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## REACH Legislation -

Opportunities and Threats for R&D in Electroplating

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### What is REACH ?

**REACH** - Regulation on **R**egistration, **E**valuation, **A**uthorisation and **R**estriction of **C**hemicals

New European Chemistry Regulation, entered into force on June 1st, 2007

**Main objectives:**


- Ensure a high level of protection of human health and the environment from the risks caused by chemicals
- the promotion of alternative test methods
- the free circulation of substances on the internal market and enhancing competitiveness and innovation.



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### How REACH works

- All manufacturers or importers must file a **registration** dossier for substances => 1 tonne at European Chemicals Agency (ECHA)
- authorities may also select substances for a broader substance **evaluation** to further investigate substances of concern.
- foresees an **authorisation** system aiming to ensure that **substances of very high concern (SVHC)** are properly controlled, and progressively replaced by suitable alternative substances or technologies where these are economically and technically viable. Where this is not possible, the use of substances may only be authorised where there is an overall benefit for society of using the substance.




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### Impacts of REACH on Plating Industry

#### Registration

- low volume materials (but > 1 tonne/year) will disappear from the market, for suppliers decide to avoid registration effort and cost.
- even low volume materials may generate a huge impact on preparations, which contain those materials in small quantities
- often this decisions are made short term, which generates additional pressure on substitution work
- suppliers may save costs for registration by offering „transported, isolated intermediates“. Those intermediates need strictly controlled handling in closed systems (e.g. sodium dichromate).




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### Impacts of REACH on Plating Industry

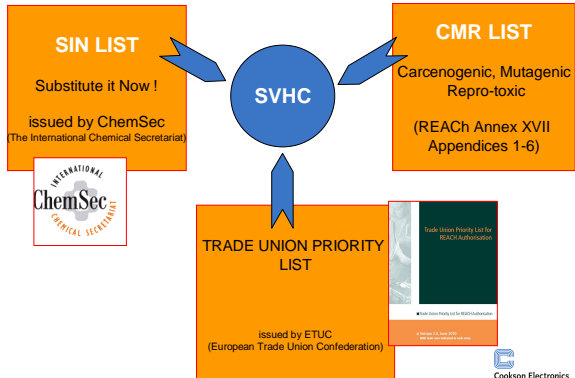
#### Authorisation

- Authorisation process will be applicable to a significant number of SVHC
- the use of SVHC will be strictly limited and the goal is to get rid of them
- Suppliers will stop manufacturing of those substances due to business limitations
- we would need to spend time and money to obtain an exemption



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### Sources for Selection of SVHC Candidates

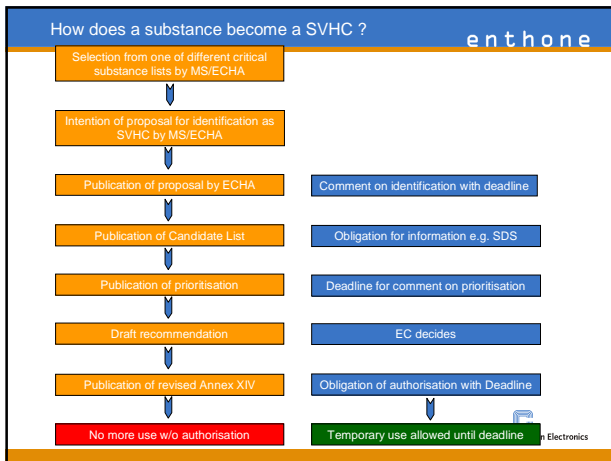


**SIN LIST**  
Substitute it Now!  
issued by ChemSec  
(The International Chemical Secretariat)

**CMR LIST**  
Carcinogenic, Mutagenic  
Repro-toxic  
(REACH Annex XVII  
Appendices 1-6)

**TRADE UNION PRIORITY LIST**  
issued by ETUC  
(European Trade Union Confederation)





### Threats for Electroplating Industry

~ 1000 substances are on different lists like CMR, SIN, ETUC, etc., dynamically growing

~ 150 substances of these 1000 are used in Electroplating Industry

Currently 13 (7 proposals & 6 candidates) are in use in this industry

### Current interesting candidates

We see currently six candidates on the candidate list which have an impact on the Electroplating Industry

Boric Acid	(Toxic for reproduction)
Cobalt dichloride	(carcinogenic)
Diarsenic trioxide	(CMR)
Potassium dichromate	(Toxic for reproduction)
Disodium tetraborat-anhydrous	(CMR)
Sodium dichromate	(CMR)

### Current consultations

And some more under consultation.....

Substance name	EC number	CAS number	Proposing authority	Reason for proposing	Date of publication	Deadline for commenting	Link to the Annex XIV report	Link to commenting form
Cobalt(II) sulphate	233-334-2	10124-43-3	Netherlands	CMR	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
Cobalt(II) dihydrate	233-402-1	10141-05-6	Netherlands	CMR	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
Cobalt(II) carbonate	208-169-4	513-79-1	Netherlands	CMR	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
Cobalt(II) diacetate	200-755-8	71-49-7	Netherlands	CMR	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
2-Methoxyethanol	203-713-7	109-86-4	Austria	CMR	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
2-Ethoxyethanol	203-804-1	110-80-5	Austria	CMR	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
1,3,5-Trichlorobenzene	203-608-6	108-70-3	Germany	PBT like substance (equivalent level of concern)	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
1,2,3-Trichlorobenzene	201-757-1	87-61-6	Germany	PBT like substance (equivalent level of concern)	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
1,2,4-Trichlorobenzene	204-428-0	120-83-1	Germany	PBT like substance (equivalent level of concern)	30/09/10	14/10/10	<a href="#">[X]</a>	The consultation is now over
Chromium trioxide	215-607-8	1333-82-0	Germany	CMR	30/09/10	14/10/2010	<a href="#">[X]</a>	The consultation is now over
Acids generated from Chromium trioxide and their oligomers	-	-	Germany	CMR	30/09/2010	14/10/2010	<a href="#">[X]</a>	The consultation is now over
Group containing Chromium acid	231-601-5	7739-94-5	-	-	-	-	-	-
Dichromic acid	236-661-5	13030-68-2	-	-	-	-	-	-
Oligomers of chromic acid and dichromic acid	-	-	-	-	-	-	-	-

From the ECHA Website: [http://echa.europa.eu/consultations/authorisation/svhc/svhc\\_cons\\_en.asp](http://echa.europa.eu/consultations/authorisation/svhc/svhc_cons_en.asp)

- ### Tasks for R&D in Electroplating
- 
- Avoid further use of critical substances (CMR, SIN etc. ) for new developments
  - Find replacements for substances in these lists
  - Concentrate on fast replacement of candidates and substances under consultation
  - avoid substances which require „save use“, this is what customers want

### Importance of substances for Plating Industry

Substance(s)	Importance	Applications	Status of Replacement
Chrome trioxide and related Salts	Very High	Passivations for Zinc and Zinc-Alloys Chromic acid etch for plastics Decorative Chromium Plating Hard Chromium Plating	Most passivations replaced by Cr (III)-type Research ongoing for ABS & PC/ABS First comparable Chromium(III) available No sufficient solution existing!
Cobalt salts	High	High performance Cr (III)-Passivations Cobalt plating	Under research, first prototypes developed Minor importance, no replacement possible
Boric Acid	High	Buffer substance in Nickel, Zinc plating etc.	Replacement work started, no general solution expected, very critical!
Disodium tetraborat	High	Component of Pretreatment/Cleaners	Under investigation
Diarsenic trioxide	Low	Brightener in precious metal processes	Complete replacement ongoing

### Importance of chromium trioxide and related salts

**CrO<sub>3</sub>**

Chromic trioxide and related salts have multiple use in Electroplating/Surface Finishing with enormous importance

**Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>**  
**K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>**

Hardchrome Plating

Decorative Chrome Plating

Passive Pretreatment (Etch)

Passivation for Zn/Zn-Alloys etc.

### Examples for successful replacement

#### Decorative Chrome Plating

- The final layer of a decorative, corrosion resistant coating sequence is a thin layer of Chromium (e.g. 0.3 µm for microporous chrome).
- This final layer is normally plated from Chromium (VI)-electrolytes and provides characteristic properties like colour, brightness and overall corrosion properties to the surface.

### Examples for successful replacement

#### Decorative Chrome Plating

- Beside **corrosion** properties **colour** is the biggest challenge
- New developed Chromium(III) electrolytes could overcome the colour mismatch of older systems
- Corrosion properties are good but not as good as from Cr(VI) solutions
- Automotive application is still critical (72 h CASS)
- Cr(VI) post dip improves, but makes no sense
- Work is ongoing with SAM technology to achieve optimum corrosion properties

No	Type	L*	a*	b*
1	Hex Chrome	84	-1.07	-1.56
2	TRILYTE® CF	83	-0.9	-0.9
3	Silver	86.8	+0.7	5.3
4	Copper	84	11.8	14.3

### Ongoing replacement work

#### Passivation for Zn & Zn-Alloys

- Change from Cr(VI) passivations to Cr(III) passivations almost complete
- This was driven e.g. by ELV (Directive 2000/53/EC)
- High performance passivations (> 240 h NSS) are mostly thick film passivations using cobalt salts
- These cobalt salts are under threat too
- Replacement work is ongoing and has delivered first promising results

### Ongoing replacement work

#### Passivation for Zn & Zn-Alloys

First results Co-free

- Temperature of 60°C delivers iridescent passivation layers**
  - Up to 600 h NSS to first WR
  - Better on alkaline than acid zinc
  - Good longtime performance – passivation fulfills requirements also after >10m<sup>2</sup>/L through-put
  - Wide working window
  - Low pH- sensitivity, easy handling
  - Iron – contaminations cause yellowish layers
    - Control by suitable Fe-inhibitor or ion exchange
- Temperature of 45 °C delivers lighter colour**
  - Corrosion resistance NSS >200 h to first, voluminous WR

### Ongoing replacement work

#### Passivation for Zn & Zn-Alloys

Metal Content & Thickness by GDOES

**Co – based thickfilm passivation**  
Approx. 13 % Cr (at 100 nm thickness)  
260 nm (1% Cr)  
2,5% Co (orange curve)

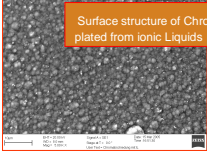
**Co – free passivation**  
ca. 12% Cr (at 100 nm thickness)  
220 nm (1% Cr)

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**Electroplating of Hardchrome**

- Hardchrome has enormous importance for manufacturing of tools, automotive & aerospace parts etc.
- Hardchrome is plated from Cr (VI) solutions
- all approaches based on Cr(III) have not delivered satisfying results so far
- there are e.g. some results based on ionic liquids, using Cr (III)
- this is in a **very first stage of research**
- a long way to go to technical mass production
- replacement by other alloy questionable

Surface structure of Chrom plated from ionic Liquids



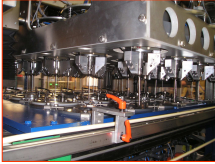
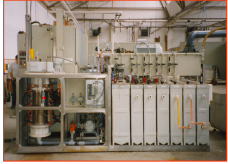
Plating Cr from Cr(III) / IL-system (e.g. Cholinechloride or BMImCl) leads to blackish & semibright Cr-layers. Layer thicknesses > 5 µm can be achieved.



Hardchrome ? enthone


**Electroplating of Hardchrome**

- a different approach is to achieve a maximum safety in handling
- part specific reactors with closed loop systems are already in use
- applicable for mass production parts of simple geometry

source: Fa. LPW (left) , Fa. Gramm (right)


➔ **A replacement of Chrome trioxide for Hardchrome is not very likely in near future ! Authorisation is needed until replacement is possible.**




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**SUMMARY**

- Registration and Authorisation, both will have impact on availability of raw materials
- R&D's avoid use of critical substances for current and future developments
- Replacement work is ongoing and accelerated for (proposed) candidates
- some processes like decorative chrome and cobalt-free passivates show promising results, first replacement products are available
- others are in very first stage of research
- Hardchrome plating is a field , where we see need for exemption of Cr (VI) compounds



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Thank you for  
your attention