Sulfochromic pickling substitution solutions for surface treatment on aluminium and alloys

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Cr^{6+}

- Health hazard
  - Known human Carcinogen
  - Target Organs :
    - Blood, respiratory system, liver, kidneys, skin, eyes
  - Strict Occupational exposure limits
- Environmental Hazard
  - Major water polutant
  - Also present in the air

Most commonly found water pollutants

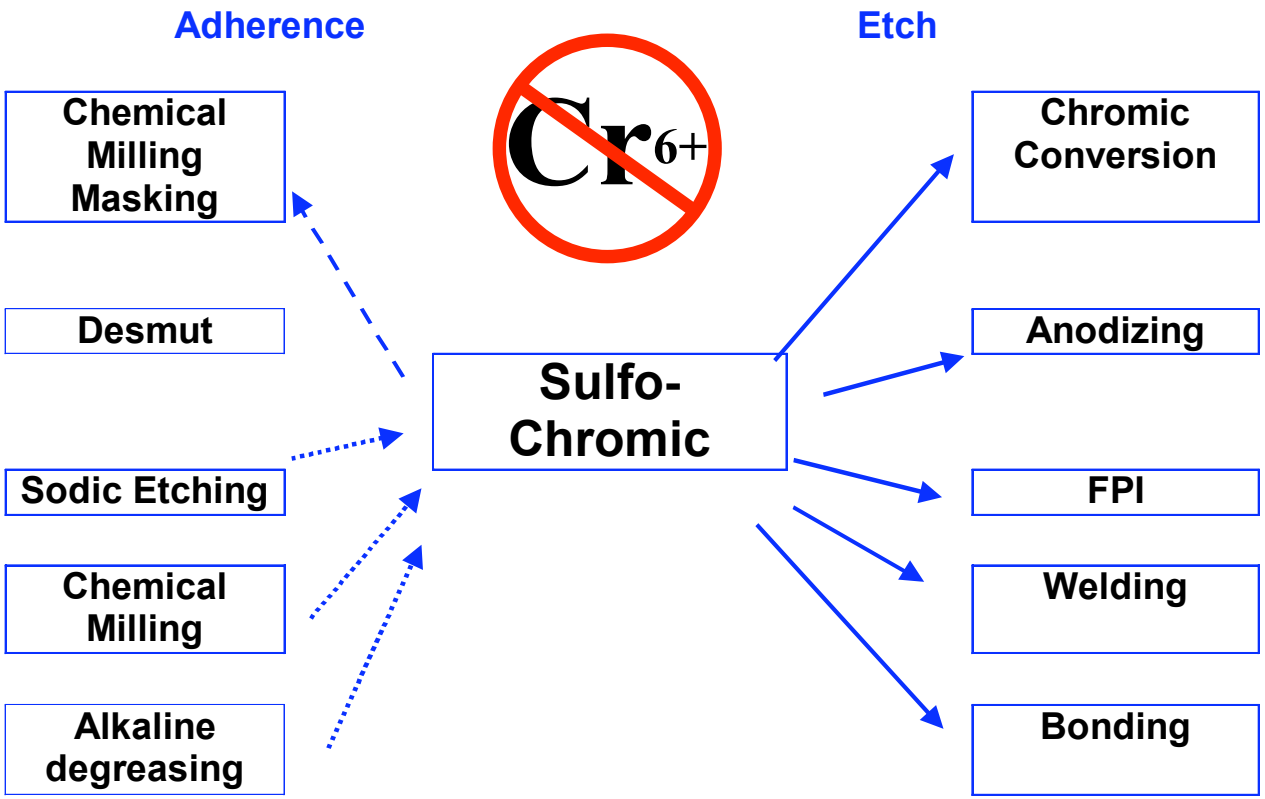
Hydrocarbons	24, 3%
Poly-cyclic Aromatics	11,1 %
Lead	9,1 %
Zinc	7,5 %
Chlorinated solvents	7,5 %
Chromium	6,6 %
Copper	5,9 %
Arsenic	5,4 %
Nickel	4,1 %
Cadmium	3,3 %

Atmospheric release of Heavy Metals

(Estimation, for France in 2002)

- Zinc 1570 t
- Lead 387 t
- Chromium 256 t
- Nickel 218 t
- Copper 90,8 t
- Mercury 33,8 t
- Arsenic 18,5 t
- Cadmium 14,1 t
- Selenium 12,1 t

A central step:



Engineering Requirements

- Chemical Milling + Sodic etching
  - Maskant adherence to substrate and milling coefficient
  - Neutralisation and desmut : removal of all surface deposit
- Non-Destructive Testing (FPI)
  - Compatibility with Penetrants. Remove all surface deposit.
- Welding
  - Conductivity
- Bonding
  - Shear Resistance, Cohesive failure.
- Chromic conversion, anodising and painting
  - Salt Spray , Corrosion Tests :
    - 168 h Chromic conversion
    - 750 h Sulfuric anodising ; 500 h Chromic anodising
  - Paint adherence
  - Filiform corrosion
  - Fatigue test following Chromic Anodising

Industrial Requirements

- 3 year bath lifetime
  - Etching should not be affected even when Aluminum concentrates (20 g/ l maximum)
- Easy bath monitoring
  - Titration should be performed with simple tools .
- Compatibility with all aluminum alloys : 2xxx, 7xxx,5xxx,6xxx.
  - Test should be performed on all nuances
- Compatibilty with tanks and equipment
  - Inventory and test of all the involved materials
- Water Treatment.
  - Fluoride free system
- Economical Balance

Different Substitution technologies

- Phosphoric acid based
  - Lower etching rates
  - Insoluble surface deposits
  - Insufficient desmut properties
- Sulfo-Nitro-Ferric
  - Best compromise so far
  - Requires heating (40-60°C)
- Fluorides ?
  - Increase etching rates
  - Safety issues
  - Water treatment issue
  - Intergranular attack

Base mechanisms of aluminum etching
(2XXX and 7XXX series alloys)

Al

Cu

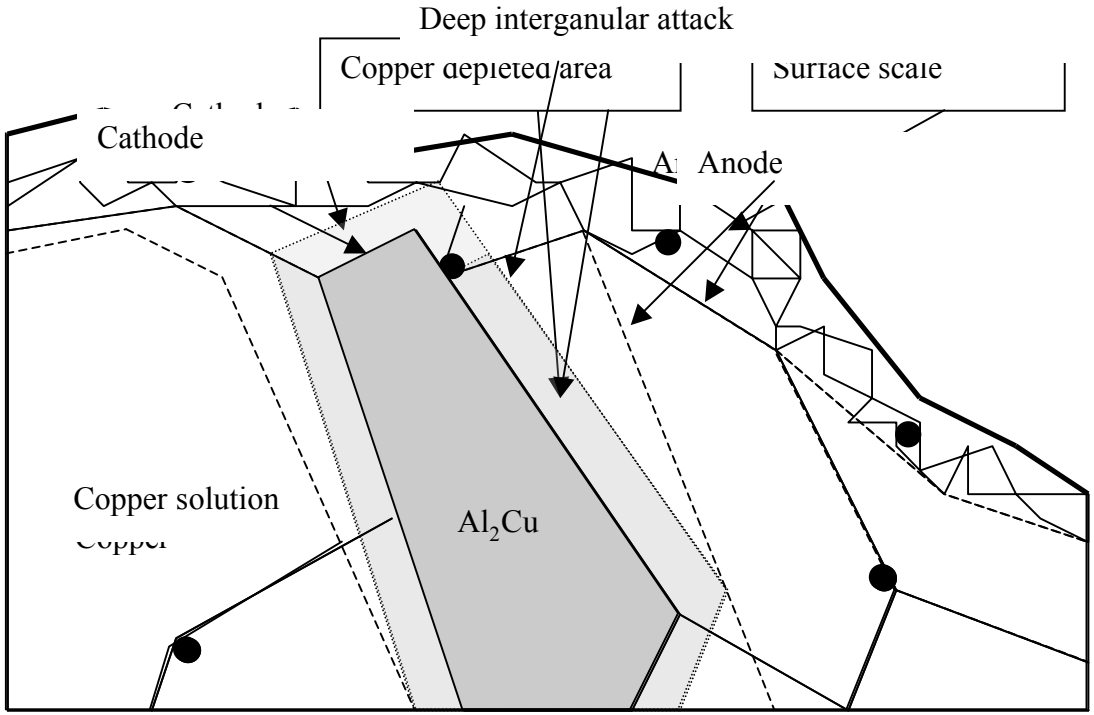
$Al + 6\ H^+ \rightarrow 2\ Al^{3+} + 3H_2$ Very quick reaction

$Cu + Ox^{(n)} \rightarrow Cu^{2+} + Red^{(n-2)}$ Slow reaction

- Risk : preferential attack on aluminum
- Consequences :
  - Copper concentrates on the surface
  - Deterioration of corrosion resistance

- Control and limit attack on aluminum
- Enhance attack on copper

Fluorides and Inter-granular attack

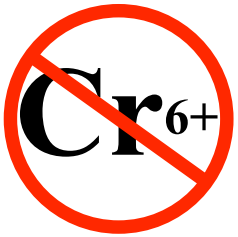


Deeper look into mechanisms

- H_2SO_4
  - $2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2$ (1)
- HNO_3
  - $Al + 6H^+ + 3NO_3^- \rightarrow Al^{3+} + 3NO_2 + 3\ H_2O$ (2)
  - $Al + NO_3^- + 4H^+ \rightarrow Al^{3+} + NO + H_2O$ (3)
  - $Cu + 2NO^{3-} + 4H^+ \rightarrow Cu^{2+} + 2NO_2 + H_2O$ (4)
  - $3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4\ H_2O$ (5)
- Fe^{3+}
  - $2Al + 2Fe^{3+} \rightarrow 2Al^{3+} + 2(Fe)$ (6)
  - $2(Fe) + 6H^+ \rightarrow 2Fe^{3+} + 3H_2$ (7)
  - $(Fe) + 6H^+ + 3NO_3^- \rightarrow Fe^{3+} + 3NO_2 + 3\ H_2O$ (8)
  - $(Fe) + NO_3^- + 4H^+ \rightarrow Fe^{3+} + NO + H_2O$ (9)

SOCOMOR dedicated solution

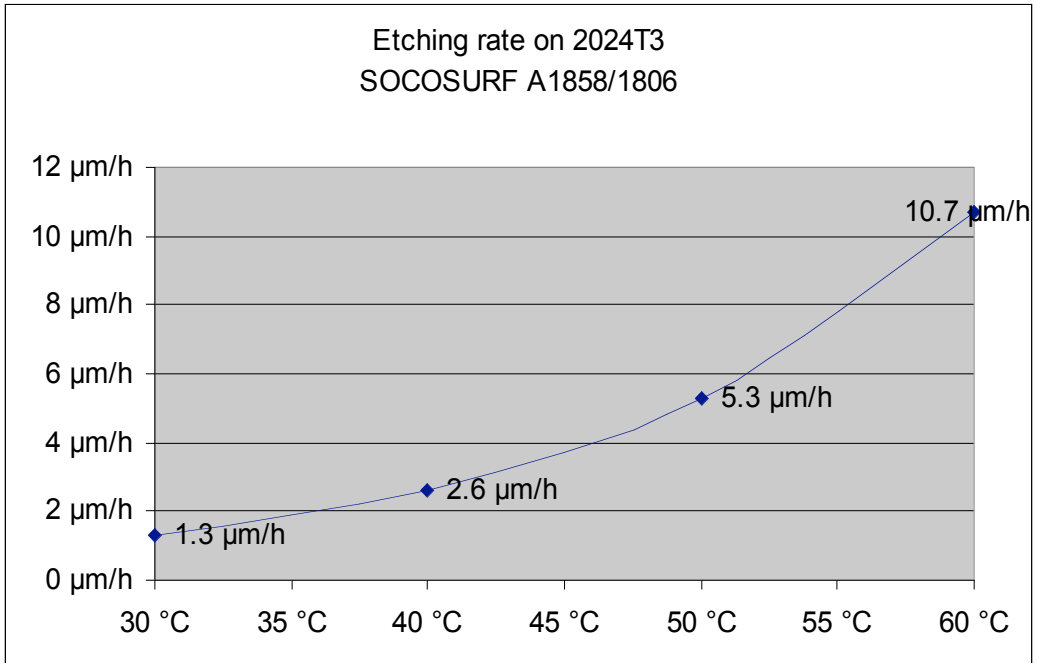
- Bi-Component : Sulfo- Nitro - Ferric
  - **Socosurf A 1858** 40 - 50 %
  - **Socosurf A 1806** 6 - 10 %
- Working conditions :
  - Temperature : 40 - 60 °C
  - Typical etch time : 1 - 10 minutes
  - Air agitation, or spray systems.
- Demin. water rinse (3 minutes)



Typical etching rates on 2024 T3 with Socosurf A1858/A1806

- Temperature dependent value. The rate doubles for each 10°C
- Example :

  immersion 5 minutes at 40°C → 0,2 µm removal



Bath Monitoring
Socosurf A1858/A1806.

- Acid Base titration for H_2SO_4 and HNO_3
- Oxydo-reduction titration for Fe^{3+}
- Chelating titration for Al^{3+}.
- Colorimetry for Cu^{2+}

Current Approval Scheme

- SOCOSURF Product range has been evaluated by
  - AIRBUS / EADS
  - DASSAULT
- Final results are pending / available
- SOCOMOR are seeking to extend approval scheme to further OEM's

Future challenges

- In a treatment line, any change can affect all the other steps
- Other major technological shifts will come, motivated by new and harsh environmental constraints
- Before Cr^{6+} has totally disappeared, we expect much work
  - New products
  - Processes adjustment
  - Industrial Know-how acquisition

Sulfo-chromic subsitution connected developments

- Chemical milling maskants :
  - Perchlo to toluene based maskants
  - High solid content maskants
- Surface conversion :
  - From chromium conversion coating to the Sol-Gel technology
- Degreasing :
  - Chlorinated solvent vapor degreasing ban
  - Surfactant EC regulations

Conclusion

- Sulfo-Nitro-Ferric etching / desmutting shows big potential
- We believe Fluorides are globally a nuisance :
  - Environmentally
  - Safety
  - Surface properties
- Our development policy also covers adjacent areas
- The next big step will be total elimination of Cr^{6+} from workshops