Workshop

on implications of use of trivalent chromium in functional plating with decorative character

Experience of the company Kesseböhmer

Racks with articles for trivalent chrome plating

System: Coating of steel materials (several 10,000 products/day)

-> High placement density and high throughput

Requirements Kesseböhmer

Chrome III (Light) - Establish as a stable process

- Ensuring colour stability
- Ensuring corrosion stability
- Ensuring the layer thickness
- Ensuring of the process stability
- Determination of influences of process parameters on layer thickness and colour
- Determination of the long-term behaviour of the coated surfaces
- Determining the possible applications of the process used by Kesseböhmer

Requirements Customers

The demands on the chromium III surface result from:

- Customer requirements and delivery conditions
- Operating standards, e.g. TL 203 from VW
- Specific requirements of further OEM's
- National and international standards e.g. DIN/ISO1456
- …

Working parameters

Parameter	Area	Optimal
Temperature [°C]	50 - 60	55
Cathodic current density [A/dm^2]	3 - 10	5
Anodic current density [A/dm^2]	1 - 5	2
Deposition rate [µg/min]	0,02 - 0,05	Depending on individual system installation
Voltage [V]	8 - 20	Depending on individual system installation and distance cathode - anode
pH value	3, 5 - 3,9	3,7 (Borat buffer)
Density at 55°C [g/cm^2]	1,18 - 1,24	1,21
Conc. Sulphate [g/L]	1.100 - 170	140
Conc. Borate [g/L]	80 - 100	90
Conc. Cr(III) [g/L]	7,5 - 12,5	10

Anodes & Technical Requirements

Sophisticated equipment and process management:

- Mixed oxide coated titanium anodes
- Goods movement of complex products with e.g. cavities
- Electrolyte movement controllable
- Precipitation of salts in areas with little movement should be avoided (Work close to solubility limits of Boric acid)

Available electrolytes

Tabelle 1: Auswahl an Substanzen, die in Chrom(III)-Elektrolyten eingesetzt werden. Die Aufstellung ist unterteilt nach Chrom(III)-chlorid und Chrom(III)-sulfat-basierten Systemen.

Kategorie	Chlorid-Elektrolyte	Sulfat-Elektrolyte
Chromsalze	Chrom(III)-chlorid [58]	Chrom(III)-sulfat [59], Kaliumchrom(III)-sulfat [78], basische Chrom(III)-sulfate [79]
Leitsalze	Natriumchlorid, Kaliumchlorid, Ammoniumchlorid [58]	Natriumsulfat, Kaliumsulfat [59], Ammoniumsulfat [78]
Puffersubstanzen	Borsäure [58], Aluminiumchlorid [80]	Borsäure [59], Aluminiumsulfat [14]
Netzmittel	Natriumdodecylsulfat [14, 58], Sulfosuccinate, Alkylbenzensulfonate [58, 59]	
Komplexbildner	Formiat [81, 82], Acetat [83, 84], Oxalat [85, 86], Glycin [87, 88], Harnstoff [89, 90], Malonsäure [91], Diethanolamin [92]	
Weitere Zusätze	Saccharin [19, 79], Malonsäure [93, 94], Polyethylenglykol [95, 96], Polyvinylpyrrolidon [97, 98], Natriumhypophosphit [99, 100], Thiosalicylsäure [101], Natriumallylsulfonat [102], Bis-3-sulfopropyl-disulfid [103]	
Metallsalze der VIII. Nebengruppe	Eisen(II)-chlorid [104], Nickelchlorid [105]	
Bromide	Kaliumbromid [80], Ammoniumbromid [58]	

Compare lecture Dr. Heermann
Dissertation M. Leimbach,
TU Ilmenau 2021

Large number and variety of additives
lead to more conscious and demanding handling

Experience

- System:
  Coating of steel materials (several 10,000 products/day)

- Experience:
  1. Boric acid concentration:
     Strong influence on layer quality
     Reason: Boric acid changes surface properties,
     e.g. by gloss formation.
  2. Iron ions:
     Strong influence on coating quality and corrosion properties
     Reason: Incorporation in metallic layer
     Influence of boric acid: Complexation of iron ions
  3. Loading of ion exchangers for electrolyte processing:
     Currently available systems do not show sufficient performance

Opportunities and risks

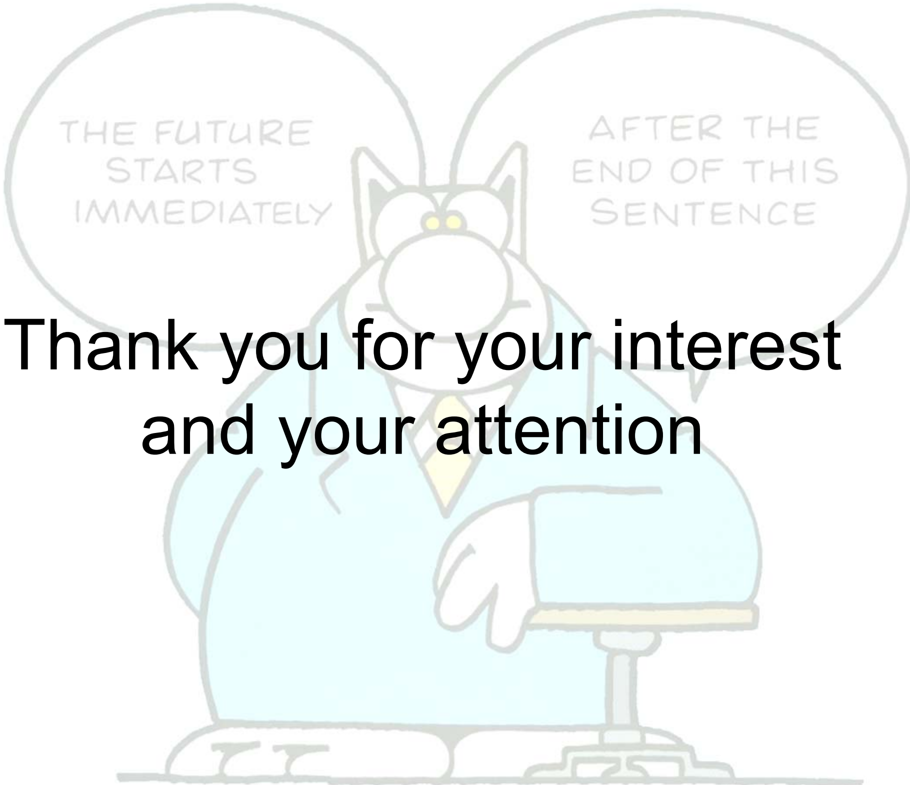
- Exposure measurements
  - Borates below the detection limit
    (Measurement methodology and assessment:
    occupational exposure limits D and A)
  - Measurements Cr(III) and Cr(VI) are carried out on all employees
  - Experience with other systems (e.g. nickel, zinc) using boric acid does not show a recognisable increased risk.
- Employee protection is based on extensive experience of other systems as well
- The amount of waste produced in Cr(III) technology is significantly higher than in Cr(VI) technology.
  In both cases, there is no evidence of risk in the waste..

Developments

- Acceptance: Currently, a limited proportion of Cr(III) based products is accepted by customers. Corresponding products are offered in all cases.
- Consequence: Control the influence of the substances used on coating quality due to chemical interactions.
- Realisation of high throughput -
  Control concentration of iron ions by suitable complexing agents.
- Improvement of the systems for electrolyte processing and wastewater treatment.

Perspectives

- Cr(III) technology is not yet generally applicable:
  - Use of boric acid still to be adapted
  - Process conditions dominated by a large number of additives
- Cr(III) based coatings on steel components are currently only accepted to a limited extent by customers, mainly due to colour and gloss effects as well as insufficient corrosion protection.
- An increased risk due to borates cannot be detected (measurements below detection limit), essentially due to the experience in other system
- Further technical development and conversion is actively pursued and necessary



Thank you for your interest
and your attention