Reactivity and Management of Chromium(III) Processes

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Solutions for Electroplating

Content

- Short introduction of the Schlötter company
- Chromium(III) and chromium(VI) processes
- Typical composition of chromium(III) electrolytes
- Process performance and parameters
- Function of boric acid / borates in the process
- Conclusions

Overview

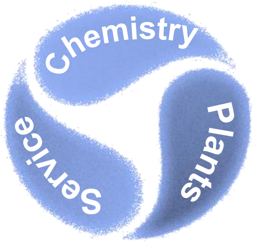
Schlötter is a leading solution provider of surface technology.

With chemistry, service and plants we offer integrated coating solutions in the fields of electronics and printed circuit boards, cathodic corrosion protection as well as decorative surfaces.

Chemistry

350 processes from own development;
60 employees in research and development + service;
customers in all areas of electroplating technology

Plant engineering



more than 800 rack and barrel systems realised as complete solutions;
45 employees (mechanics, electrics and control)

- since 1912
- headquarter in Geislingen

- family owned in 4th generation

- appr. 320 employees worldwide

Locations

Kian Teck Drive
Singapore


Wuxi, Dongguan,
China


Headquarter, **Germany**

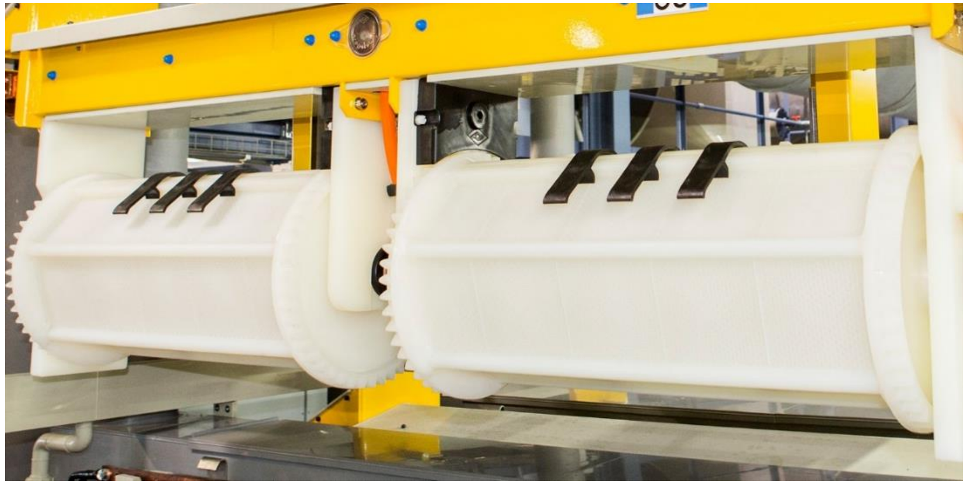

Newbridge, **Ireland**


Hillerstorp, **Sweden**


Pershore, **Great Britain**

Applications

Industries
Automotive, drive train
Automotive interieur / exterieur
Electric / Electrics
Building technology
Consumer goods
Aerospace
Mechanical Engineering
Metalworking



Processes
Pre treatment
Copper
Nickel
Chrome
Silver
Gold
Zinc and Zinc alloys
Passivates and Sealers
Tin and Tin alloys
Metallisation of non conductive
Anodising

Metallic Chromium

Facts about chromium:

- chromium as a in German so-called “Tausendsassa”, means a “jack of all trades”
- variety of useful properties, such as high hardness, high wear resistance, high chemical stability, high corrosion resistance and so on
- application in a wide variety of industries, e.g. automotive, sanitary, furniture industry
- The melting metallurgical processing of pure, metallic chromium is very complex due to its high melting point.
- In addition, the high brittleness prevents mechanical forming of chromium layers.
- Therefore, chromium is usually used on a large technical scale as a metal coating.
- Chromium coatings are porous and cracked due to mechanical and thermal stress. This allows corrosive attack on the base material and the formation of local elements.
- In order to be able to guarantee a high level of corrosion protection, chromium coatings are therefore generally used together with nickel intermediate layers.
- To date, the simplest way to produce chromium coatings is by means of galvanic chromium(VI) processes.
- However, chromium trioxide, which is listed in Annex XIV of the REACh Regulation, is used for this purpose.
- substitution of hexavalent by trivalent chromium aspired: class objective: primarily high corrosion resistance and colouring as with chromium(VI) processes

Chromium(III) Processes

Types of electrolytes:

- chloride electrolytes
- sulphate electrolytes
- methansulfonate electrolytes
- fluoride electrolytes
- mixed electrolytes

Use of these electrolytes:

- functional chrome plating (layer thickness: few micrometres up to several millimetres)
- functional chrome plating with decorative character (layer thickness: 0.1 up to 0.5 micrometres)

- All these electrolytes are operated with boric acid as an essential component of the electrolyte formulation.
- The aim of decorative chromium plating is to achieve a (mirror-)bright, corrosion-resistant deposit.

Process Flow

Typical process sequence for chromium plating:

- degreasing of the substrates (electrolytic degreasing)
- acidic pickling
- copper plating (if levelling is necessary, better thermal expansion)
- deposition of bright nickel (adjustment of the gloss level of the chromium surface)
- chromium plating
- rinsing processes as intermediate steps

Process equipment:

- conventional coating plants with usually open production troughs equipped with exhaust devices
- special anode materials
- automatic transfer units or lifters
- waste water treatment

Boric acid is especially used as a buffer substance in electroplating nickel baths, weakly acidic zinc baths, and chromium baths based on trivalent chromium compounds. The concentration in the electrolytes is less than 5.5 wt.%.

Typical Chromium(VI) Process

Chemical composition and function of the ingredients:

- chromium trioxide (up to 500 g/L, decorative use: 100 up to 400 g/L), chromium(VI) source
- sulphuric acid (1 up to 4 g/L), catalyst for the formation of the cathode film during deposition
- foreign acids like hydrofluoric acid, hexafluorosilicic acid or methansulfonic acid, increasing of the current efficiency and influencing the layer properties by changing the structure of the cathode film
- fluorosurfactants like per- and polyfluorinated alkyl compounds, e.g. PFOS, avoidance of spray mists and aerosols
- further additives (usually organic substances) for adjusting the layer properties

Operating conditions of the electrolytes:

- current density: 5 up to 20 A/dm^2
- temperature: 30 up to 50 °C
- pH value: < 1
- deposition rate: 50 up to 150 nm/min
- anodes: lead tin, lead antimony alloys or platinised titanium (reduction of overvoltage for the oxidation of trivalent to hexavalent chromium on lead oxide)

Typical Chromium(III) Process

Chemical composition and function of the ingredients:

- chromium salts as chromium(III) source (45 up to 155 g/L, i.a. depends on the used salt)
- conducting salts for the increasing of conductivity
- buffer substances for the compensation of changes in the pH value in the near-electrode area
- wetting agents for the reduction of surface tension and avoidance of aerosol formation
- complexing agents
- further additives for the increasing of the current efficiency or for the influencing of the layer properties

additionally used for chloride electrolytes:

- salts of metals of the 8th subgroup (PSE) for increasing the current efficiency
- bromides for the preventing of the oxidation of chromium(III) to chromium(VI) at the anode

Operating conditions of the electrolytes:

- current density: 15 up to 30 A/dm²
- temperature: 25 up to 60 °C
- pH value: 1 up to 4
- deposition rate: ca. 40 nm/min
- anodes: special mixed oxide materials

Active Ingredients

Selection of substances used in chromium(III) electrolytes:

category	chloride electrolytes	sulphate electrolytes
chromium salts	chromium(III) chloride	chromium(III) sulphate, potassium chromium(III) sulphate, alkaline chromium(III) sulphate
conducting salts	sodium chloride, potassium chloride, ammonium chloride	sodium sulphate, potassium sulphate, ammonium sulphate
buffer substances	boric acid, aluminium chloride	boric acid, aluminium sulphate
wetting agents	sodium dodecyl sulphate, sulfosuccinates, alkylbenzenesulfonate	
complexing agents	formiates, acetates, oxalates, glycine, urea, malonic acid, diethanolamine	
further aditives	saccharin, malonic acid, polyethylene glycol, polyvinyl pyrrolidone, sodium hypophosphite, thiosalicylic acid, sodium allyl sulphonate, bis-3-sulfopropyl disulfide	
metal salts of the 8th subgroup	iron(II) chloride, nickel chloride	
bromides	potassium bromide, ammonium bromide	

M. Leimbach, doctoral thesis, University Ilmenau, 2022.

Function of Boric Acid

State of the art:

- buffer system in chromium(III) electrolytes
- gloss-forming effect (a kind of „supporting effect“)
- complexing effect
- corrosion resistance of chromium layers based on hexavalant better than based on trivalent processes, especially if "larger quantities" of iron from the base material to be coated get into the electrolyte

Influence of boric acid on:

- cathode film
- deposition process
- (grain) structure
- morphology of the chromium surface (alternative: pulse plating)
- layer properties such as colour, brightness, gloss and corrosion resistance

Advantages and Disadvantages of Chromium(III)

- a lot of investigations in the last 10 years in order to substitute the buffer system boric acid by an alternative such as carboxylic acids or other substances: results not as successful as desired or expected so far

Problems of chromium(III) electrolytes with:

- brightness, colouring, and corrosion resistance
- current efficieny (increase possible by modifying the electrolyte composition with carboxylic acids as complexing agents, but associated with high incorporation of carbon in the chromium layer)
- current density
- 3 up to 4 times lower deposition rate
- influence of the morphology on the optical appearance
- spare part problem because of other colouring
- colouring: somewhat darker, yellish shade (difficult to maintain certain colour shade in large-scale technical process)
- relatively extensive electrolyte management

Advantages:

- currently no use of substances requiring authorisation
- better throwing power

Conclusions

Important statements:

- Boric acid is an indiensable ingredient in chromium(III) electrolytes.
- Boric acid and chromium(III) electrolytes belong together, because there exists no technical adequate solution to produce chromium surfaces with a trivalent instead of a hexavalent chromium electrolyte so far.
- The investigations on chromium(III) electrolytes will still take some further time, until a chromium(III) electrolyte, which is equal to the chromium(VI) process in all respects or in at least the essential respects, will be available for electroplating.
- With regard to success announcements and marketing strategies, one should currently remain sceptical about statements made by the market.
- In principle, environmental and occupational health and safety problems with boric acid can only occur in the production, because boric acid is not present on the electrodeposited surfaces. Safe handling of boric acid can be guaranteed. The end user cannot come into contact with boric acid at all.
- And do not forget: Boric acid is not only used for chromium plating, but also for nickel and zinc plating.

Schlötter
Galvanotechnik

Thanks for your attention!

Solutions for Electroplating