Hexavalent Chromium Processes

Hard Chromium Process SurTec® 875
Decorative Chromium Process SurTec® 871

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1. Introduction

1.1. General outline and applications
1.2. Process engineering
1.3. Equipment technology

1.1. General outline and applications

Chromium processes:

- Hard chromium
  for parts with high mechanical stress
- Bright decorative chromium
  for decorative applications
- Trivalent chromium processes
  for decorative and for mechanically stressed parts
- Black chromium
  functional and decorative applications

Chromium processes in comparison

	Hard chromium	Bright chromium	Trivalent chromium process	Black chromium
metal content	100-400 g/l chromic acid	180-400 g/l chromic acid	ca. 30 g/l chromium sulfate / chromium chloride	ca. 250 g/l chromic acid
other compounds	sulfate catalyst	sulfate (fluoride)	ammonium sulfate boric acid sodium thiocyanate	acetic acid Ba-acetate
pH value	< 1	< 1	2-4	< 1
deposition rate	1-1.5 μm/min	ca. 0.2 μm/min	0.1-5 μm/min	ca. 0.2 μm/min
bath maintenance	easy	easy	complicated	complicated
layer thicknesses	20-150 μm	0.3-0.8 μm	0.3-150 μm	0.3-0.8 μm
appearance	bright	bright bluish	less brightness	black, dull

1.2. Process engineering

material to be plated: steel, brass, copper, zinc die cast, aluminium

Examples for the pretreatment:

steel:	chemical hot degreasing SurTec 194 + SurTec 415 pickling HCl 1:1, maybe inhibited with SurTec 424 electrolytical (anodic) cleaning SurTec 194 + SurTec 419
brass, copper zinc die-cast	chemical hot degreasing SurTec 151 electrolytical (cathodic) cleaning SurTec 177 fluoride containing acid dip SurTec 481
aluminium:	chemical hot degreasing SurTec 133 high alkaline pickling SurTec 181 acid dip in nitric acid zincate treatment SurTec 652 (cyanide free)

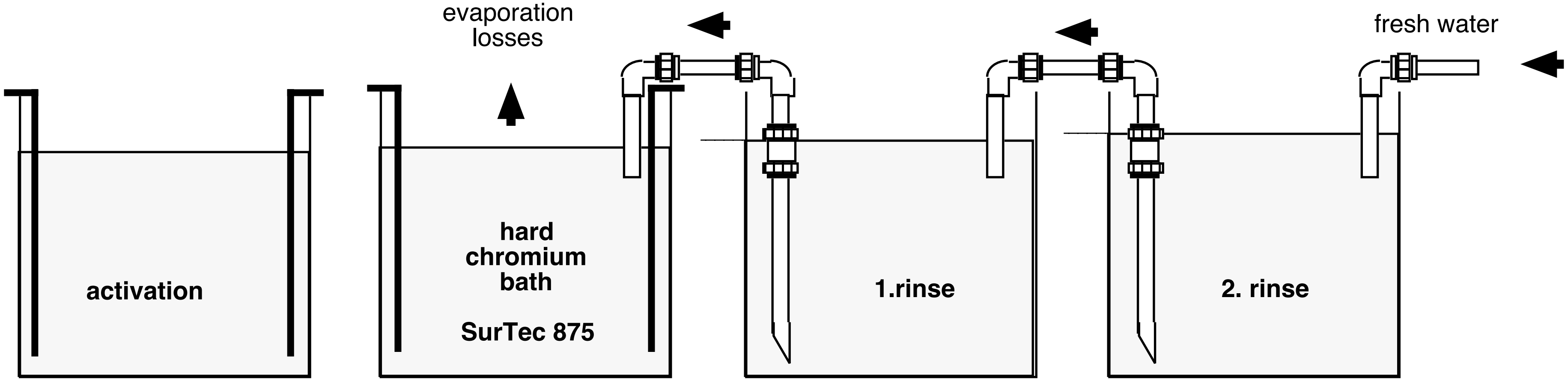
Examples for the sequence of layers for parts plated with hard chromium:

material	**steel**	**steel**	**copper**
possible process sequence	cyanide or noncyanide Cu SurTec 866 or 864 3-5 µm		
	acid Cu SurTec 869 ca. 20 µm		
	hard chromium SurTec 875 20-50 µm	hard chromium SurTec 875 20-150 µm	hard chromium SurTec 875 20-50 µm
examples	roto press cylinders	piston rings hydraulic cylinders	copper tubes for casted metals

Examples for the sequence of layers for parts plated with decorative chromium:

material	steel	steel	zinc die cast	brass / copper	aluminium
possible process sequence	cyanide or noncyanide Cu SurTec 866 or 864 3-5 μm	cyanide or noncyanide Cu SurTec 866 or 864 3-5 μm	cyanide or noncyanide Cu SurTec 866 or 864 5-8 μm		zincate treatment SurTec 652
	acid Cu SurTec 869 10-20 μm		acid Cu SurTec 869 15-25 μm		cyanide or noncyanide Cu SurTec 866 or 864 5-8 μm
	semibright Ni SurTec 854 10-15 μm				
	bright Ni SurTec 857 10-15 μm	pearl Ni SurTec 852 10-15 μm	bright Ni SurTec 857 10-15 μm	bright Ni SurTec 857 10-15 μm	bright Ni SurTec 857 10-15 μm
	bright chromium SurTec 871 0.3 μm	bright chromium SurTec 871 0.3 μm	bright chromium SurTec 871 0.3 μm	bright chromium SurTec 871 0.3 μm	bright chromium SurTec 871 0.3 μm
examples	furniture fittings motorcycle parts	furniture fittings	door handles (car) luggage fittings	bathroom fittings	rims of cars

Sequence of the baths before and behind the chromium bath



activation dip:	3 g/l chromic acid, possible with anodic current support (also possible with pole reversal)
hard chromium:	high evaporation losses, therefore counter flow is possible
rinsing:	demin. water rinses with counter flow the usage of SurTec 870 R as reduction compound is possible

Calculation of drag out

the following steps are necessary for the calculation of the drag out:

- new make up of the rinse behind the active bath
- measure the volume of the rinsing tank exactly
- stir well the active bath and the rinsing at the beginning and take 100 ml bath sample
- 10-50 racks or barrels with different parts should be plated and counted
- take and analyse samples in regular intervals

calculation of the drag out:

$$V_{A,n} = \frac{c_{S,n} - c_{S,0}}{c_B} \cdot V_S$$

there is: $V_{A,n}$ = dragged out volume

$c_{S,n}$ = concentration of the rinse after n racks (barrels)

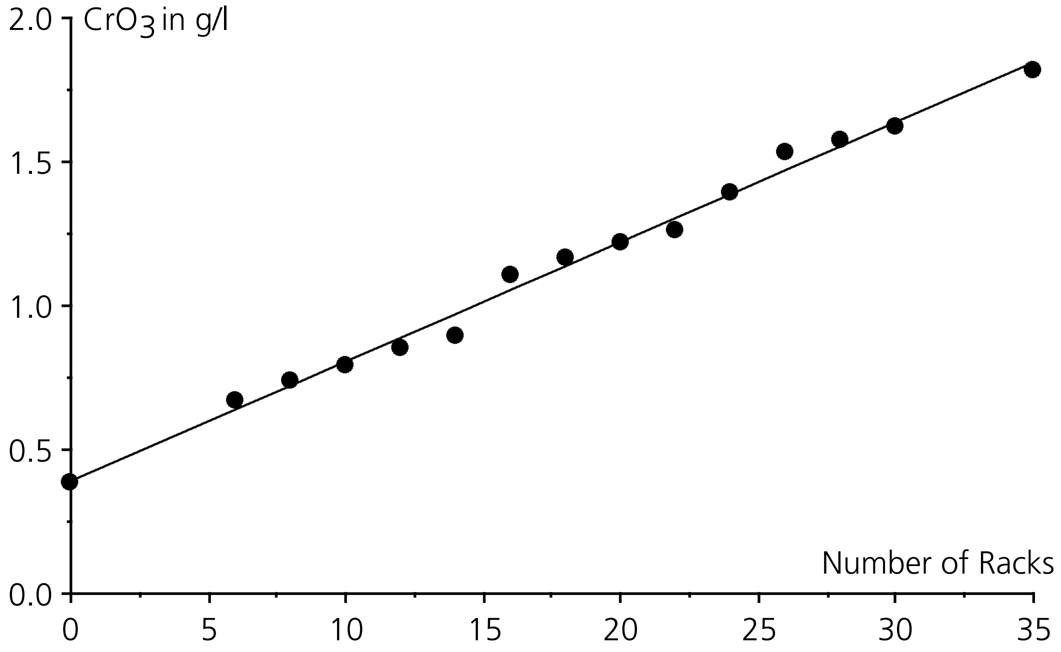
$c_{S,0}$ = concentration of the rinse at the beginning

c_B = bath concentration

V_S = volume of the rinsing

example: calculation of the drag out of a chromium bath (Fa. Kronenberger)

WT	CrO_3 in g/l	$V_{A, cum}$ in l	V_A in l/Rack
0	0,38		
6	0,67	3,28	0,55
8	0,74	4,07	0,51
10	0,79	4,71	0,47
12	0,85	5,39	0,45
14	0,89	5,87	0,42
16	1,10	8,32	0,52
18	1,16	9,00	0,50
20	1,22	9,61	0,48
22	1,26	10,12	0,46
24	1,39	11,62	0,48
26	1,53	13,23	0,51
28	1,57	13,72	0,49
30	1,62	14,26	0,48
35	1,81	16,51	0,47
Bath:	260	**Average:**	**0,485**



1.3. Equipment technology

tank material:	steel with chromic acid resistant coating e.g.: hard rubber (T-Gomit, PVC...)
heating/cooling:	necessary, material: Teflon, PVC (only for cooling), glass only for nonfluoride electrolytes
worker´s protection:	foam on the bath surface (SurTec 870 AK) or plastic balls, exhaustor, eye protection, protective gloves
rectifier:	must be powerful enough, ripple should be less than 2 %
position of anodes:	the distance between anodes and cathodes should be as high as possible maybe auxiliary anodes, dimming devices or form anodes are required

2. Deposition out of Hexavalent Chromium Electrolytes

2.1. Cathode Reactions

2.2. Anodes and Anode Reactions

2.3. Composition of Chromic Electrolytes

The following reactions take part at the cathode (at the parts):

Deposition reaction:

a) Reduction of Cr(VI) down to metallic chromium:

$$2\ CrO_3 + 2\ H_2O \rightarrow 2\ H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O$$

$$(Cr_2O_7)^{2-} + 12\ e^- + 14\ H^+ \rightarrow 2\ Cr^0 + 7\ H_2O \qquad (10\text{-}20\ \%)$$

Secondary reaction:

b) Hydrogen evolution:

$$2\ H^+ + 2\ e^- \rightarrow H_2 \qquad (80\text{-}90\ \%)$$

c) Reduction of chromium(VI) to chromium(III):

$$(Cr_2O_7)^{2-} + 6\ e^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 7\ H_2O \qquad (0\text{-}5\ \%)$$

Calculation of deposition rate:

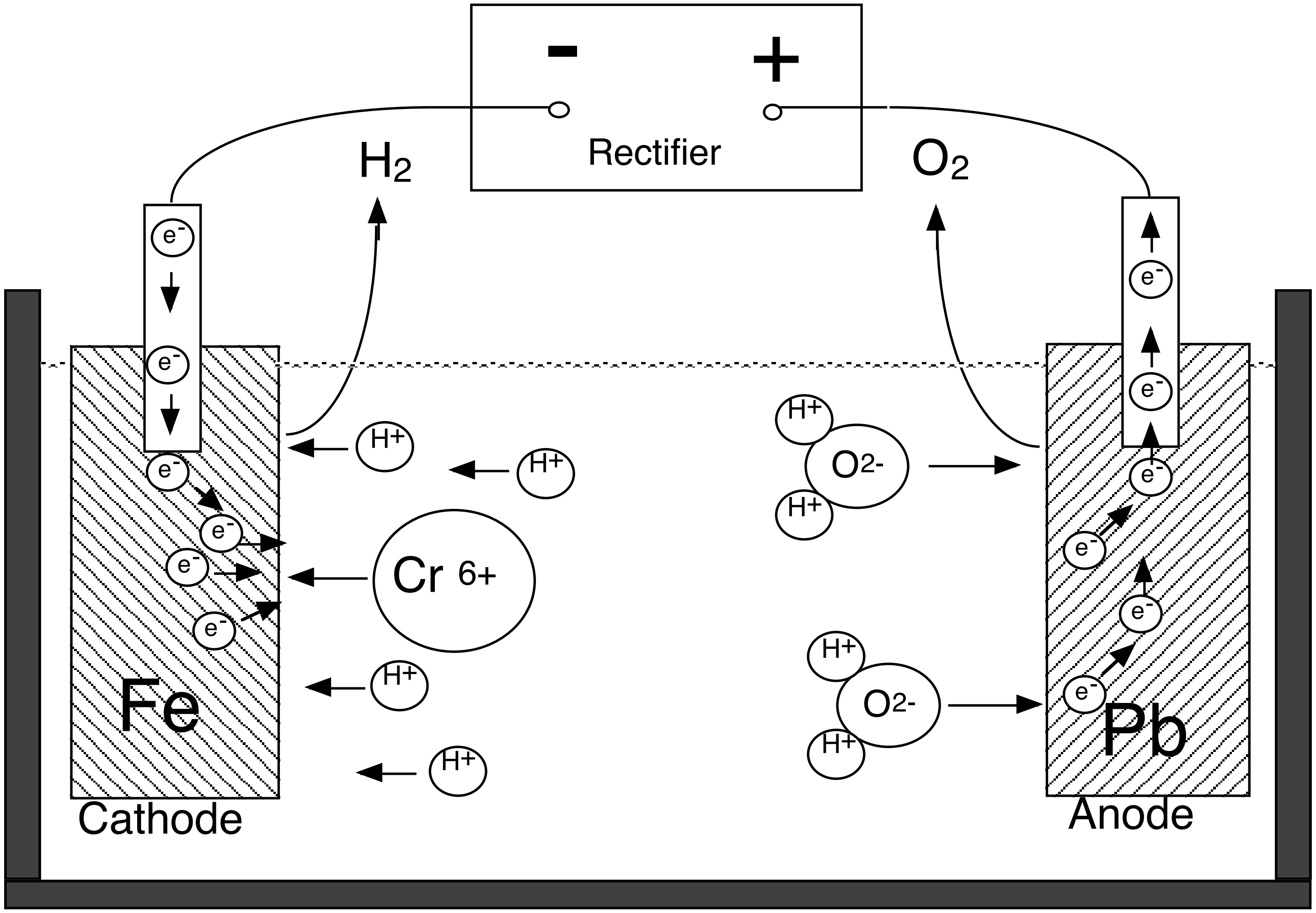
1.) deposited amount of chromium by square measure and time

$$\frac{\overbrace{0.2}^{\text{current efficiency}}\ \text{mol}}{\underbrace{6}_{\text{equivalent electrones}} \cdot 96485\ \text{As}} \cdot \overbrace{\frac{6\ \text{A}}{100\ \text{cm}^2}}^{\text{current density}} = 20.73 \cdot 10^{-9}\ \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}}$$

2.) layer thickness by time

$$\underbrace{\frac{52\ \text{g}}{\text{mol}}}_{\text{molar mass chromium}} \cdot \underbrace{\frac{\text{cm}^3}{7.19\ \text{g}}}_{\text{density chromium}} \cdot \frac{20.73 \cdot 10^{-9}\ \text{mol}}{\text{cm}^2 \cdot \text{s}} \cdot \underbrace{\frac{60\ \text{s} \cdot 10^4\ \mu\text{m}}{\text{min} \cdot \text{cm}}}_{\text{conversion of units}} = 0.09\ \frac{\mu\text{m}}{\text{min}}$$

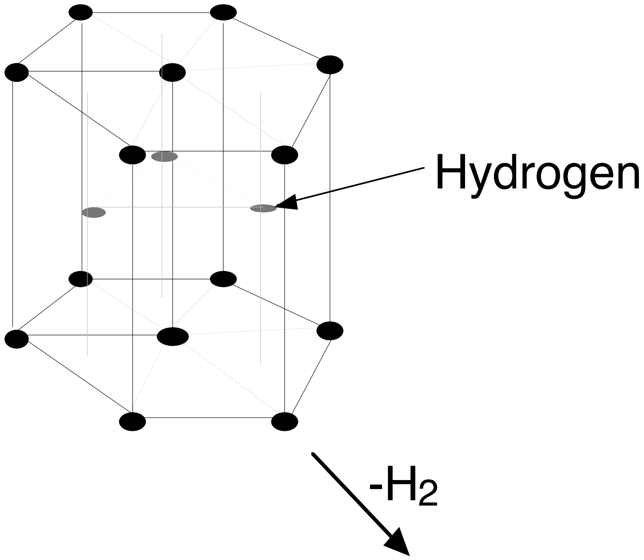
Reaction Schema:



2.1. Cathode Reactions

Why does the layer become cracks:

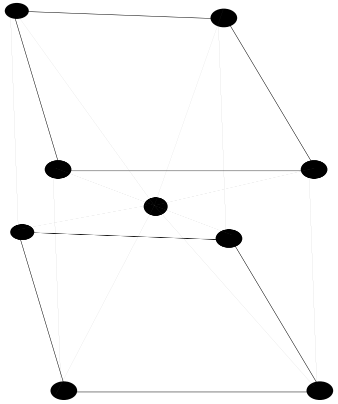
$Cr(VI) + x\,H^{+}\,(6+x)\,e^{-} \rightarrow CrH_x$



β-Cr (meta-stable)

(hexagonal face centered)

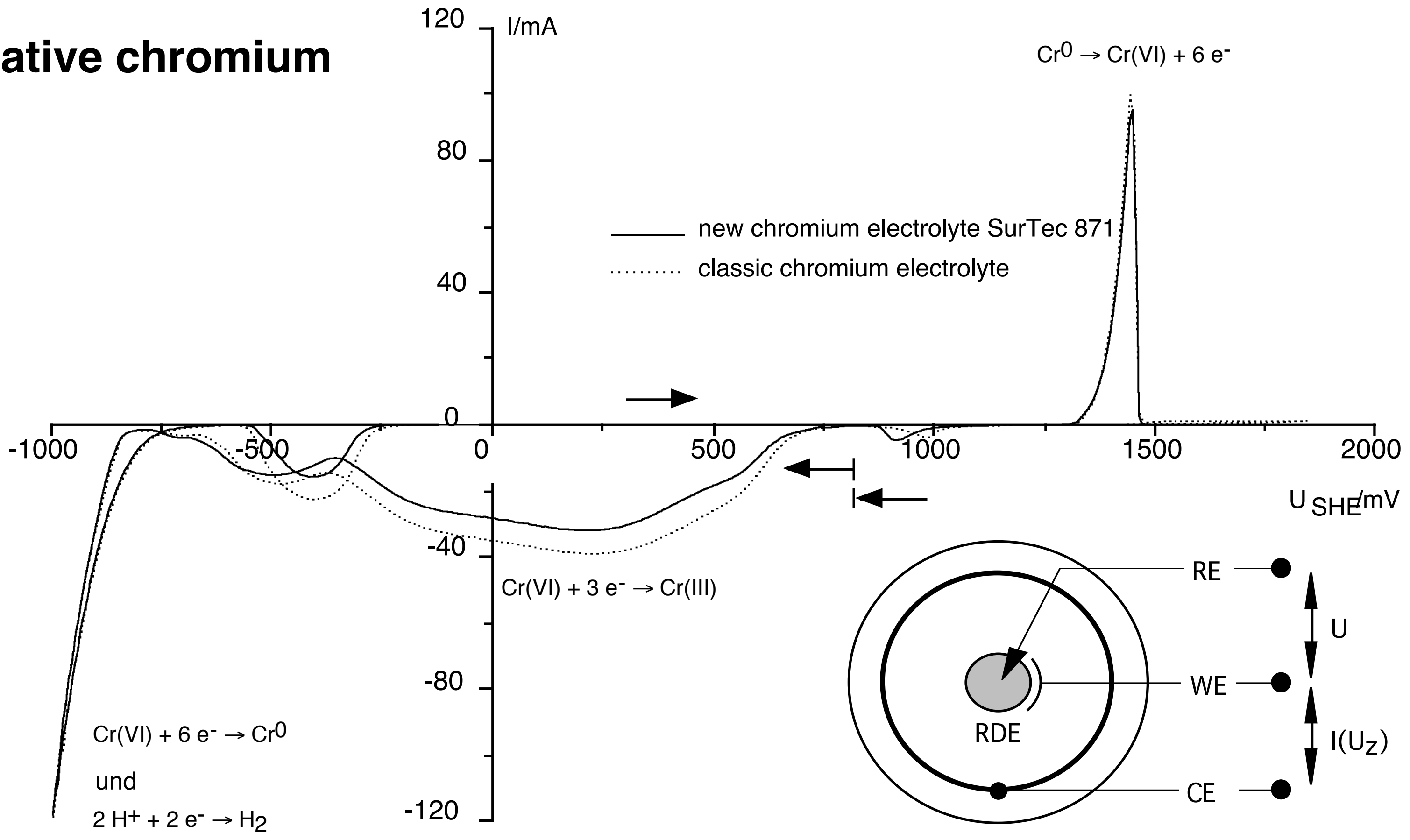
Re-crystalisation: $CrH_x - x\,H \rightarrow Cr + x/2\,H_2$



α-Cr (stable)

(cubic body centered)

Decorative chromium



Cyclic voltammogrammes at 10 mV/s; rotating gold disc, 0,196 cm^2, 1250 rpm

280 g/l Chromic acid, 28 °C

RDE = rotating disc electrode, **WE** = working electrode, **RE** = reference electrode,

CE = counter electrode, **U** = potential, **I** = current, **U_Z** = cell potential

During plating the following reactions take place at the anodes:

a) Oxygen generation:

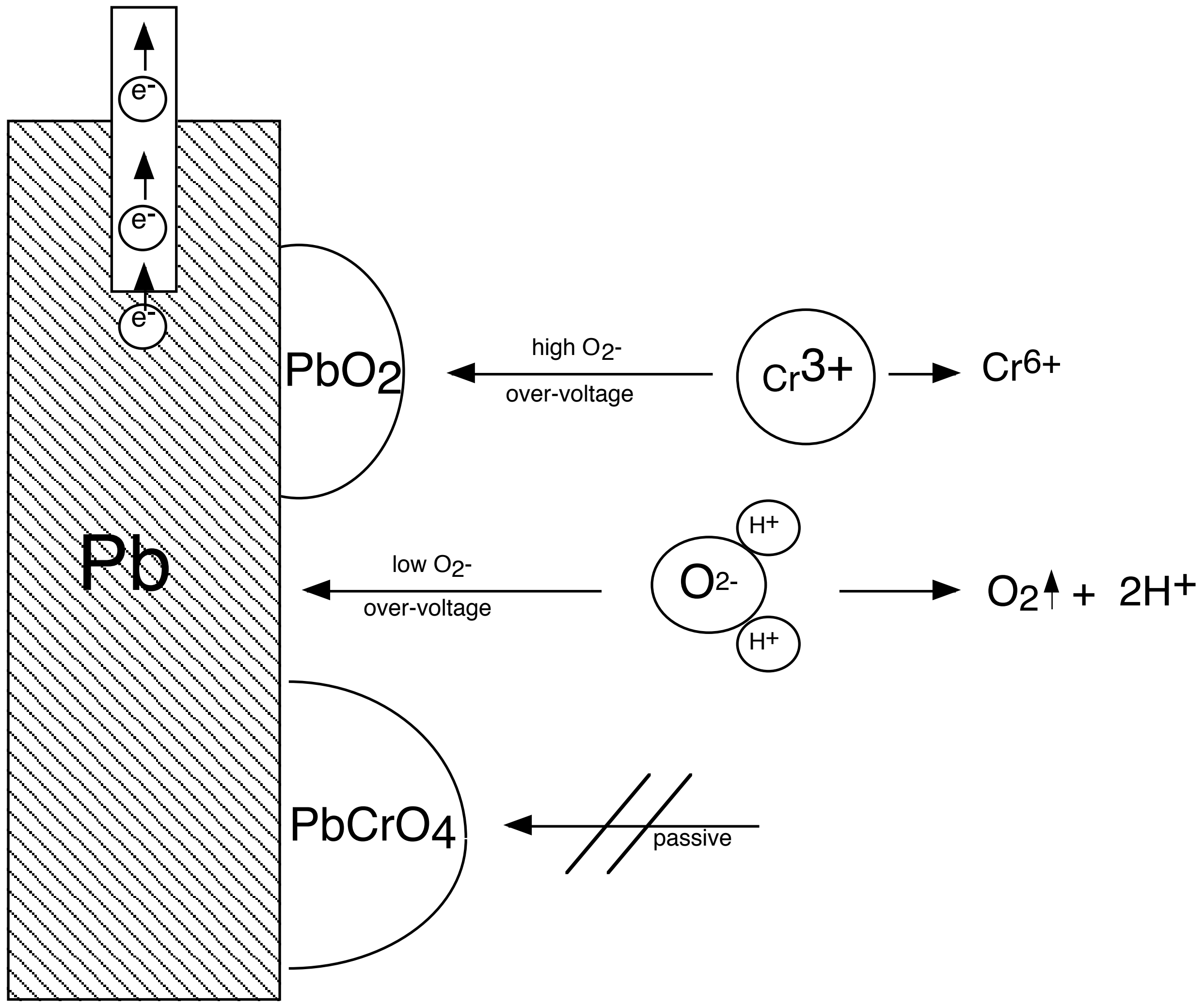
$$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$$

b) Oxidation of trivalent chromium:

$$Cr^{3+} + 3\ H_2O \rightarrow CrO_3 + 6\ H^+ + 3\ e^-$$

Using anodes of platinised titanium causes a low proportion of the second reaction. In this case, trivalent chromium must be oxidised by other means, e.g. electrodialysis (see chapter 6.)

Reaction schema:



Relation between anode and cathode surface:

in practice 2/1.

Anode material:

commonly used: lead anodes

Advantages:

- high oxygen over-voltage caused by formation of lead oxide at the anode´s surface
- high efficiency of oxidising Chrom(III) to Chrom(VI)
- low-cost material

Disadvantages:

- ‘working in’ before starting the process
- mechanical activation after long breaks is necessary
- anode corrosion → lead chromate mud as waste product
- heavy metal, toxic

Alternative anode materials:

- platinised titianium
- expended metal plated with ca. 2,5 μm platinum

Advantages:

- stable dimensions
- no corrosion
- no anode mud → no waste products
- not toxic, easy to handle

Disadvantages:

- high material costs
- cannot be used in fluoride electrolytes → platinised niobium
- cathodic hydrogen evolution destroys titanium
  → no pulse reverse plating
- low efficiency of oxidising Cr(III) → additional installation necessary

Anode materials for chromium electrolytes:

type of electrolyte	Anode material	
	various materials	platinised titanium
sulfuric acid (sulfuric acid only)	PbSb2 PbSb5 PbSn6	applicable
mixed acid (sulfuric acid / fluorides)	PbSn6 PbSn2Ag2 (*)	**inapplicable** (alternative: platinised niobium)
fluoride free (e.g. SurTec 875)	PbSn6 PbSb5	applicable

(*) for drag-in of chloride preferred -> precipitation as silver chloride

Remarks: the number behind the element stays for its mass percent inside the alloy
in practice PbSn6 commonly is used because of its low cost

2.3 Composition of chromic electrolytes

Chromic electrolytes, hard and bright chromic bathes consist of:

- chromic trioxide
- acid (other than chromic acid)
- chromium (III)
- surfactant

2.3 Composition of chromic electrolytes

Chromic trioxide / chromic acid

main component - metal carrier

◇ plating out of pure chromic solutions is not possible

- dense film of chromic chromates at the cathode prevent the access of chromium aniones and their reduction to metal

- only hydrogen formation

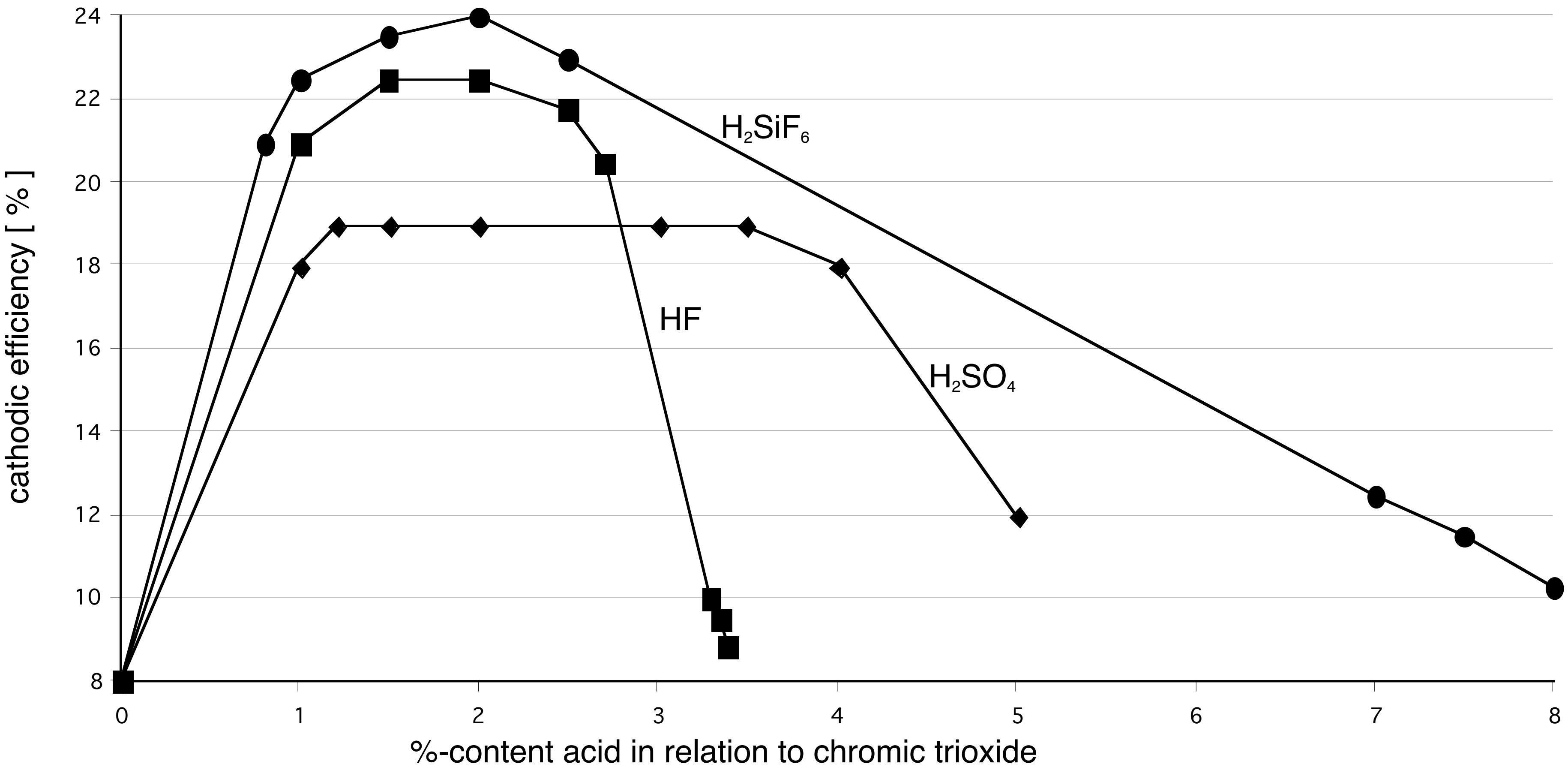
2.3 Composition of chromic electrolytes

Acids (other than chromium)

◇ Effective acids:

- H_2SO_4 (sulfuric acid)
- HF (hydrofluoric acid)
- H_2SiF_6 (silicic hydrofluoric acid)
- mixture of sulfuric acid and silicic hydrofluoric acid or their salts

2.3 Composition of chromic electrolytes



2.3 Composition of chromic electrolytes

◇ Advantages of chromium bathes with fluoride, silicofluoride and mixtures of both salts with sulfate:

- higher efficiency
- higher current density applicable
- very hard chromium deposits
- current density range for bright chromium deposits are considerably extended
- coverage and throwing power are extremely improved

◇ Disadvantages:

- corrosive effect on bath material and anodes
- at partial chroming - penetration by the electrolyte
- more sensitive to impurities.

2.3 Composition of chromic electrolytes

Chromium (III)

◇ low amounts of Cr^{3+} improve the throwing power

◇ Cr^{3+} is generated at the cathode by reduction of Cr^{6+}

◇ at the anode Cr^{3+} is oxidized to Cr^{6+}

◇ the Cr^{3+} - content is controlled by the anode-area

2.3 Composition of chromic electrolytes

Surfactant

- due to strong gasformation at anode and cathode drops of electrolyte are pulled in the atmosphere
  - bath vapors are strongly corrosive and
  - for people toxic/carcenogen/sensitizing/corrosive
- surfactants are used to reduce bath vapors and for better rinsing properties
  - surfactans reduce the surface tension
  - they generate a foam cover

3. Operating conditions

- 3.1. Influence of bathparameters on the deposition conditions
- 3.2. Hard chromium plating SurTec 875
- 3.3. Bright chromium plating SurTec 871

3.1 Influence of bathparameters on the deposition conditions

◇ the plating range of bright and hard chromium deposits depends on the current density and temperature

◇ outside this plating range the chromium deposit is grey, dull and brittle or milky dull and soft

◇ For example:

$\vartheta = 70$ °C, $j = 10$ A / dm^2 : milky dull and soft chromium deposit

$\vartheta = 30$ °C, $j = 20$ A/ dm^2 : grey, dull and brittle chromium deposit

3. Operating conditions

	chromic acid	**temperature**	**current density**
higher current efficiency	+	+	+
better coverage	+	-	+
lower burning limit	+	+	-
better throwing power	✳	+	+
higher hardness	-		+

+ high - low

✳ throwing power depends on the conductivity of the electrolyte

3.2 Hard chromium plating SurTec 875

The hard chromium process SurTec 875 consists of two products:

SurTec 875 A: (make-up)	50 weight % CrO_3 + catalyst + SurTec 870 AK sulfuric acid is added separately
SurTec 875 V: (maintenance)	50 weight % CrO_3 + catalyst + SurTec 870 AK

Examples for make up:

Rated value in g/l CrO_3 x 2 = addition in g/l SurTec 875 A

Rated value 120 g/l CrO_3 = 240 g/l SurTec 875 A

3. Operating conditions

- Operating conditions (practice-values):

SurTec 875 A:	200 - 500	g/l
sulfate	1 - 2	% from chromic acid content
temperature:	55 - 65	°C
voltage:	appr. 6 - 8	V
current density:	appr. 50 - 60	A/dm^2

- For strongly profilated parts it is necessary to use auxiliary anodes
- dimmings are used

- maintenance:
  - SurTec 875 V had to be added according to CrO_3 analysis
  - H_2SO_4 is added separately as required, if sulfate content is too high, sulfate has to be precipitated with $BaCO_3$

3. Operating conditions

◇ Conversion:

- a conversion from competitive chromic bathes is possible (also fluoride containing bathes)
- at high metal impurities (10 - 15 g/l) conversions are not useful
- after conversion analysis at SurTec, the catalyst (and/or $Ca(OH)_2/BaCO_3$, respectively) are added by a SurTec-technician

◇ Comparison to competitive processes:

- competitive processes work generally at 250 g/l CrO_3
- although SurTec 875 contains less CrO_3 it shows comparable to better coverage and higher deposition rate
- brightness and properties of the layer are comparable to the competitive processes

3. Operating conditions

3.3 Bright chromium plating SurTec 871 (practice-values)

CrO_3: 200 - 280 g/l
sulfate: 1 - 1,5 g/l = 25-37 ml/l SurTec 871 I
fluoride: ca. 0,2 g/l = 25 ml/l SurTec 871 II
SurTec 870 AK (surfactant): 2,5 ml/l

temperature: 28 - 35 °C
voltage: appr. 5 V
applicationtime: appr. 5 min
layer thickness: 0,3 - 0,8 μm

- auxiliary anodes are only necessary for very strongly profilated parts

- dimmings are used

3. Operating conditions

◇ Maintenance:

- CrO_3 is added corresponding to the analysis
- SurTec 871 II and SurTec 870 AK are added corresponding to the drag-out
- consumption of SurTec 871 I is low to nothing
- if the sulfate concentration is too high, it had to be precipitated with $BaCO_3$

◇ comparison to competition processes:

- competition processes work with higher chromic acid concentration and higher temperature
- brightness (depends on the Ni-deposit) and colour is comparable
- coverage and throwing power is better than the competition processes

4. Layer properties

4. Layer properties

chromium deposits are:

- bright with a bluey white colour
- hard
- smooth
- nonmagnetic

chromium deposits have:

- a good wear resistance and abrasion protection
- high tensile stress. At mechanical strain the deposit is less ductile and high crack sensitive (e.g.: bending, deforming)
- a good reflectivity

4. Layer properties

Effects of atmospheric oxygen on chromium deposits, is:

- a thin, dense oxidation film without changing the metallic appearance,

because of this:

- ☐ the chromium deposit dissolves at approx. 1,3 V
- ☐ chromium has low wetting and adhesive poperties
- ☐ is chromium resistant to tarnish until 500 °C
- ☐ chromium could not be soldered
- ☐ chromium is badly conductive

chromium is

chemical resistant	**less chemical resistant**	**not chemical resistant**
organic acid	hydrofluoric acid	hydrochloric acid
phosphoric acid / salts	sulfuric acid	chlorides
nitric acid / salts		
alkali solution / salts		

4. Layer properties

Formation of cracks in chromium deposits

- during the chromium plating mainly chromium hydride is formed
- at dissociation of the chromium-hydride (hexagonal structure) the body-centered cubic chromium is formed with a smaller volume than the chromium-hydride
- as a result of the volume reduction there are very high internal tensions in the deposit and from a certain layer thickness the deposit cracks
- therefore in thicker deposits several cracked layers lay on top of each other
- from approx. 20 μm layer thickness the cracks overlap and do not get to the base metal (micro-cracked chromium deposit)

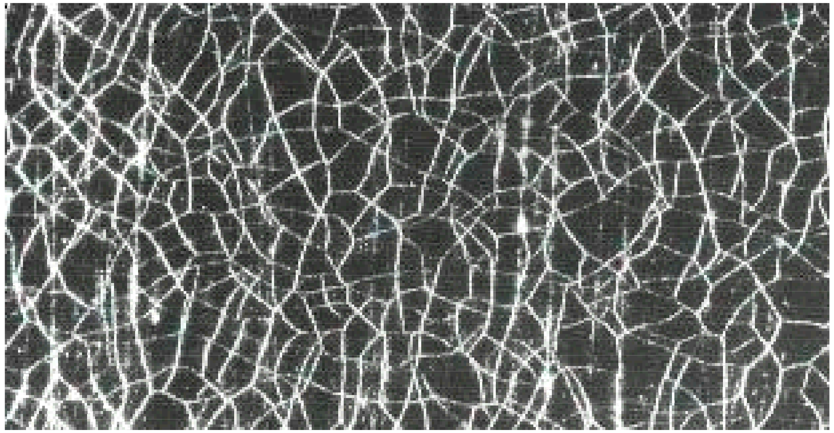
4. Layer properties

normal bright chromium bathes have 10 - 20 cracks / cm

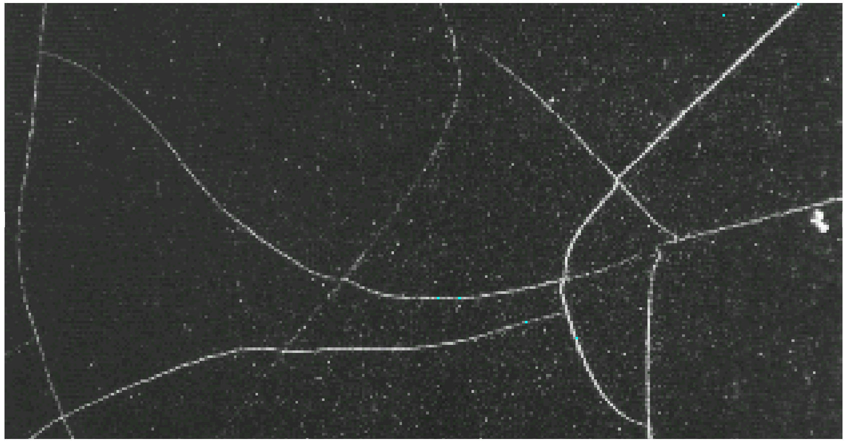
micro - cracked chromium deposits have approx. 400 - 800 cracks / cm

- the corrosion protection of micro-cracked chromium deposits is much better than macro-cracked chromium deposits

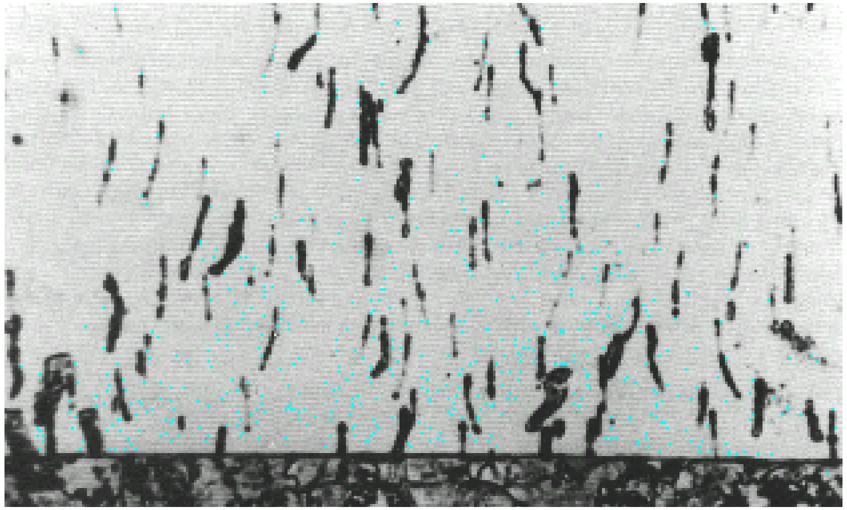
- it is possible to plate crack-free chromium deposits, but these deposits have high internal tensions and crack later
  (macro-cracks)



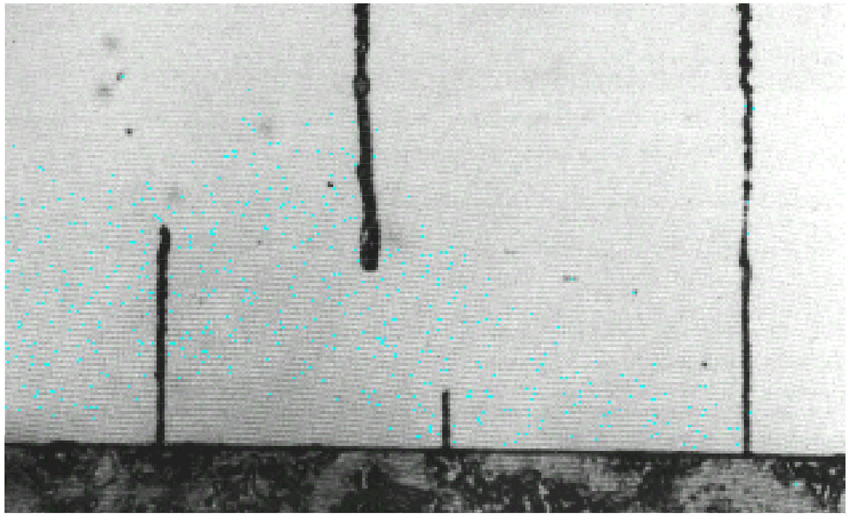
micro-cracked chromium plating with more than
300 cracks / cm (magnified 200 times)



macro-cracked chromium plating with less than
50 cracks / cm (magnified 200 times)



micro graph of a hard chromium deposit with a lot
of short cracks (magnified 1000 times)



micro graph of a hard chromium deposit with a few long
cracks (magnified 1000 times)

Hard chromium plating SurTec 875

area of application:

- wear protection
- abrasion resistance
- hardness
- sliding property
- layer thickness: 1 μm to several mm

SurTec 875

hardness:	900 - 1100 HV
cracks:	approx. 400 cracks / cm - after grinding 400 - 600 cracks / cm
brightness:	well

4. Layer properties

Bright chromium plating SurTec 871

decorative application (decorative chromium plating)

0,3 - 1,0 μm layer thickness

with this layer thickness the chromium has only low corrosion protection

that is why layer systems like Ni / Cr or Cu / Ni / Cr are plated

pitting free nickel deposits protect the basis material

corrosion test: Corrodkote-process to DIN 50958

5. Analysis and bath control

5.1. Analysis for hard chromium baths

Analysis of chromic acid:

- titration: addition of hydrochloric acid and potassium iodide, subsequently titration with sodium thiosulfate solution and starch as indicator
- by way of the bath density
- correction: addition of chromic acid

Analysis of the trivalent chromium:

- oxidising of Cr-III to Cr-VI with peroxide under alkaline conditions, then analysis of the total amount of chromic acid as described above
- analysis via AAS (total amount of chromic acid)
- the previously measured amount of chromic acid must be subtracted from the total amount and multiplied with a factor to get the amount of Cr-III

Analysis of sulfate:

- precipitation with Ba-chloride, filtrate and complex the precipitation with EDTA, the excess of EDTA is titrated back with zinc chloride solution
- precipitation with Ba-chloride and centrifugation
- analysis by the way of ion chromatography
- correction: addition of the missing quantity sulfuric acid or precipitation of 0.1 g/l sulfate with the addition of 0.2 g/l $BaCO_3$

Impurity metals (Fe, Cu, Ni)

- analysis by the way of AAS

Catalyst of the hard chromium bath

- analysis only by the way of ion chromatography possible (not possible to analyse at the customer´s site)

5.2. Methods to adjust hard chromium baths

Hull cell test

to check the coverage and the burning limit

- 250 ml bath sample (at working temperature), Hull cell out of porcelain
- platinised titanium anode
- using a Hull cell panel freshly plated with bright nickel
- plating with 10 A (if not possible then use 5 A) for 5 min

HEEF SurTec 875

Analysis of current efficiency (OUR method):

- 600 ml beaker with a round anode (platinised titanium), filled with 500 ml bath sample at working temperature
- plate a rod of stainless steel with exactly 60 A/dm^2 (for 2,5 min)
- compare brightness and possible burnings with a standard plated rod
- dissolve anodically the chromium layer quantitatively in 5 % sodium hydroxide solution
- titrate the content of chromium with thiosulfate solution

Calculation of the current efficiency:

$$\frac{0.1\ \text{mol} \cdot \text{ml thiosulfate} \cdot 96485\ \text{As/mol} \cdot 6 \cdot 100\ \%}{1000\ \text{ml} \cdot 60\ \text{A} \cdot 150\ \text{s} \cdot 3} = \text{current efficiency}$$

or: $$\text{ml thiosulfate} \cdot 1.0756 = \text{current efficiency}$$

Experimental setup for the analysis of the current efficiency:

5.3. Analysis for decorative chromium baths

chromic acid, sulfate, Cr-III and metal impurities as described above

Analysis of fluoride

- measurement with fluoride sensitive electrode
- it is a comparative measuring method (standard solutions are required, like a pH measurement)
- adjustment also possible in the Hull cell

5.4. Adjustment for decorative chromium baths

Hull cell test

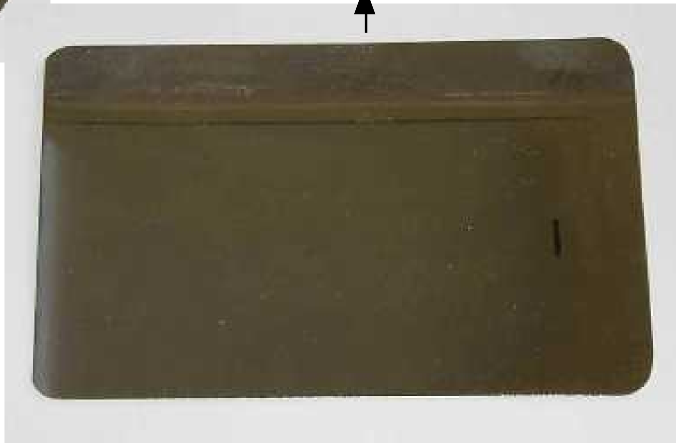
- 250 ml bath sample at 35 °C, Hull cell out of porcelain
- platinised titanium anode
- Hull cell panel freshly plated with bright nickel
- plating for 3 min with 3 A

5.4. Adjustment for decorative chromium baths

extreme lack of sulfate

lack of sulfate

optimum of sulfate



Trouble shooting list for chromium processes

problem	**possible reason**	**adequate action**
bad coverage	too much sulfate	addition of 0.2 g/l Ba-carbonate precipitates 0.1 g/l sulfate
	too low current density at the beginning	covering current for 10-20 s (ca. 1.5 times of the normal current)
	too high temperature	adjust the temperature to 30 (55)* °C
dull and brittle chromium layer at the edges rough	too low temperature	adjust the temperature to 35 (60)* °C
	too high current density	adjust the current density to 10 (50)* A/dm2
dull rough chromium layer	too low chromium content	addition of 20 g/l chromic acid
blisters, bad adhesion	insufficient degreasing	control of the pretreatment
only a small interval of brightness	too high Cr-III content	working out with small cathodic area and big anodic area to oxidise Cr-III
bad throwing power	insufficient contacting	check the contacts (corrosion...)
	passive lead anodes	check the anodes, clean them
	too low current density	check the calculation of the surface, increase the current density
	parts hanging too close on the rack	check the load on the racks, increase the distance anode - cathode
no deposition around holes in the part	strong formation of gas there	close the holes using lead or PVC
slight white clouds	impurity of chloride	addition of silver carbonate (according previous trials in the Hull cell)

* values for the hard chromium process

Additional list of trouble shooting especially for bright chromium baths

problem	possible reason	adequate action
dull grey spots	too low content of sulfate	analysis and addition of the missing amount of SurTec 871 I
dark or coloured edge between nickel and chromium	lack of fluoride catalyst SurTec 871 II	analysis or Hull cell test and addition of the missing amount SurTec 871 II
blisters, bad adhesion	insufficient pretreatment or activation	check the pretreatment, make a more aggressive activation
	impurities in the Ni electrolyte	check the Ni-bath in front of the Cr-bath
bad coverage	at correct sulfate content, temperature and using covering current: metal impurities in the Ni-bath	complex the metal impurities in the Ni-bath

6. Practical Experiences

6.1. Chromium Processes

6.2. Electrodialysis

SurTec 871 - decorative chromium process

e.g. at LKS Kronenberger in Seligenstadt (Germany).

Customer confirmed the following advantages since he switched to our process:

- better coverage of the electrolyte
- no more need of auxilliary anodes
- comparatively easy to operate:
  - determination of chromic acid and sulfate at LKS laboratory, as well as SurTec 871 II by Hull cell test
  - monthly analysis of SurTec 871 II with fluoride sensitive electrode at SurTec laboratory
- constant plating quality

SurTec 875 - hard chromium process

Current efficiency at the installations: 16,3 - 20,4 %

e.g. at COFAP / Portugal.
Comparison to former used HEEF electrolyte:

Parameter	HEEF	SurTec 875
Chromic acid	180 g/l	105 g/l
Sulfate	1,2-1,3 g/l	1,2 g/l
Bath temperature	> 60°C	> 54°C
Layer thickness at 58 A/sqdm, 143 min.	82 +/- 12 μm	94 +/- 8,5 μm -> + 14%

Results:		
	adhesion: excellent	
	microcracks (desired 400-500/**cm**):	~ 465 cracks/**cm**
	hardness (desired > 800 HV):	~ 960-1040 HV

Preferred working routine for the hard chromium process:

1. 1-5 minutes warming up the parts in the anodic etching bath (without current)
2. 20-30 seconds anodic etching at 30 A/dm^2, ca. 55°C
3. 1-5 minutes warming up the parts in the hard chromium electrolyte at a cathodic potential of about 2 V.
4. slowly increase the current from zero to the desired value
5. hard chromium plating to reach the desired coating thickness,e.g. at 55°C, 50 A/dm^2

For geometrically difficult parts:

- auxilliary anodes
- shielding devices (plastics or metal) to avoid growing edges or burnings

Despite good plating lines and process stability, on most of the parts a layer is deposited which is thicker than actually desired. Afterwards the parts are treated mechanically to reach the proper thickness (e.g. grindery).

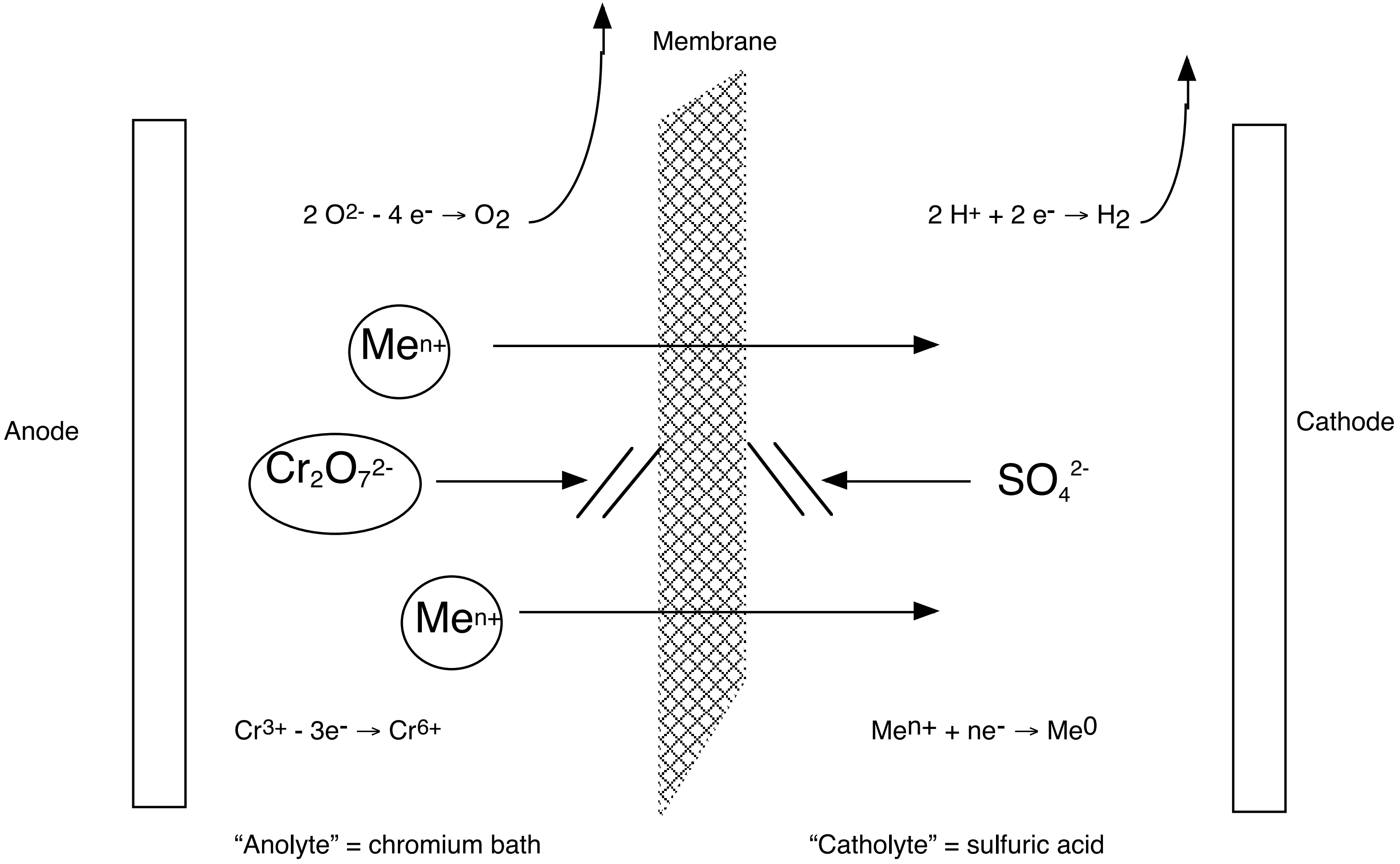
Electrodialysis to regenerate chromium baths:

- oxidation of Cr(III) to Cr(VI)
- removal of impurity metals
- recycling of the electrolyte

Working methode:

- separation process by using a cation exchange membrane in an electric field
- electrolyte contains the anode (PbO_2) to oxidize Cr(III) to Cr(VI)
- impurity metals migrate through the membrane into catholyte (diluted sulfuric acid)
- chromium(VI), as being a anion ($Cr_2O_7^{2-}$), does not penetrate the membrane and stays in the electrolyte
- the electrodialysis can be used by continuous or by batch process

Schematic principle of electrodialysis:



Advantages of continuous processing:

- constantly low concentration of impurity metals
- constant concentration of Cr(III) by regulated flow rate
- use of platinised titanium anodes
- constant layer quality
- no need to increase chromic acid with bath age

Profitability of an electrodialysis plant:

The energy costs to reduce the impurity metals to 1/5 of the start concentration are about 550 DM/m^3 chromium bath.
In comparison, the costs for disposing the bath and a new make-up are about 2000 DM/m^3 chromium bath.
Thus, the costs of the electrodialysis plant are amortised after recycling about 10-30 m^3 of chromium bath.
It is possible to rent a small mobile plant from some manufactures.

7. Summary

Presented topics:

- processes, applications and application techniques
- deposition reactions, anodic reactions, anodes
- electrolyte ingredients
- process parameters in practical use
- layer properties and parameters which influence these properties
- analysis and process control
- practical experiences that confirme the laboratory results

SurTec 875 und SurTec 871

- easy process control by easy analyses (titration and Hull cell test)
- technical support for the processes by SurTec laboratory
- positive practical experience