copper + white bronze	See above under Base material, zinc and aluminium	0.100	0.017	
Zinc + chromium (III) passivation	See above under Base material, steel	0.044	0.113	
Zinc + chromium (III) passivation + silica and wax containing topcoat	See above under Base material, steel	0.044	0.113	
	Colloidal silica at 44% SiO_2 90 g/L	n.a.	n.a.	
	Wax copolymer acrylic-Polyethylene 120 g/L	n.a.	n.a.	

From this overview, it should be noted that:

- A few substances applied in alternative plating solutions have SVHC properties: cobalt nitrate, which is classified as Carc 1B and Repr 1B, is used as an element in

chromium (III) passivation used on top of zinc plating. Furthermore, boric acid is used as an element in bright chromium plating as well as in acidic zinc plating.

- The base scenario, i.e. the use of nickel and chromium (VI) for bright chromium plating, includes use of SVHC substances and potential SVHC substances, i.e. nickel sulphate, nickel chloride, chromic acid and boric acid.
- RCR values >1 for workers (inhalation) and environment (fresh water) is observed for use of chromic acid in the presented scenarios. Also copper sulphate applied in bright acid copper plating triggers RCR values> 1 in the freshwater environment. This cannot be used to conclude that there is risk at sites using these substances but rather confirms a concern that probably has already been addressed locally through use of strict conditions in the work environment as well as environmental permits.
- Specifically with respect to use of cyanide salts, i.e. in the white bronze plating, and use of alkaline cyanide copper pre-layer, it should be noted that the high acute toxicity of these compounds may trigger requirements pertaining to the transport regulation and the 'Seveso'-directive[3]. Moreover, industry experts point to the hazards of hydrogen gas potentially evolving from non-soluble electrodes and the use of hypochlorite for neutralisation of cyanide. These hazards introduce requirements of additional safety measures at sites shifting to white bronze plating.

Title VII of the REACH legislation has the aim to progressively replace Substances of Very High Concern. Consequently, a substance or techniques identified as alternative to a SVHC substance should not itself involve substances with similar properties, i.e. CMR, 1A or 1B, or persistent, toxic and bioaccumulative (PBT or vPvB) or substances of equivalent concern.

It should further be noted that it is possible to adequately control risks where a threshold level has been determined for a CMR substance. This is the case for nickel salts and boric acid. The current preliminary risk assessment indicates a (worst-case) exposure below the DNEL values of these substances.

Finally, it is observed that, in general, the risk quotients for workers and the environment are relative low for the alternatives.

5.5 Cost-related aspects of alternatives

The aim of the current section is to provide indication on the relative costs of the alternatives and to provide rough estimations of the cost ratio. An extensive cost assessment will require an approximation of the costs of chemicals and additives, labour, energy, treatment of waste streams and equipment amortization. All these expenses depend on a range of factors including local regulations as well as and market-related issues.

A simplified approach would be to consider metal prices as key figures and compare the costs of the various layers by focusing mainly on two issues:

- A precise but non-complete way: The metal costs included the specialty chemicals that could have a major influence (e.g. white bronze)
- The global plating costs

[3] Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances

5.5.1 Nickel plating

Composition

Normally, nickel electroplating is using the conventional Watt electrolyte. It contains sulphate, chloride and borate ions. Sulphate and chloride are replenished by drag-in of acidic activation or by pH adjustment. The nickel content is maintained by nickel anode dissolution. As the anodic current efficiency is slightly higher than the cathodic current efficiency, close to 100%, the metallic content of the electrolyte is supposed to increase if the drag-out of nickel solution is recycled. The costs of the raw materials of the nickel electrolyte are practically the costs of the nickel anodes in pellets or in buttons plus the costs of the drag-out of boric acid.

Productivity

The deposition rate is high approx. 1 µm/min and, normally, the plating time does not exceed 10 min. An automatic plant produces one rack every five minutes and the volume of the nickel bath does not exceed two positions.

Specialty chemicals

Specialty chemicals include mainly various brighteners and wetting agents. The market of these chemicals is large and the costs have been dramatically reduced in the last decades. The price setting depends partly on the level of the supporting services that go together with the supply of the specialty chemicals. Many suppliers provide a full service of Quality Control including analysis of the plating bath (salts, brighteners and practical test in Hull Cell), technical assistance on the plating line, technical assistance for the end users and various tests on plated parts according the quality control. Rough calculations indicate average costs of EUR 40/10 kAh for serving automatic plants of an industrial production.

Costs of metal and specialty chemicals/plating costs

This includes evaluation of the costs of a specific deposit. The prices of the main raw materials, i.e. the deposited metal used in electroplating, are calculated on the basis of market prices, which accounts for approximately one third of the global plating costs. The other main costs are roughly 4% for other chemicals used in the plating line (cleaners, pickling, activation, post treatments and water rinses), 7% for the amortization of the equipment, 40% is costs of labour for production, control and maintenance, 8% for treatment of the wastes etc. and 4% for energy consumption.

By end of 2012, the costs were EUR 1.5/m^2 of nickel metal at a thickness of 10 µm and including specialty chemicals while the global plating costs are approx. EUR 4/m^2.

5.5.2 White bronze plating

Composition

The main users are purchasing ready-to-use cyanide-containing chemicals for make-up, replenishing and maintenance. Insoluble anodes are used in this process. Consequently the electrolyte will accumulate the side ions while the metals are consumed at the cathode. The working life of these electrolytes is limited to a couple of dozens of turn-over before a new make-up is necessary.

Productivity

The deposition rate is more or less 4 times lower than for nickel. With about 0.25 µm/min, the plating time is about 12 min for 3 µm. By considering an automatic plant producing 1 rack every 5 min, the required volume of the cyanide white bronze bath is higher than for the nickel: 3 positions instead of 2.

Costs of metal and specialty chemicals/plating costs

If only the metal costs are considered, white bronze is cheaper than nickel plating but the costs of the cyanide and sophisticated specialty chemicals are very high. Currently, the market of white bronze is strictly limited to small parts in contact with the human skin. The volume of the electrolyte exceeds rarely 200 L and the volume of the production is much lower than nickel plating.

Consequently, costs of EUR 0.5/g of plated white bronze is frequently encountered as the service linked to the production and the maintenance of an alloy of 3 elements is much more comprehensive than for a single nickel bath.

By considering a possible large industrial scale production, the costs will be approx. EUR 0.25/g of plated white bronze. Even at this price, the metal and specialty chemicals costs add up to EUR 7.7/m² for an alternative of 10 µm of copper plus 3 µm of white bronze compared with 10 µm of nickel, i.e. more than 4 times higher.

The global plating costs are estimated to be EUR 10/m², i.e. 2.5 times higher than nickel at EUR 4/m².

5.5.3 Palladium plating

Composition

Plating with palladium or palladium alloys requires sophisticated electrolytes with insoluble anodes. All chemicals are supplied by specialists and the electrolytes are very costly. However, the costs of the metal represent the main part of the costs.

Productivity

The deposition rate is very low at 0.06 µm/min but the low thickness requirement at 0.1 µm compensates the low rate and one station is enough.

The main problem is the potential contamination of the electrolytes by the drag-out of the previous bathes or by the dissolution of metals into the ammonia-containing alkaline bath. Consequently, the prior rinse bath must be very efficient and the parts must be dipped under current in order to avoid dissolution of copper. In order to make sure that the racks are perfectly rinsed and free of contaminants, the rinse time is increased, which reduces the productivity of the plating line.

Costs of metal and specialty chemicals/plating costs

The costs of palladium represent more than 66% of the global costs and are much higher than nickel. Plating with palladium is, however, still feasible as basis for further precious metal plating, e.g. on luxury goods, writing elements, jewellery, watches, eye wears. The palladium layer is thus considered part of the total precious metal plating. The production of palladium is limited to a few countries and the risk of unstable market prices on palladium is high.

At the end of 2012 the plating costs of 0.1 µm of palladium on acid copper were EUR 22.7/m² while the global plating costs were EUR 25.2/m².

5.5.4 Zinc plating

Composition

Zinc plating is dedicated to plating on steel and can be made with various electrolytes. Except for the cyanide version, the most efficient zinc plating is the alkaline and acid chloride zinc plating types. Acid chloride zinc offers a better appearance but cannot offer the same corrosion protection than alkaline zinc. Even if the appearance is slightly less bright, the alkaline plating is preferred because it offers a longer working life and a

longer sustainability of the appearance of the plated parts. By using new passivation methodologies plus topcoats, zinc plating offers additional properties in terms of friction and wear resistance that counterbalance some of the weaknesses of the appearance.

An alkaline electrolyte is relatively cheap with caustic soda and low zinc content. The zinc anodes are dissolved separately in a dissolving tank. Specialty chemicals can provide a high quality of the plating with an outstanding metal distribution.

Productivity

The deposition rate is two times lower than for nickel, i.e. 0.5 µm/min. Zinc thus needs larger volume of electrolytes but does not have a high sensitivity to contaminants and the costs are considerably cheaper than nickel.

Costs of metal and specialty chemicals/plating costs

Zinc is by far the cheapest alternative and represents the largest production volume within electroplating. There are many highly sophisticated plating lines in Europe which combines zinc with Cr(VI)-free passivation and topcoats, which provide additional properties in term of friction and wear resistance. The combination is competitive e.g. for corrosion protection of fasteners, supermarket trolleys and window frames. Many electroplaters who faced legal constraints due to ban of chromate (VI) have successfully converted to zinc plating.

The metal and specialty chemicals costs are estimated to be EUR 0.37/m^2, thus lower than EUR 1.5/m^2 for nickel.

The global plating costs of zinc + chromium (III) passivation + a suitable topcoat are estimated to be EUR 3/m^2, thus lower than EUR 1.5/m^2 for nickel.

5.5.5 Copper plating

Copper is already very frequently used as a base coating for plating of nickel on Zamak, aluminium, copper alloys and plastics. Cyanide is practically mandatory for many of these applications because of high demands with respect to adhesion and a low number of rejected parts. Consequently, alkaline cyanide-free copper, which is expensive due to the costs of the copper complex, is mainly used on steel and copper alloys.

The acid copper can alone offer a high levelling and brightness which is comparable to nickel. It would be the ideal alternative if copper was not sensitive to oxidation. Furthermore, copper tends to migrate through other metal layers and can tarnish the topcoat.

Composition

The acid copper electrolyte is very simple and based on sulphate. An additional small quantity of chloride helps the depolarization of the Cu-P (0,06% w/w in P) anodes. The bath is replenished with sulphuric acid and chemicals as leveller, wetting agents and grain refiner.

Productivity

The deposition rate of 0.6 µm/min is slightly higher than for nickel but copper is more sensitive to the risk of 'burning' at high current density and is usually considered to have the same deposition rate as nickel.

Costs of metal and specialty chemicals/plating costs

The market of the copper brightener is very competitive and the costs per 10 kAh can be as low as EUR 30, depending on the technical services that the specialty chemicals supplier is providing. The treatment of the wastes is well known and effective. The

costs of a copper layer of 10 µm are estimated to be EUR 0.75/m² for metal and specialty chemicals, compared with EUR 1.5/m² for nickel. The global plating costs of 10 µm of acid copper are approx. EUR 3.3/m², thus lower that EUR 4/m² for nickel.

6 Conclusions

The aim of the current report was to identify and preliminary evaluate potential alternatives to nickel used in plating. The evaluation presented here is by nature generic and covers a wide range of different applications where metal plating is used to provide decorative qualities to an item. Ultimately, a potential alternative to nickel needs to be evaluated against a set of specific requirements, which are defined by the use of the coated item, e.g. technical qualities as resistance to corrosion and wear, in addition to the quality of the design and appearance. The main issue in the report is an evaluation and discussion of alternatives to nickel, which are currently used and available for industrial scale production. The analysis can be used as the basis of further specific analysis of individual cases of alternatives.

In the following paragraphs, some of the main findings and conclusions of the evaluation are highlighted:

- Among the few possible alternatives for nickel, white bronze seems far the best candidate. However, the process involves use of cyanide-containing baths. But a survey of patents indicates that efforts are made to develop cyanide-free and cheaper white bronze. It may, however, take years before a suitable solution is available for industrial production.

- White bronze is suitable for plated articles intended for contact with human skin, e.g. watches, eye-wear and jewellery, although the plating costs are 2.5 times the price of nickel plating. The replacement of nickel is the general trend for such products including the manufacture outside the EU because of the legal restriction and awareness of dermatological effects of nickel release from such articles. Normally, these articles do not require the levelling effect of nickel (or alternatively acid copper) because they already have a polished surface. Moreover, the volume of the plating baths is much smaller than for other industrial applications.

- For other uses than watches, eye-wear and jewellery, white bronze has a number of limitations:

    1) White bronze cannot replace a multilayer of nickel as subcoat to chromium (VI) plating as it does not fulfil the specifications on corrosion resistance, e.g. as required in the automotive industry, and corrosion and wear requirements for sanitary fittings used in bathrooms.

    2) The white bronze coating process involves use of cyanides. It needs to be noted that use of cyanide in quantities above 5 tonnes cyanide per year triggers requirements according to the 'Seveso'-directive. The plating sequence of white bronze is short and thus there is a risk by acid drag-out in cyanide which also presents a risk.

    3) White bronze is more costly than an equivalent nickel coating

- Zinc plating on steel with trivalent chromium, a cobalt-free passivation layer plus additional topcoat can be a convenient solution for fasteners, supermarket trolleys and windows frame mechanisms. This solution has outstanding corrosion resistance and a convenient friction coefficient but as zinc is supposed to be corroded over

time, it does not, however, preserve the same bright appearance as a nickel + bright chromium (VI) coating.

- It is very difficult to replace nickel plating as subcoat for chromium (VI) plating on furniture. Copper cannot be used instead because it does not apply to steel pipes and tubes. No alternative has been identified for industrial scale production.

The hazard and risk evaluation in this report is focused on properties that may trigger identification as SVHC under REACH. This includes carcinogenic, reprotoxic and mutagenic properties. In addition, it is noted in the table whether the current preliminary assessment resulted in risk characterization ratios higher than 1, indicating a risk to humans or the environment.

The substitution of SVHC is a main objective of REACH Title VII on authorization. The table highlights the plating types where substances have already been or may in future be identified as SVHC.

High RCR values are observed where copper is used in plating of a 'bright acid copper'. This is due to the conditions set in the exposure scenario used for the calculations where a default release rate emission from a plating process is relatively high. The result confirms what the plating industry has already experienced in terms of quite strict requirements regarding release of copper via waste water. Cyanide-containing baths are used in plating of alkaline copper and white bronze and, due to the high toxicity, they will trigger strict reduction measures in order to control possible risks in the work environment. In addition, industries with more than 5 tonnes cyanide have to comply with the provisions of the 'Seveso'-directive. From the exposure scenarios and the calculated RCR values, it seems that the risk can be controlled.

In addition to the hazard and risk assessments made, the following should be noted:

- Out-phasing nickel plating in the EU may move plating business outside the EU and may lead to increasing import of plated items from non-EU countries. This may be true for applications where the item is not subject to corrosive environments but where the alternative white bronze is more expensive and European industry will experience loss of market shares to non-EU manufacturers. This includes indoor lighting, indoor locks and door handles, furniture, sanitary fittings, souvenirs, fasteners, hinges, tools and home appliances.

- The use of cyanide salts in white bronze plating and the use of alkaline cyanide copper pre-layer involve handling highly acute toxic compounds and may trigger additional legal requirements pertaining to the transport regulation and the 'Seveso'-directive[4]. Moreover, there is a pressure on industry to replace cyanide due to the toxicological hazards. Furthermore, industry experts point to the hazards of hydrogen gas potentially evolving from non-soluble electrodes as well as the use of hypochlorite for neutralisation of cyanide. These hazards introduce requirements of additional safety measures at sites shifting to white bronze plating.
- Cost issues need be evaluated based on specific cases and must include the investments needed at the level of each company

In the table below, the column 'Plating unit costs' indicates estimated prices per m^2 for the different plating types. The estimate takes into consideration the costs of metals and specialty chemicals as well as the plating efficiency. Other relevant site specific costs could be a reduction of capacity due to lower plating efficiency and introduction

[4] Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances

of additional measures for wastewater treatment (copper). Moreover, maintenance costs may increase by substitution of nickel, e.g. copper tanks that need to be more frequently replaced due to acid corrosion from some of the alternatives.

The table below summarizes the main findings.

Table 6. Summary of the evaluation of alternatives to nickel used in decorative plating

Plating type	Uses	Hazards and risk[1]	Plating unit costs and other cos t issues
Base scenario, main uses of nickel in decorative plating			
Nickel subcoat under bright chromium (VI)	Wide application. Not suitable on white bronze bronze	Use of nickel and chromium (VI) substances (Carc 1A) and boric acid (Repr. 1B). High RCR (workers) and RCR (environ)	Nickel global plating costs approx. EUR 4/m²
Nickel sub-coat as subcoat under precious metals	Jewellery, eye wear, watch, luxury goods, souvenirs, sanitary fittings, fashion industry, buckles, locks	Use of nickel substances (Carc 1A) and boric acid (Repr. 1B). High RCR (environ) due to chromium	Nickel global plating costs approx. EUR 4/m²
Black nickel + lacquer on bright nickel or on copper	Fashion industry, luxury goods, souvenirs, locks	Use of nickel substances classified as Carc 1A and boric acid (Repr. 1B). High RCR (environ)	Nickel global plating costs approx. EUR 4/m² & copper EUR 3.3/m²
Alternatives to nickel plated on base materials of steel			
Bright acid copper, white bronze	Not suitable on tubes and pipes	High RCR (environ) due to copper	Copper + white bronze overall plating costs EUR 10/m²
Zinc + clear chromium (III) passivation	Fasteners	May involve use of cobalt nitrate (Carc 1B and Repr 1B) and boric acid (Repr 1B)	Approx. global plating costs of EUR 2.8/m²
Zinc + chromium (III) passivation + topcoat	Supermarket trolleys, window frame mechanisms, fasteners, hinges, small parts by bulk plating	Can involve use of cobalt nitrate (Carc 1B and Repr 1B) and boric acid (Repr 1B)	The global plating costs of zinc + chromium (III) passivation + a suitable topcoat are estimated to be EUR 3/m²
Alternatives to nickel plated on base materials of copper alloys			
Bright acid copper white bronze	Jewellery, medals, buttons, eye wear, watches, lighting (but not pipes)	High RCR (environ) due to copper	The global plating costs of 10 µm of acid copper approx. EUR 3.3/m² but increases to EUR 10/m² with white bronze
Copper + palladium or palladium alloys	Jewellery, luxury items, watches, eye wear, medals	High RCR (environ) due to copper	Costs of palladium are very high and only feasible on luxury goods
Alternatives to nickel plating on base materials of zinc and aluminum			
Cyanide copper, acid copper, white bronze	Only indoor door handles, locks, fashion goods, trinkets, souvenirs	High RCR (environ) due to copper	Copper + white bronze overall plating costs of EUR 10/m²
Alternatives to nickel used in plating on plastics (POP)			

Plating type	Uses	Hazards and risk[1]	Plating unit costs and other cos t issues
Copper and white bronze	Perfume caps, electronic equipment (razors, telephones, cameras, writing pens	High RCR (environ) due to copper	Copper + white bronze overall plating costs EUR 10/m²
Alternatives to nickel prior to last metallic finish			
Bright acid copper + white bronze	Gold-plated parts, writing goods, jewellery, fashion industry, watches, luxury items	High RCR (environ) due to copper	Copper + white bronze overall plating costs EUR 10/m²
Bright acid copper + palladium or palladium alloys as undercoat to precious metal layer	Small market segment: 3 µm gold-plated items (plaqué or)	High RCR (environ) due to copper	Costs of palladium are very high and only feasible on luxury goods
Alternatives to nickel in case of further deposits as top-coating or last passivation			
Acid copper + white bronze prior to cataphoretic lacquer or top finish paint	Lightings (except pipes and tubes), furniture, eye wear	High RCR (environ) due to copper	Copper + white bronze overall plating costs EUR 10/m²
Acid copper+ palladium + PVD/CVD	Jewellery, luxury items, watches, eye wear	High RCR (environ) due to copper	Costs of palladium are very high and only feasible on luxury goods
Acid copper + Antique finishes + eventual lacquer	Trinkets, souvenirs, medals	High RCR (environ) due to copper	Copper global plating costs EUR 10/m²
Alternatives to bright nickel when used as last finish			
White bronze	Fasteners, small items, hinges, tools		White bronze overall plating costs EUR 10/m²
Zinc + chromium (III) passivation	Fasteners, small items, hinges, tools	May involve use of cobalt nitrate (Carc 1B and Repr 1B) and boric acid (Repr 1B)	Approx. global plating costs of EUR 2.8/m²
Zinc + chromium (III) passivation + silica and wax-containing topcoat	Fasteners, small items, hinges, tools	May involve use of cobalt nitrate (Carc 1B and Repr 1B) and boric acid (Repr 1B)	The global plating costs of zinc + chromium (III) passivation + a suitable topcoat are estimated to be EUR 3/m²

1 Toxicological hazards other than those referred to in REACH Article 57 are not mentioned, i.e. carcinogenic, reprotoxic; mutagenic hazards, and similar concerns. PBT properties are not relevant for inorganic compounds. Carc. = carcinogenicity; Repr. = reprotoxicity; Mut. = mutagenicity. Use of cyanide is a serious concern in the work environment. However, the current assessment indicates that risks are controlled for use in plating.

APPENDIX A

Classification of the applied substances

Process	Substance	Hazard classification
Bright, semi-bright and satin nickel	Nickel sulphate $NiSO_4$ 250 g/L	Carc. 1A;H350i Muta. 2;H341 Repr. 1B;H360D STOT RE 1;H372 Acute tox. 4;H332 Acute tox. 4;H302 Skin irrit. 2;H315 Resp. sens. 1;H334 Skin sens. 1;H317 Aquatic acute 1;H400 Aquatic chronic 1;H410
	Nickel chloride $NiCl_2$ 60 g/L	Carc. 1A;H350i Muta. 2;H341 Repr. 1B;H360D Acute tox. 3;H331; Acute tox. 3;H301 STOT RE 1;H372 Skin irrit. 2;H315 Resp. sens. 1;H334 Skin sens. 1;H317 Aquatic acute 1;H400 Aquatic chronic 1;H410
	Boric Acid H_3BO^3 45 g/L	Repr. 1B, H360; (Annex VI)
	Nickel metal anode Maintenance	Repr. 1B; H360FD
Bright chromium (VI)	Chromic acid $Cr0_3$ 250 g/L	Ox. sol. 1 H271 Carc. 1A H350 Muta. 1B H340 Repr. 2 H361 Acute tox. 2 H330 Acute tox. 3 H311 Acute tox. 3 H301, STOT RE 1 H372 Skin corr. 1A H314 Resp. sens. 1 H334 Skin sens. 1 H317 Aquatic acute 1 H400 Aquatic chronic 1 H410
	Sulphuric acid H_2SO_4 1.5 g/L	Skin corr. 1A, H314 Skin corr. 1A H314: C ≥15% Eye irrit. 2 H319: 5% ≤ C <15% Skin irrit. 2 H315: 5% ≤ C <15%
Alcaline cyanide-free copper (pre-layer)	Copper hydroxide $Cu(OH)_2$ 20 g/L	Acute tox 4;H302 - Eye irrit. 2;H319 Aquatic acute 1 H400: Very toxic to aquatic life (From registration dossier on copper hydroxide nitrate)
	1-hydroxyethylidene-1,1,-diphosphonic acid HEDP 180 g/L	Acute tox. 4 H302: Harmful if swallowed Eye damage 1 H318: Causes serious eye damage

Process	Substance	Hazard classification
Bright acid copper	Copper sulphate $CuSO_4$, 5 H_2O 220 g/L	Acute tox. 4;H302 Eye irrit. 2;H319 Skin irrit. 2;H315 Aquatic acute 1;H400 Aquatic chronic 1;H410
	Sulphuric acid	As above
	Sodium chloride NaCl 0.12 g/L	Not classified
White bronze	Copper cyanide CuCN 11 g/L	Acute tox. 2;H300 Acute tox. 1;H310 Acute tox. 2;H330 Aquatic chronic 1;H410 Add lab.: EUH032: Contact with acids liberates very toxic gas.
	Potassium stannate K_2Sn0_3 86 g/L	Skin irrit. 2;H315 Eye irrit. 2;H319 STOT SE 3;H335
	Zinc cyanide $Zn(CN)_2$ 1.8 g/L	Acute tox. 1;H310; Acute tox 2;H300; H330; Aquatic acute;I H400; Aquatic chronic;1 H410 Add lab.: EUH032:Contact with acids liberates very toxic gas
	Potassium cyanide KCN 45 g/L	Acute tox. 2; H330 Acute tox. 1; 310 Acute tox. 2; H300 Aquatic acute 1; H400 Aquatic chronic 1;H410
Zinc + chromium (III) passivation + topcoat	Zinc chloride $ZnCl_2$ 65 g/L	Acute tox. 4;H302 Skin corr. 1B;H314 Aquatic acute 1;H400 Aquatic chronic 1;H410
	Potassium chloride KCl 220 g/L	Not classified
	Boric acid H_3BO_3 25 g/L	As above
	Colloidal silica at 44% SiO_2 90 g/L	Not classified (registration dossier)
	Wax copolymer acrylic polyethylene 120 g/L	The waxes contain polymere substances and are often available as an emulsion based on non-ionic tenside
Chromium (III) passivation	Chromium (III) chloride $CrCl_3$ 50 g/L	Acute tox. 4;H302 Skin irrit. 2;H315 Eye irrit. 2;H319 Acute tox. 1;H330
	Sodium nitrate $NaNO_3$ 100 g/L	Eye irrit. 2 H319 Acute iox. 4, H302
	Cobalt nitrate $Co(NO_3)_3$ 3 g/L	Carc. 1B;H350i Muta. 2;H341 Repr. 1B;H360F Resp. sens. 1;H334 Skin sens. 1;H317 Aquatic acute 1;H400 Aquatic chronic 1;H410
Alcaline cyanide-free copper (pre-layer)	See above under Base material, steel	
Bright acid copper	See above under Base material, Steel	
White bronze	See above under Base material, Steel	

Process	Substance	Hazard classification
Bright acid copper + palladium or palladium alloys	Palladium tetramino chloride $Pd(NH_3)4Cl_2$ 4.5 g/L	Met. corr. 1;H290 Acute tox. 4;H302 Skin sens. 1;H317 Eye irrit. 2;H319 Aquatic chronic 1;H410
	Ammonium chloride NH_4Cl 50 g/L	Acute tox. 4;H302 Eye irrit. 2;H319
	Di potassium phosphate K_2HPO_4 35 g/L	Not classified
Alcaline cyanide copper (pre-layer)	Copper cyanide CuCN 30 g/L	Acute tox. 2;H300 Acute tox. 1;H310 Acute tox. 2;H330 Aquatic chronic 1;H410 Add lab.: EUH032: Contact with acids liberates very toxic gas.
	Potassium cyanide KCN 55 g/L	Acute tox. 2; H330 Acute tox. 1; H310 Acute tox. 2; H300 Aquatic acute 1; H400 Aquatic chronic 1; H410
	Potassium hydroxide	Acute Tox. 4;H302 - Skin Corr. 1A;H314
Bright acid copper	See above under Base material, zinc and aluminium	
White bronze	See above under Base material ,zinc and aluminium	
Alcaline cyanide copper (pre-layer)	See above under Base material, zinc and aluminium	
Bright acid copper	See above under Base material, zinc and aluminium	
White bronze	See above under Base material, zinc and aluminium	
Alcaline cyanide copper (pre-layer)	See above under Base material, zinc and aluminium	
Bright acid copper	See above under Base material, zinc and aluminium	
White bronze	See above under Base material, zinc and aluminium	
Bright acid copper + palladium or palladium alloys	See above under 'Base material, copper alloys'	
Acid copper + white bronze prior to cataphoretic lacquer or top finish paint	Pre-layer, acid copper and white bronze as above	
Acid copper+ palladium + PVD/CVD	Pre-layer and acid copper as above	
	PVD/CVD could include a range of different metals (in their metallic form)	
Acid copper + antique finishes + potential lacquer	Pre-layer of alkaline cyanide copper + bright acid copper as above	
Zinc	Zinc chloride Potassium chloride Boric acid	As above
Chromium (III) passivation	Chromium (III) chloride	As above
Bright acid copper + white bronze	See above under Base material, zinc and aluminium	
Zinc + chromium (III) passivation	See above under Base material, steel	

Process	Substance	Hazard classification
Zinc + chromium (III) passivation + silica and wax containing topcoat	See above under Base material, steel	
	Colloidal silica at 44% SiO_2 90 g/L	Not classified (registration dossier)
	Wax copolymer acrylic polyethylene 120 g/L	The waxes contain polymere substances and are often available as an emulsion based on non-ionic tenside

APPENDIX B

OEL, derived DN(M)ELs and PNEC values and preliminary risk assessment of identified alternative

Process	Substance	OEL/DNEL, ihl long-term (mg/m³)	RCR, long-term inhalation	PNEC, fresh water (mg/L)	RCR, water environment
Bright, semi-bright and satin nickel	Nickel sulphate NiSO4 250 g/L	0.05 (Ni reg. dossier, as Ni-ion)	0.400	0.0036 (Nickel reg. dossier)	0.928
	Nickel chloride NiCl2 60 g/L				
	Boric acid H_3BO_3 45 g/L	0.5 (German OEL)	0.015	1.35 (reg. dossier)	0.001
Bright chromium (VI)	Chromic acid CrO_3 250 g/L	0.01 (reg. dossier)	4.098	0.0034 (reg. dossier)	2.013
	Sulphuric acid H_2SO_4 1.5 g/L	0.05 (SCOEL recomm.)	0.005	0.0025 (reg. dossier)	0.164
Chromium (III)	Chromium(III) sulphate Cr4(SO4)5(OH)2 125 g/L	Based on OEL for Cr III ion: DK + NO	0.023	Based on Cr(III) OH SO4 (reg. dossier)	0.728
	Potassium bromide KBr 35 g/L	n.a.	n.a.	n.a.	n.a.
	Boric acid H_3BO_3 45 g/L	0.5 (German OEL)	0.015	1.35 (reg. dossier)	0.001

Process	Substance	OEL/DNEL, ihl long-term (mg/m³)	RCR, long-term inhalation	PNEC, fresh water (mg/L)	RCR, water environment
Alternative coating processes					
Base material, steel					
Alkaline cyanide-free copper (pre-layer)	Copper hydroxide $Cu(OH)_2$ 20 g/L	Estimated value: 1.6 (OEL $CuSO_4$ (FL): 1 mg/m³)	0.002	0.012 (recalculated from CuSO4 reg dossier	0.046
	1-hydroxy-ethylidene -1,1,-diphosphonic acid HEDP 180 g/L	No value identified	-	PNEC , reg. dossier: 0.136	0.036
Bright acid copper	Copper sulphate $CuSO_4$, 5 H_2O 220 g/L Sulphuric Acid	1 (OEL: FI)	0.036	0.078 (reg. dossier)	1.158
White bronze	Copper cyanide CuCN 11 g/L	1 (as cyanide, SCOEL advise)	0.100	0.005 (UK-DEFRA EQS for hydrogen cyanide	0.017
	Potassium stannate K_2Sn0_3 86 g/L	2 (as tin, inorganic, OEL: UK, SW, GER, FI	0.007		n.a.
	Zinc cyanide Zn(CN)2 1.8 g/L	1 (as cyanide, SCOEL advise)	0.000	0.005 (UK-DEFRA EQS for hydrogen cyanide	0.002
	Potassium cyanide KCN 45 g/L	1 (as cyanide, SCOEL advise)	0.003	0.005 (UK-DEFRA EQS for hydrogen cyanide	0.493
Zinc + chromium (III) passivation + topcoat	Zinc chloride $ZnCl_2$ 65 g/L	1 (OEL: UK, BE, SW, FL, a.o.)	0.011	0.0061 (reg. dossier)	0.292
	Potassium chloride KCl 220 g/L	1064 (reg. dossier)	0.000	0.1 (reg. dossier)	0.060
	Boric acid H_3BO_3 25 g/L	0.5 (German OEL)	0.008	1.35 (reg. dossier)	0.001
Chromium (III) passivation	Chromium (III) chloride $CrCl_3$ 50 g/L	0.06 (OEL, Cr(III) salts: DK, NO)	0.044	4.7 (NL national EQS)	0.113
	Sodium nitrate $NaNO_3$ 100 g/L		na		na
	Cobalt nitrate $Co(NO_3)_3$ 3 g/L	0.0196 (estimated from Col reg. dossier DNEL)	0.004	0.0051 (reg. dossier)	0.016

Process	Substance	OEL/DNEL, ihl long-term (mg/m³)	RCR, long-term inhalation	PNEC, fresh water (mg/L)	RCR, water environment
Base material, copper alloys					
Alkaline cyanide-free copper (pre-layer)	See above under Base material, steel		0.002		0.046
Bright acid copper	See above under Base material, steel		0.036		1.158
White bronze	See above under Base material, steel		0.100		0.017
Bright acid copper + palladium or palladium alloys	Palladium tetra-amino chloride $Pd(NH_3)4Cl_2$ 4.5 g/L	n.a.	n.a.	n.a.	n.a.
	Ammonium chloride NH_4Cl 50 g/L	10 (OE, UK, FR, DK, NO)	0.001	n.a.	n.a.
	Di potassium phosphate K_2HPO_4 35 g/L		0.001	n.a.	n.a.
Base material, zinc and aluminium					
Alkaline cyanide copper (pre-layer)	Copper cyanide CuCN 30 g/L	1 (as cyanide, SCOEL advise)	0.005		0.158
	Potassium cyanide KCN 55 g/L	1 (as cyanide, SCOEL advise)	0.004		0.602
	Potassium hydroxide	2 (OEL, FR; FL, UK, SW)	n.a.		n.a.
Bright acid copper	See above under Base material, zinc and aluminium		0.036		1.158
White bronze	See above under Base material, zinc and aluminium		0.100		0.017
Plastic (POP)					
Alkaline cyanide copper (pre-layer)	See above under Base material, zinc and aluminium		0.005		0.602
Bright acid copper	See above under Base material, zinc and aluminium		0.036		1.158
White bronze	See above under Base material, zinc and aluminium		0.100		0.017
Nickel prior last metallic finish					
Alkaline cyanide copper (pre-layer)	See above under Base material, zinc and aluminium		0.005		0.602
Bright acid copper	See above under Base material, zinc and aluminium		0.036		1.158

Process	Substance	OEL/DNEL, ihl long-term (mg/m³)	RCR, long-term inhalation	PNEC, fresh water (mg/L)	RCR, water environment
White bronze	See above under Base material, zinc and aluminium		0.100		0.017
Bright acid copper + palladium or palladium alloys	See above under Base material, copper alloys		n.a.		0.000
Nickel in case of further deposits as top-coating or last passivation					
Acid copper + white bronze prior to cataphoretic lacquer or top finish paint	Pre-layer, acid copper and white bronze as above		0.036		1.158
White bronze	Pre-layer, acid copper and white bronze as above		0.100		0.017
	Colloidal silica at 44% SiO_2 90 g/L		n.a.		n.a.
	Wax copolymer acrylic polyethylene 120 g/L		n.a.		n.a.
Acid copper+ palladium + PVD/CVD	Pre-layer and acid copper as above		0.036		1.158
	PVD/CVD could include a range of different metals (in their metallic form)		na.		na.
Acid copper + antique finishes + potential lacquer	Pre-layer of alkaline cyanide copper + bright acid copper as above		0.036		1.158
Zinc + chromium (III) passivation + topcoat	Zinc chloride, as above		0.011		0.292
	Potassium chloride, as above		0.000		0.060
	Boric acid, as above		0.008		0.001
Chromium (III) passivation	Chromium (III) chloride, as above		0.044		0.113
	Cobalt nitrate, as above		0.026		0.016
Bright nickel when used as last finish					
Bright acid copper + white bronze	See above under Base material, zinc and aluminium		0.100		0.017
Zinc + chromium (III) passivation	See above under Base material steel		0.044		0.113

Process	Substance	OEL/DNEL, ihl long-term (mg/m³)	RCR, long-term inhalation	PNEC, fresh water (mg/L)	RCR, water environment
Zinc + chromium (III) passivation + silica and wax containing top-coat	See above under Base material, steel		0.044		0.113
	Colloidal silica at 44% SiO_2 90 g/L		n.a.		n.a.
	Wax copolymer Acrylic polyethylene 120 g/L		n.a.		n.a.