Surface Technology White Papers
100 (4), 1-26 (April 2013)

The 50th William Blum Lecture
Presented at NASF SUR/FIN 2012 in Las Vegas, Nevada,
June 11, 2012

Hexavalent Chromium
What Else?

by
Patrick Benaben
Recipient of the 2011 William Blum
NASF Scientific Achievement Award

With commentary by
Dr. James H. Lindsay – NASF Technical Editor

Since its inception in 1958, under the auspices of the AES, the NASF Scientific Achievement Award has been given annually to a person who has contributed to the advancement of the theory and practice of electroplating, metal finishing and the allied arts or has raised the quality of the profession or has been involved in a combination of these. In 2011, the award was given to Dr. Patrick Benaben, Full Professor at École Nationale Supérieure des Mines, in St. Étienne, France. Over the years, he has been a prolific contributor to the surface finishing science and technology, and has focused his research on new electrolytic processes, in particular, on the use of ionic liquids in hard chromium plating and on such materials as high ordered alumina obtained by anodic oxidation. He has authored or co-authored about 100 papers and is inventor or co-inventor of ten international patents. He has been a member of NASF (AESF) since 1990 and served six years as 1st Vice-President of the AESF International Branch. He has been awarded both the Silver and Gold medals for outstanding papers published in Plating & Surface Finishing.

Dr. Benaben's lecture title was "*Hexavalent Chromium - What Else*?," a rather timely topic. He first described the nature of chromium, and the uses of chromium metal in industry and in commerce. Applications in surface engineering included decorative and hard chromium plating, chromium anodizing, chemical conversion and passivation, sealing and etching.

He then went on to note the risks involved in its use, including chromates, fumes from welding of stainless steel and ferrochromium alloys, chromium fumes during electroplating, and others. This led to a discussion of the toxicity, health and regulatory issues of the day.

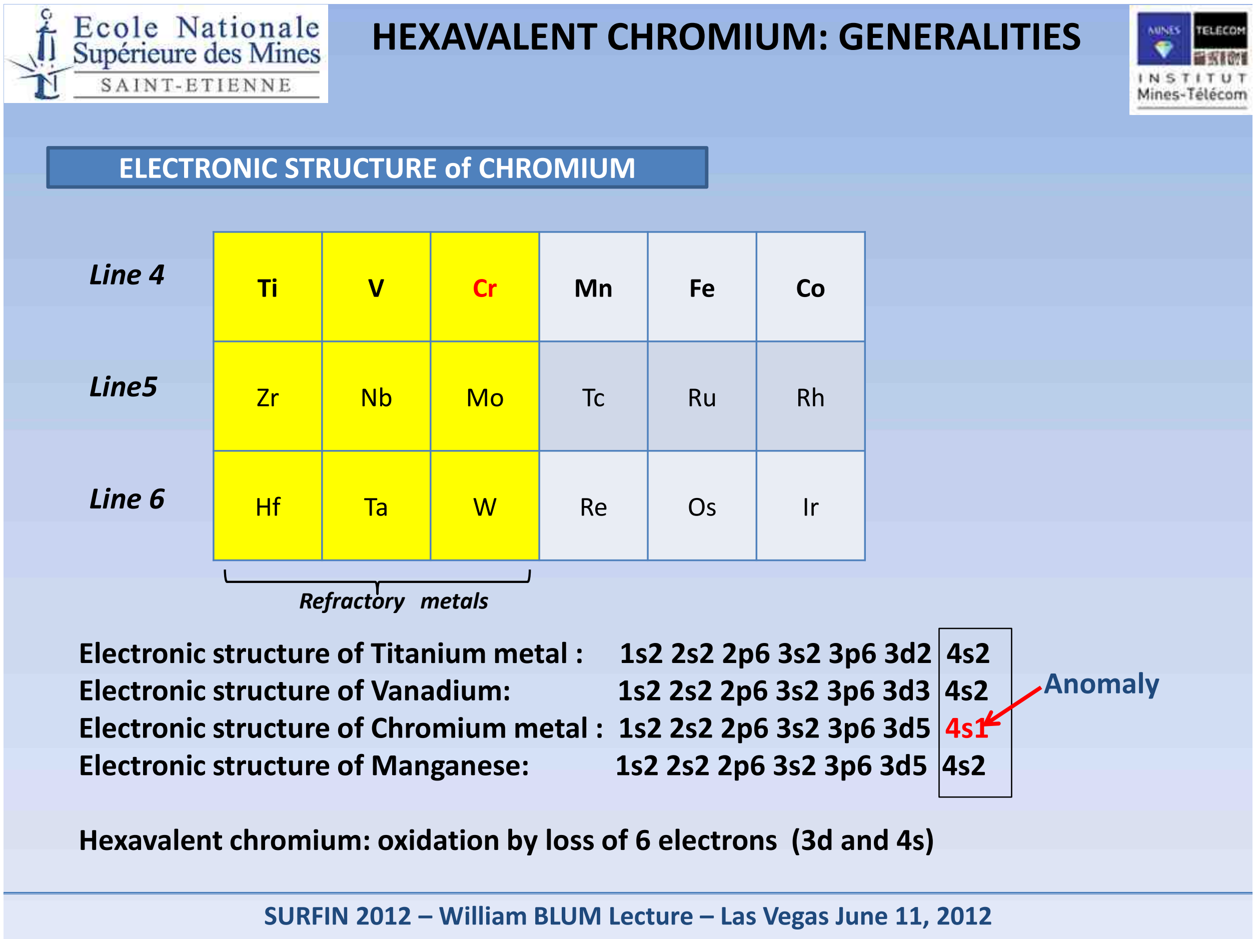
Given those problems, Dr. Benaben discussed "what else" would serve as substitutes for chromium and its deleterious health effects. He stressed that there are two regimens to consider when considering exposure to toxic forms of chromium: (1) exposure during the processing and (2) exposure in the end product to the general public. The difference is significant, and is often ignored (or at least discounted) in the ongoing debate on such issues.

He notes that, since hexavalent chromium is recognized as one of the more toxic forms of chromium, products that have the potential to release Cr(VI) to the public must be banned, and important work must be done to find alternative processes across the board. On the other hand, in other applications, the public is not directly exposed to Cr(VI). Stainless steel is an obvious example. Dr. Benaben noted that decisions and regulations must be discussed by all interested parties, although he added that such a constructive goal is very difficult to achieve.

What follows is an edited version of his presentation, along with commentary provided by Dr. James H. Lindsay, Technical Editor for the NASF.

Dr. Benaben began his 2012 William Blum Memorial Lecture with a brief review of his work at Ecole Nationale Supérieure des Mines and an outline of the material that he would be covering in the lecture, beginning with a general discussion of hexavalent chromium and the issues involved, followed by a survey of the options involved in meeting regulatory issues – the "What Else?" in his title.

In the slide below, he noted that the electronic structure of chromium was anomalous with the other elements sharing Row 4 in the Periodic Table, in the filling of the 3d shell as one advances along the row. Going from vanadium to chromium, two electrons are added to the 3d shell, and the 4s shell is only partially filled with one electron. This given configuration is the most probable but there is a non-zero probability of having a "normal" structure: 3d4, 4s2. What would otherwise be a difficult process of oxidation by the loss of six electrons from the 3d and 4s shells becomes viable.



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HEXAVALENT CHROMIUM: GENERALITIES

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ELECTRONIC STRUCTURE of CHROMIUM

Line 4	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**
Line5	Zr	Nb	Mo	Tc	Ru	Rh
Line 6	Hf	Ta	W	Re	Os	Ir

Refractory metals

Electronic structure of Titanium metal : 1s2 2s2 2p6 3s2 3p6 3d2 4s2
Electronic structure of Vanadium: 1s2 2s2 2p6 3s2 3p6 3d3 4s2
Electronic structure of Chromium metal : 1s2 2s2 2p6 3s2 3p6 3d5 4s1
Electronic structure of Manganese: 1s2 2s2 2p6 3s2 3p6 3d5 4s2

Anomaly

Hexavalent chromium: oxidation by loss of 6 electrons (3d and 4s)

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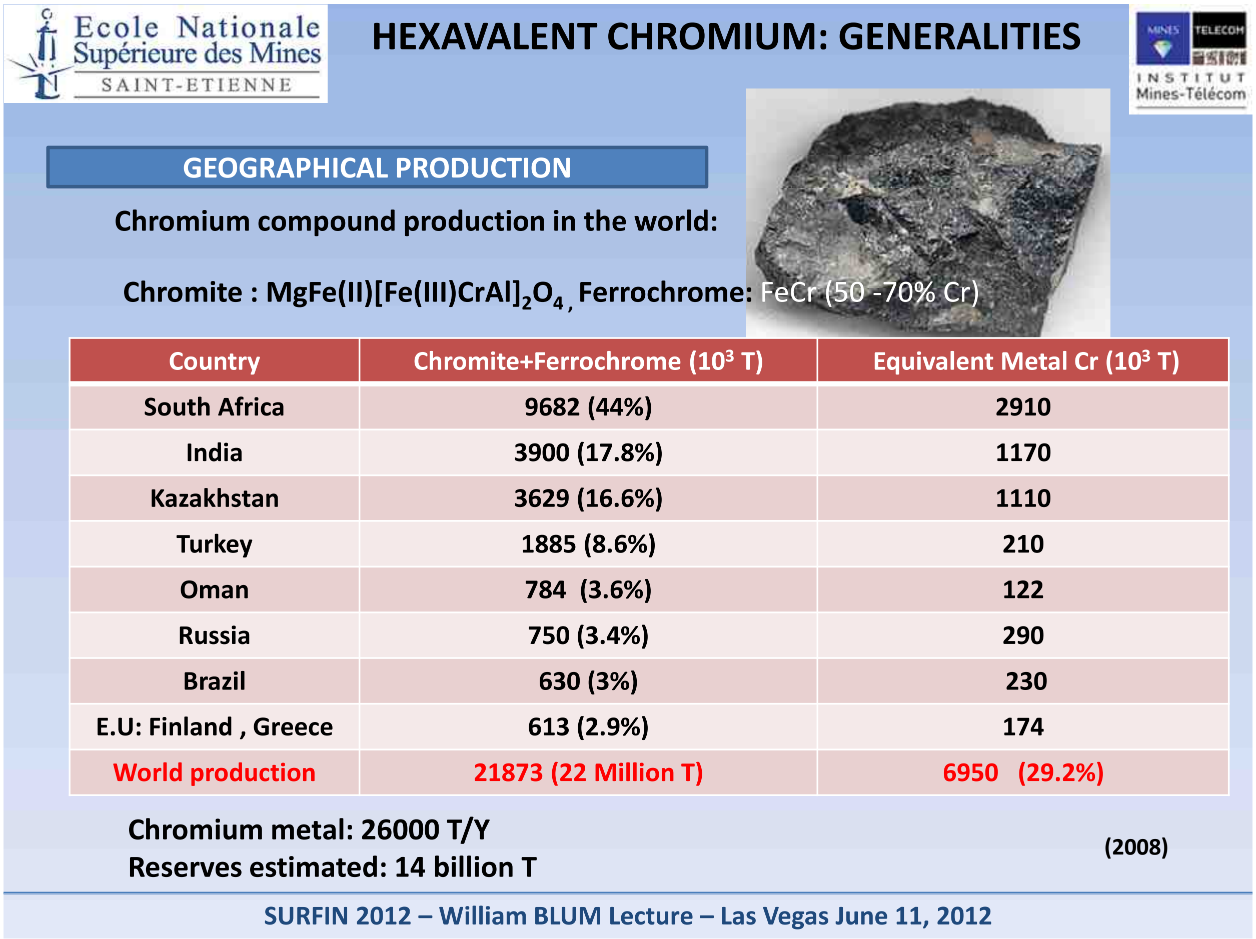
Most of the world's chromium is produced from chromite, an iron magnesium chromium oxide. The predominant supplies of chromite come from South Africa, India and Kazakhstan. Ferrochrome, most of which is used in the production of steel, is produced by the electric arc melting of chromite.



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HEXAVALENT CHROMIUM: GENERALITIES

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GEOGRAPHICAL PRODUCTION

Chromium compound production in the world:

Chromite : $MgFe(II)[Fe(III)CrAl]_2O_4$, Ferrochrome: FeCr (50 -70% Cr)

Country	Chromite+Ferrochrome (10^3 T)	Equivalent Metal Cr (10^3 T)
South Africa	9682 (44%)	2910
India	3900 (17.8%)	1170
Kazakhstan	3629 (16.6%)	1110
Turkey	1885 (8.6%)	210
Oman	784 (3.6%)	122
Russia	750 (3.4%)	290
Brazil	630 (3%)	230
E.U: Finland , Greece	613 (2.9%)	174
World production	21873 (22 Million T)	6950 (29.2%)

Chromium metal: 26000 T/Y
Reserves estimated: 14 billion T

(2008)

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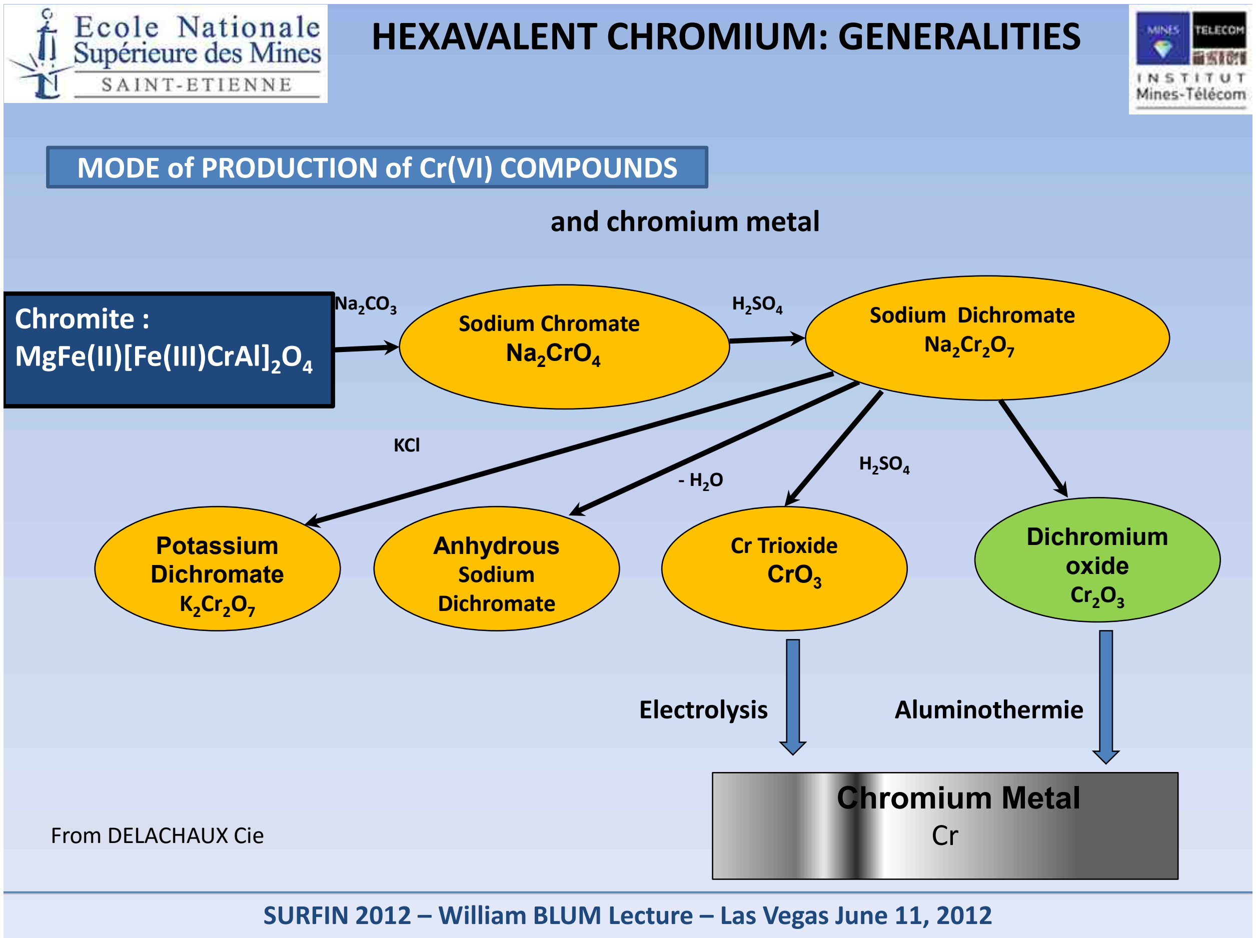
The figure below outlines the production processes for producing the common industrial hexavalent chromium compounds from chromite ore. Chromium metal is produced by electrolysis from hexavalent chromium trioxide, as well as from exothermic aluminothermic processes.



HEXAVALENT CHROMIUM: GENERALITIES

MODE of PRODUCTION of Cr(VI) COMPOUNDS

and chromium metal

From DELACHAUX Cie

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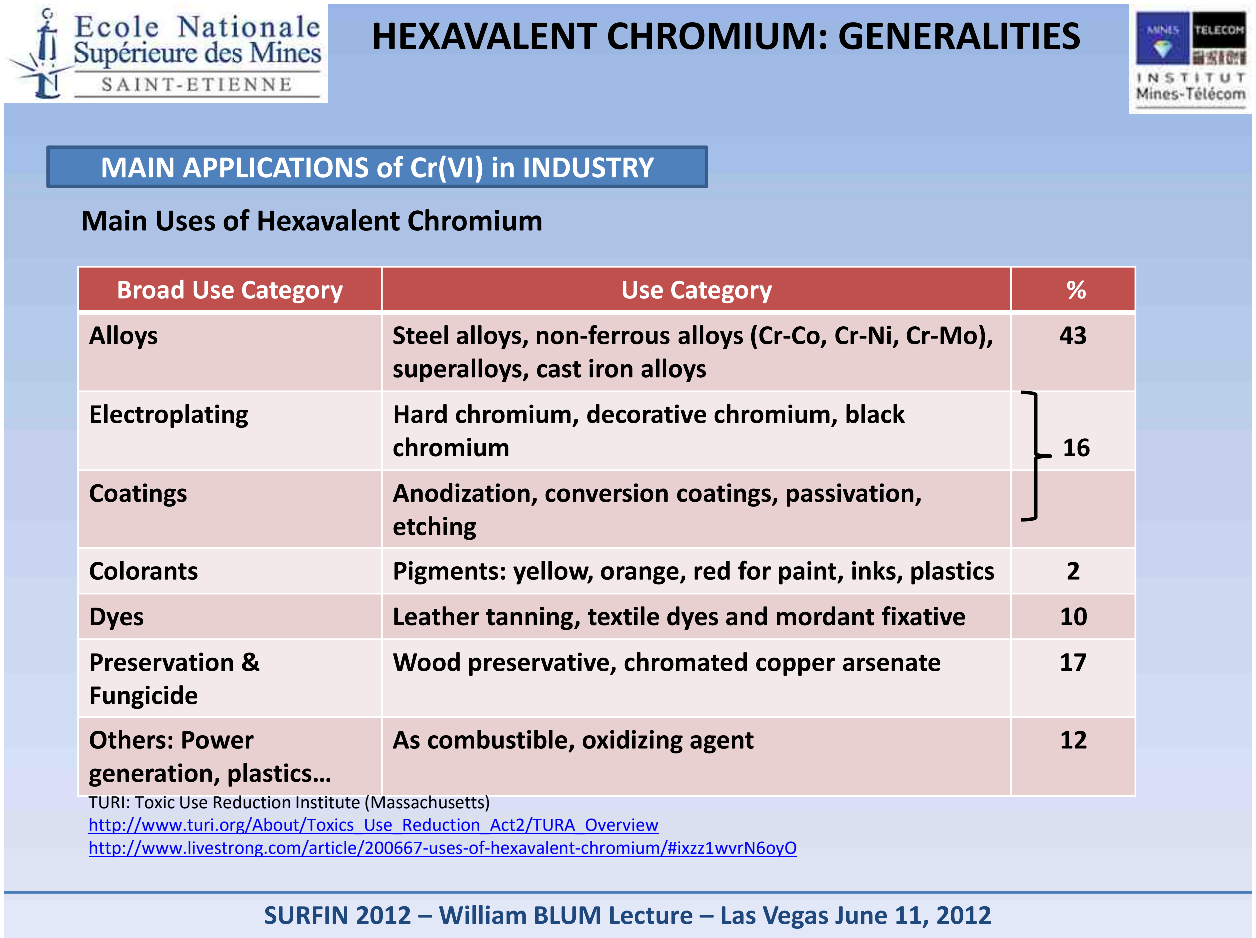
The applications of Cr(VI) in industry are many. As mentioned in the previous slide, electrolysis is used to extract chromium metal from chromic acid solution. Chromium metal is an essential ingredient in numerous essential alloys used in commerce. This application constitutes by far the largest use for Cr(VI), at 43%. The surface finishing industry uses the next largest portion , including electroplating (decorative, hard and black) as well as numerous other surface treatments (anodization, conversion, passivation and etching).



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HEXAVALENT CHROMIUM: GENERALITIES

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MAIN APPLICATIONS of Cr(VI) in INDUSTRY

Main Uses of Hexavalent Chromium

Broad Use Category	Use Category	%
Alloys	Steel alloys, non-ferrous alloys (Cr-Co, Cr-Ni, Cr-Mo), superalloys, cast iron alloys	43
Electroplating	Hard chromium, decorative chromium, black chromium	16
Coatings	Anodization, conversion coatings, passivation, etching	
Colorants	Pigments: yellow, orange, red for paint, inks, plastics	2
Dyes	Leather tanning, textile dyes and mordant fixative	10
Preservation & Fungicide	Wood preservative, chromated copper arsenate	17
Others: Power generation, plastics…	As combustible, oxidizing agent	12

TURI: Toxic Use Reduction Institute (Massachusetts)
http://www.turi.org/About/Toxics_Use_Reduction_Act2/TURA_Overview
http://www.livestrong.com/article/200667-uses-of-hexavalent-chromium/#ixzz1wvrN6oyO

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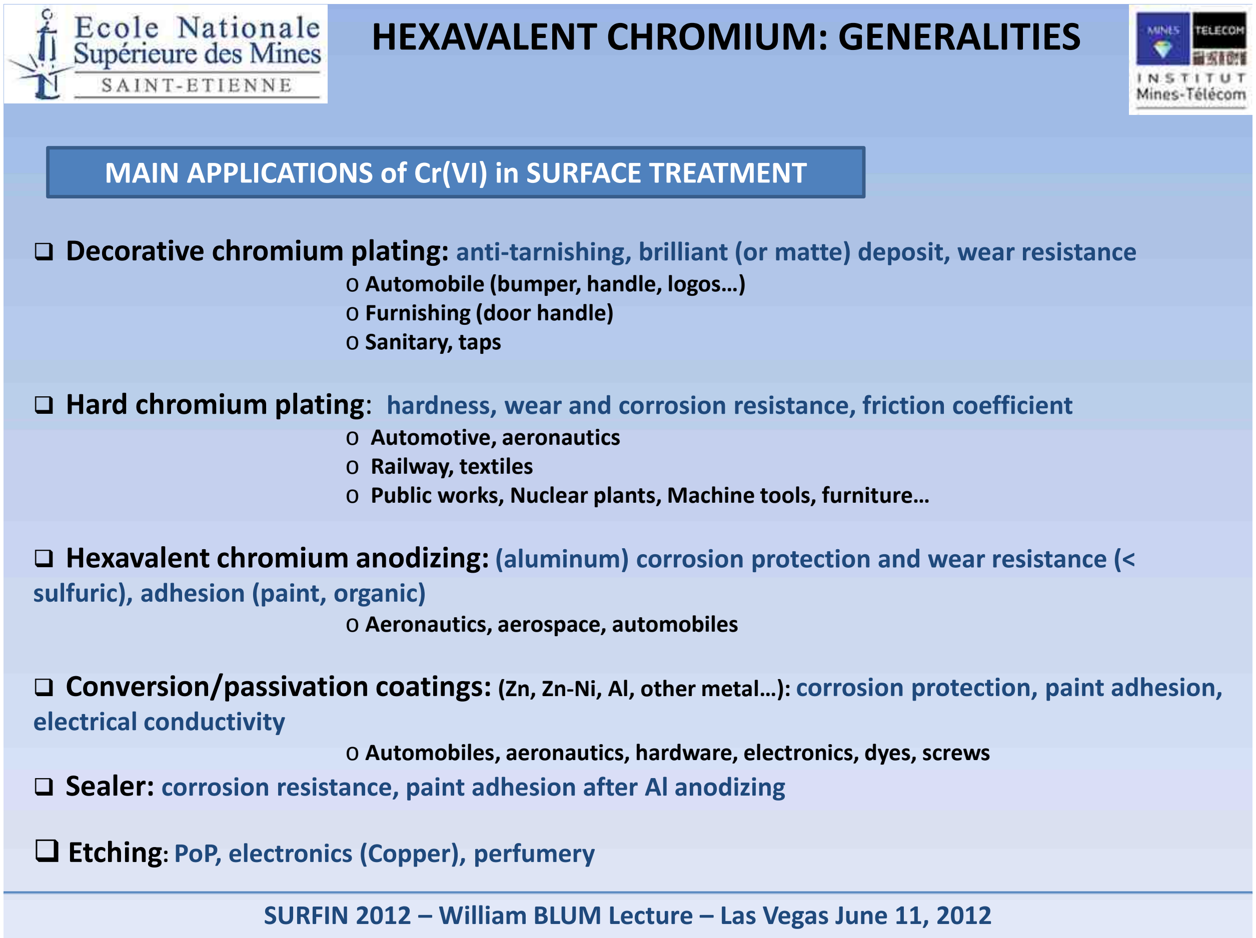
Within the surface finishing industry, Cr(VI) is applicable to many industry segments as listed below. The appearance, corrosion and wear properties of decorative chromium are important in automotive trim and many articles used in the home and in business. The robust mechanical properties of hard chromium find use in numerous heavy-duty applications. Anodizing based on Cr(VI) chemistry is used where corrosion, wear and adhesion of subsequent layers (paints) are important. Conversion and passivate coatings offer similar properties. Finally, other processes, including sealing and etching find use in a variety of processes, ranging from ABS etchants for plated plastics to perfume manufacture.



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MAIN APPLICATIONS of Cr(VI) in SURFACE TREATMENT

☐ **Decorative chromium plating:** anti-tarnishing, brilliant (or matte) deposit, wear resistance
  - Automobile (bumper, handle, logos…)
  - Furnishing (door handle)
  - Sanitary, taps

☐ **Hard chromium plating**: hardness, wear and corrosion resistance, friction coefficient
  - Automotive, aeronautics
  - Railway, textiles
  - Public works, Nuclear plants, Machine tools, furniture…

☐ **Hexavalent chromium anodizing:** (aluminum) corrosion protection and wear resistance (< sulfuric), adhesion (paint, organic)
  - Aeronautics, aerospace, automobiles

☐ **Conversion/passivation coatings:** (Zn, Zn-Ni, Al, other metal…): corrosion protection, paint adhesion, electrical conductivity
  - Automobiles, aeronautics, hardware, electronics, dyes, screws

☐ **Sealer:** corrosion resistance, paint adhesion after Al anodizing

☐ **Etching**: PoP, electronics (Copper), perfumery

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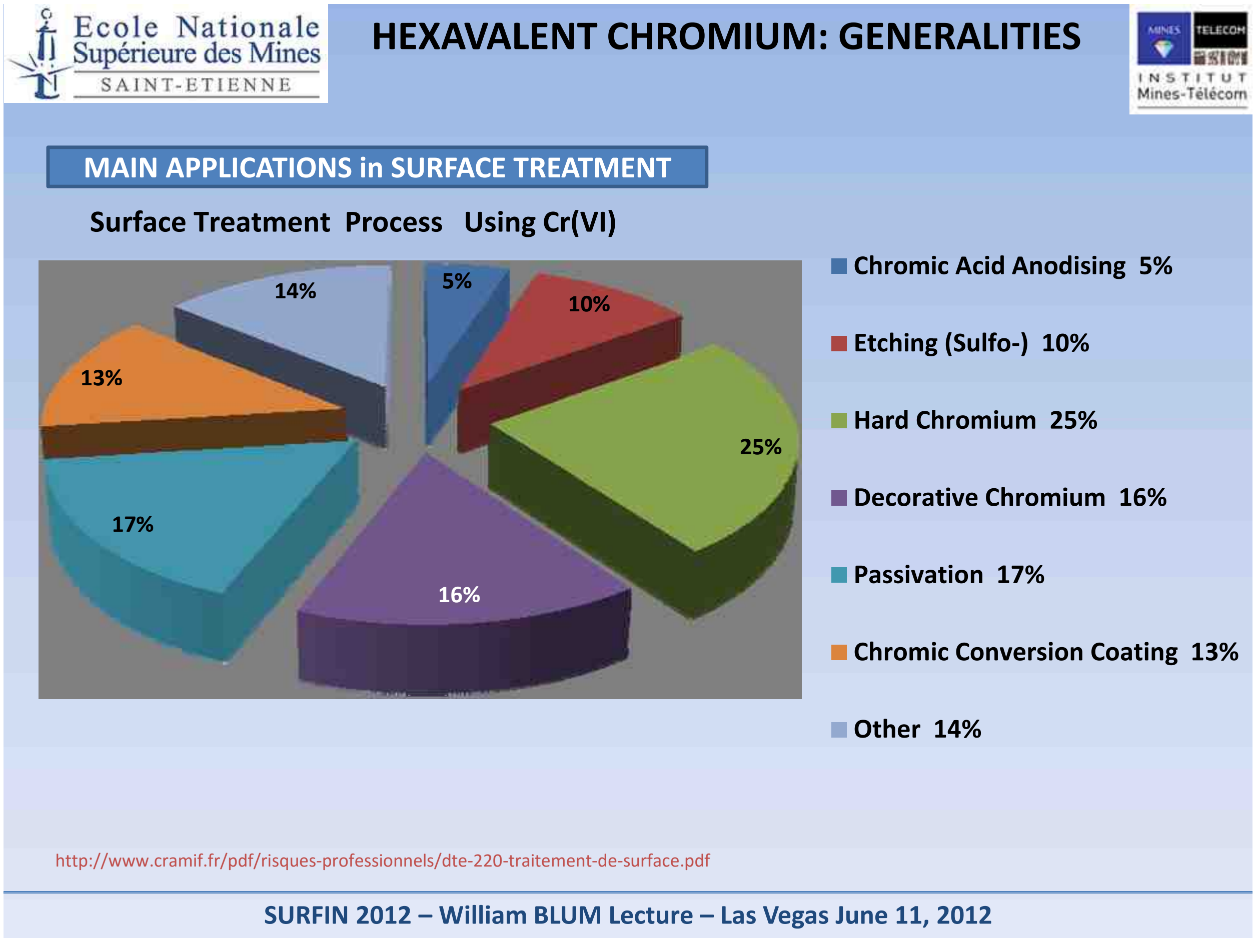
The slide below shows the relative portions of the major surface finishing processes using Cr(VI) in France. Hard chromium comprises one quarter of all Cr(VI)-based processing. Indeed, the electrolytic processes (hard and decorative plating plus chromic acid anodizing) constitute nearly half of all hexavalent chromium processing in the surface finishing industry.



HEXAVALENT CHROMIUM: GENERALITIES

MAIN APPLICATIONS in SURFACE TREATMENT

Surface Treatment Process Using Cr(VI)

■ Chromic Acid Anodising 5%

■ Etching (Sulfo-) 10%

■ Hard Chromium 25%

■ Decorative Chromium 16%

■ Passivation 17%

■ Chromic Conversion Coating 13%

■ Other 14%

http://www.cramif.fr/pdf/risques-professionnels/dte-220-traitement-de-surface.pdf

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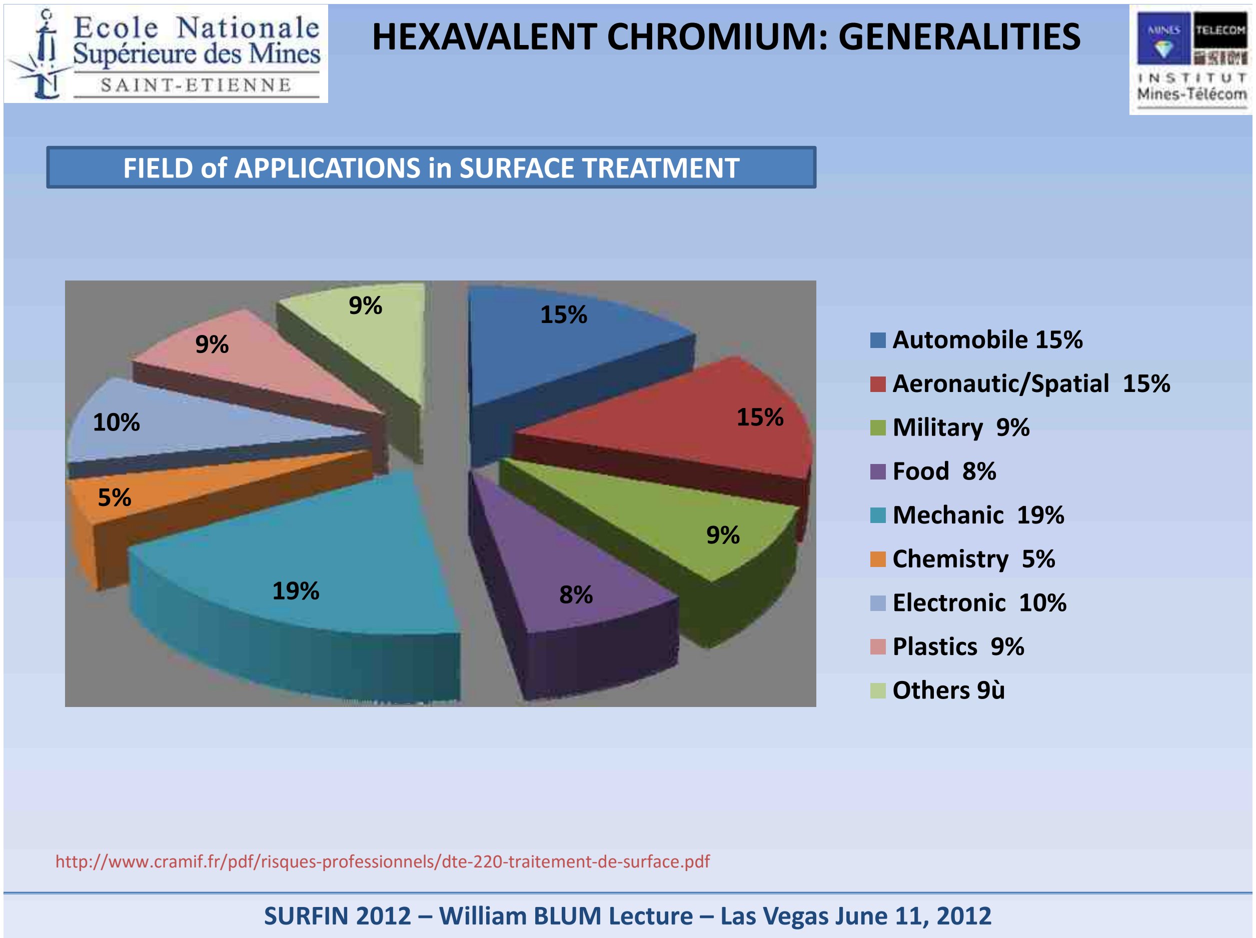
The next slide shows the various industrial sectors that use surface finishing in their operations in France. The largest usage is found in the mechanical (i.e., heavy duty machinery), aeronautics/aerospace and automotive segments. There are numerous industries dependent on surface finishing technology.



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FIELD of APPLICATIONS in SURFACE TREATMENT

- ■ Automobile 15%
- ■ Aeronautic/Spatial 15%
- ■ Military 9%
- ■ Food 8%
- ■ Mechanic 19%
- ■ Chemistry 5%
- ■ Electronic 10%
- ■ Plastics 9%
- ■ Others 9ù

http://www.cramif.fr/pdf/risques-professionnels/dte-220-traitement-de-surface.pdf

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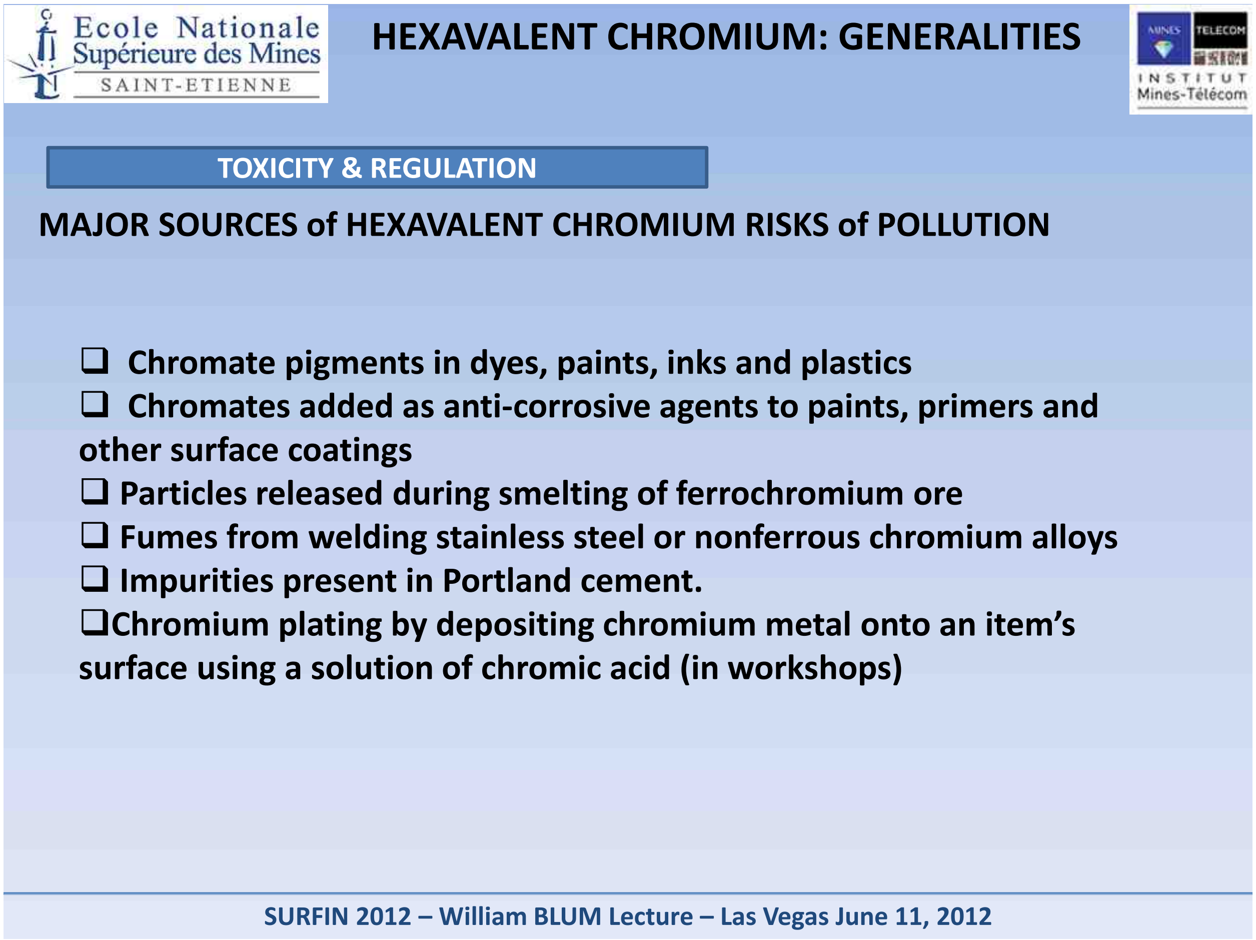
Despite the importance of hexavalent chromium chemistry in commerce, it is well established that Cr(VI) poses risks in terms of health and toxicity to humans. The pollution sources listed here go well beyond the chromium plating usage in surface finishing. There are risks involved in the metallurgical areas, including smelting and welding of chromium-bearing alloys. Hexavalent chromium in a variety of other coatings, including paints, primers, inks, dyes, etc. are also potential pollution sources.



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MAJOR SOURCES of HEXAVALENT CHROMIUM RISKS of POLLUTION

☐ Chromate pigments in dyes, paints, inks and plastics
☐ Chromates added as anti-corrosive agents to paints, primers and other surface coatings
☐ Particles released during smelting of ferrochromium ore
☐ Fumes from welding stainless steel or nonferrous chromium alloys
☐ Impurities present in Portland cement.
☐ Chromium plating by depositing chromium metal onto an item's surface using a solution of chromic acid (in workshops)

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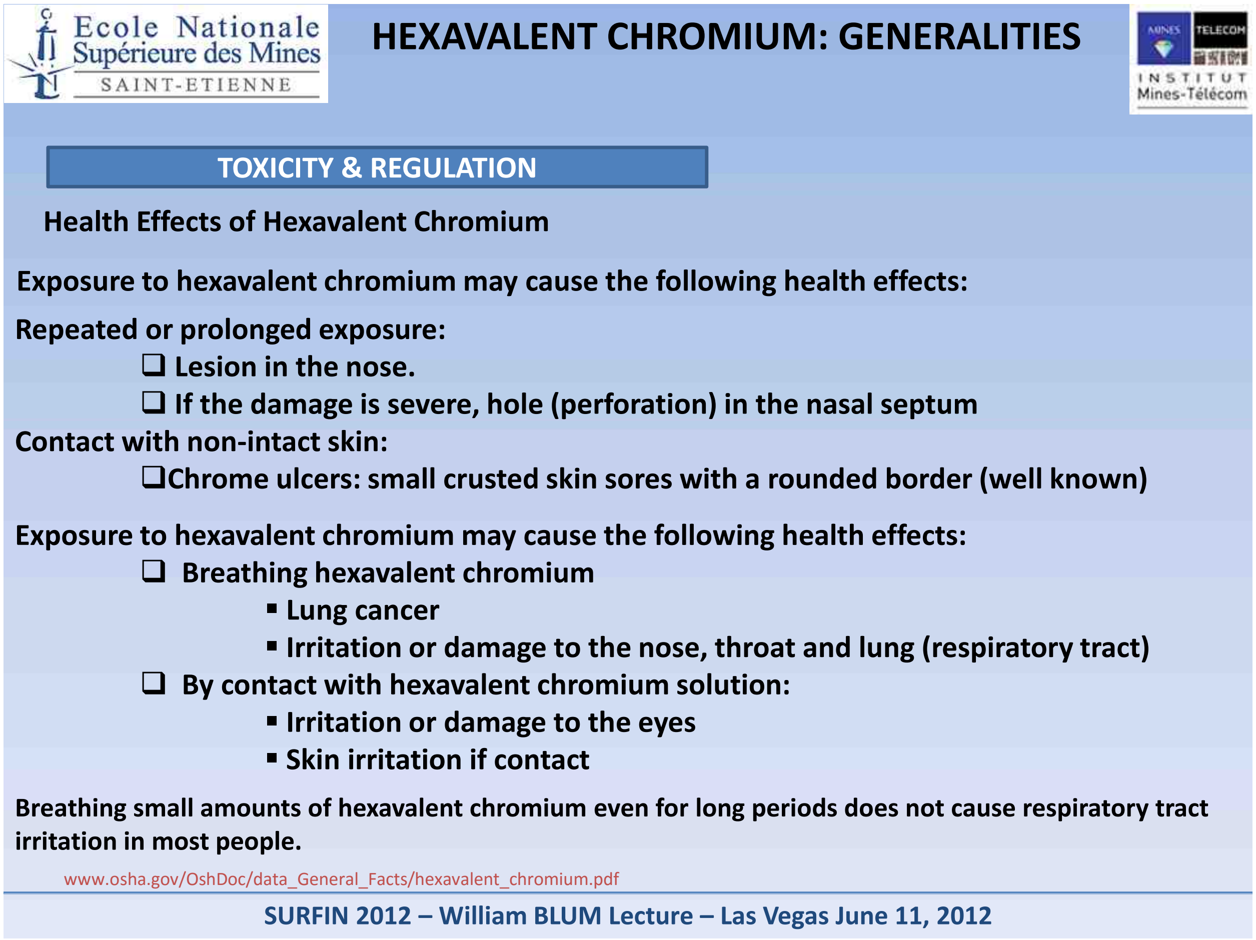
Toxicity: The health effects of exposure to hexavalent chromium, for direct contact and exposure in the air, are displayed in the slide below. Dr. Benaben stressed that for most people, “breathing small amounts of hexavalent chromium even for long periods does not cause respiratory tract infection.”



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Health Effects of Hexavalent Chromium

Exposure to hexavalent chromium may cause the following health effects:

Repeated or prolonged exposure:
- ☐ Lesion in the nose.
- ☐ If the damage is severe, hole (perforation) in the nasal septum

Contact with non-intact skin:
- ☐ Chrome ulcers: small crusted skin sores with a rounded border (well known)

Exposure to hexavalent chromium may cause the following health effects:
- ☐ Breathing hexavalent chromium
  - Lung cancer
  - Irritation or damage to the nose, throat and lung (respiratory tract)
- ☐ By contact with hexavalent chromium solution:
  - Irritation or damage to the eyes
  - Skin irritation if contact

Breathing small amounts of hexavalent chromium even for long periods does not cause respiratory tract irritation in most people.

www.osha.gov/OshDoc/data_General_Facts/hexavalent_chromium.pdf

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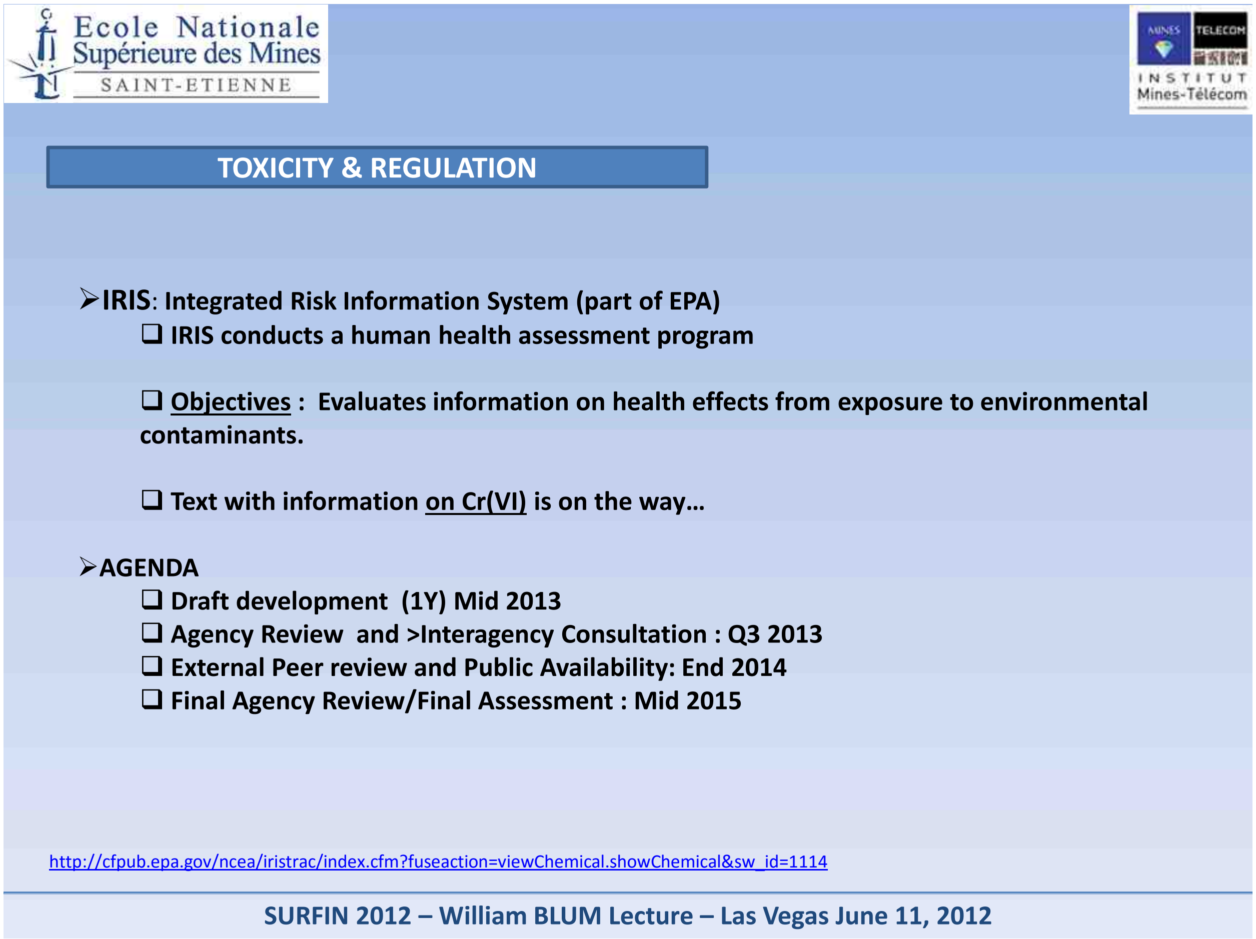
Regulation: Dr. Benaben reviewed the Integrated Risk Information System, under the auspices of the U.S. EPA, which assesses human health effects from exposure to environmental contaminants. The development of information for Cr(VI) is ongoing, with final review and assessment expected in 2015.



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➢**IRIS**: **Integrated Risk Information System (part of EPA)**

- ❑ **IRIS conducts a human health assessment program**
- ❑ **Objectives : Evaluates information on health effects from exposure to environmental contaminants.**
- ❑ **Text with information on Cr(VI) is on the way…**

➢**AGENDA**

- ❑ **Draft development (1Y) Mid 2013**
- ❑ **Agency Review and >Interagency Consultation : Q3 2013**
- ❑ **External Peer review and Public Availability: End 2014**
- ❑ **Final Agency Review/Final Assessment : Mid 2015**

http://cfpub.epa.gov/ncea/iristrac/index.cfm?fuseaction=viewChemical.showChemical&sw_id=1114

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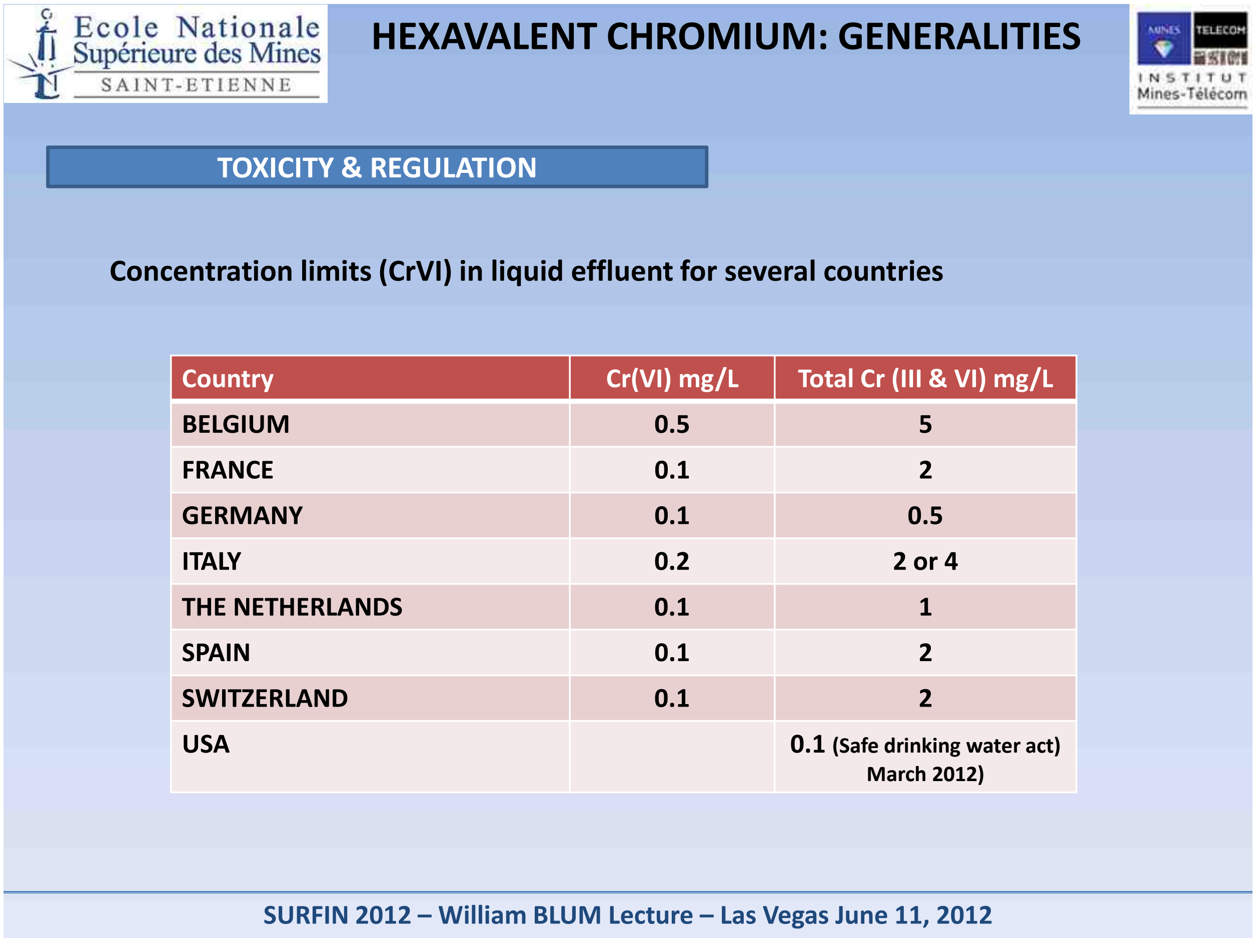
The Cr (VI) concentration limits in liquid effluents are given below in the table for several European countries and the United States.



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Concentration limits (CrVI) in liquid effluent for several countries

Country	Cr(VI) mg/L	Total Cr (III & VI) mg/L
BELGIUM	0.5	5
FRANCE	0.1	2
GERMANY	0.1	0.5
ITALY	0.2	2 or 4
THE NETHERLANDS	0.1	1
SPAIN	0.1	2
SWITZERLAND	0.1	2
USA		0.1 (Safe drinking water act) March 2012)

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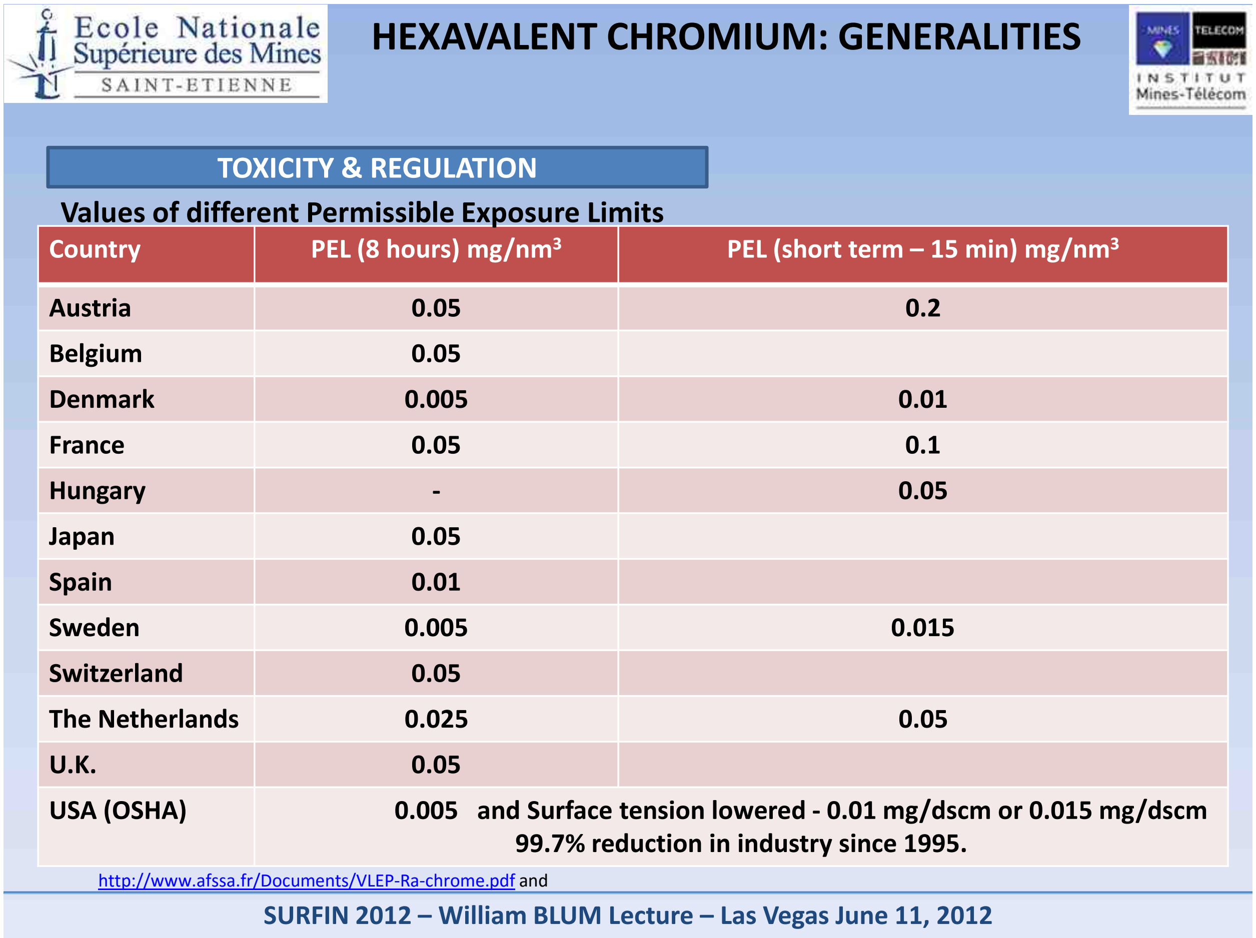
The Cr (VI) Permissible Exposure Limits in air are given in the table below for several European countries, Japan and the United States.



HEXAVALENT CHROMIUM: GENERALITIES

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Values of different Permissible Exposure Limits

Country	PEL (8 hours) mg/nm^3	PEL (short term – 15 min) mg/nm^3
Austria	0.05	0.2
Belgium	0.05	
Denmark	0.005	0.01
France	0.05	0.1
Hungary	-	0.05
Japan	0.05	
Spain	0.01	
Sweden	0.005	0.015
Switzerland	0.05	
The Netherlands	0.025	0.05
U.K.	0.05	
USA (OSHA)	0.005	and Surface tension lowered - 0.01 mg/dscm or 0.015 mg/dscm 99.7% reduction in industry since 1995.

http://www.afssa.fr/Documents/VLEP-Ra-chrome.pdf and

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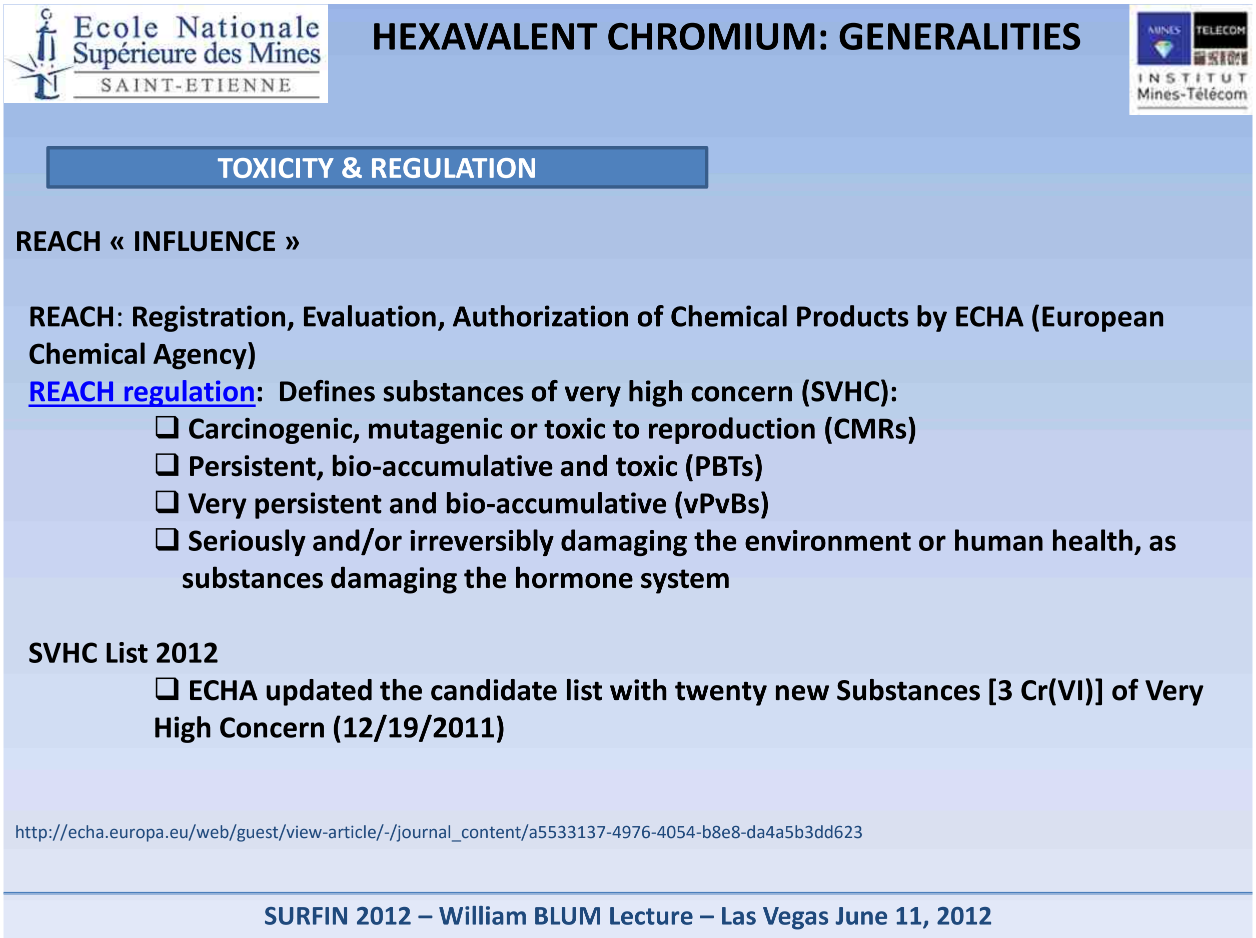
The REACH (Registration, Evaluation and Authorization of Chemical Products) regulations promulgated by the European Chemical Agency have had a profound effect on the surface finishing industry in general, and on usage of hexavalent chromium-based processes in particular. As outlined below, REACH ultimately defines Substances of Very High Concern (SVHC). In late 2011, 20 new substances were added to the SVHC list, three of which contained Cr (VI).



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REACH « INFLUENCE »

REACH: Registration, Evaluation, Authorization of Chemical Products by ECHA (European Chemical Agency)

REACH regulation: Defines substances of very high concern (SVHC):

- ❑ **Carcinogenic, mutagenic or toxic to reproduction (CMRs)**
- ❑ **Persistent, bio-accumulative and toxic (PBTs)**
- ❑ **Very persistent and bio-accumulative (vPvBs)**
- ❑ **Seriously and/or irreversibly damaging the environment or human health, as substances damaging the hormone system**

SVHC List 2012

- ❑ **ECHA updated the candidate list with twenty new Substances [3 Cr(VI)] of Very High Concern (12/19/2011)**

http://echa.europa.eu/web/guest/view-article/-/journal_content/a5533137-4976-4054-b8e8-da4a5b3dd623

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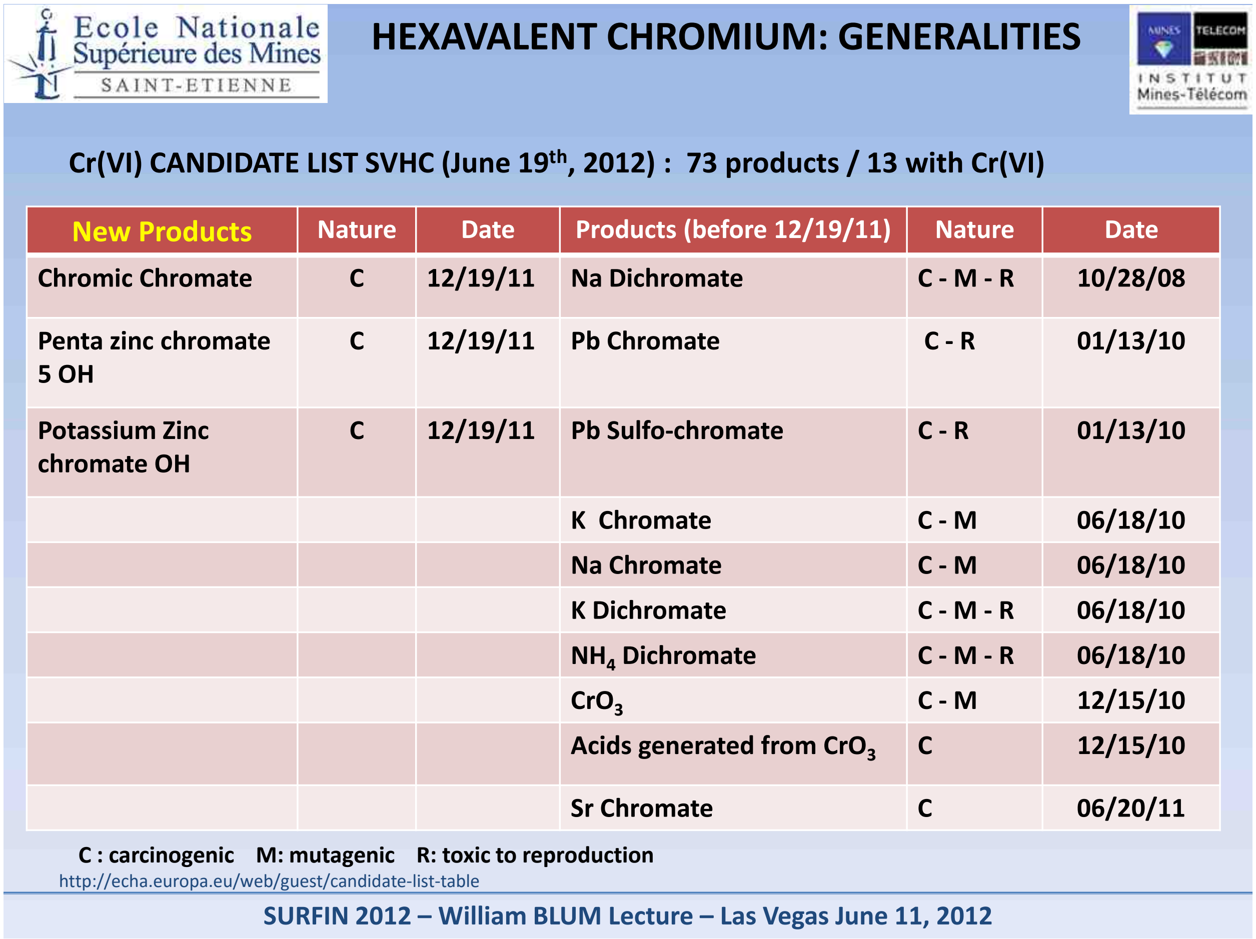
As of June 19, 2012, 73 substances were listed as Substances of Very High Concern, 13 of which contained hexavalent chromium. From a global perspective, placement on this list strongly discourages their use, and accelerates the quest for replacements.



HEXAVALENT CHROMIUM: GENERALITIES

Cr(VI) CANDIDATE LIST SVHC (June 19th, 2012) : 73 products / 13 with Cr(VI)

New Products	Nature	Date	Products (before 12/19/11)	Nature	Date
Chromic Chromate	C	12/19/11	Na Dichromate	C - M - R	10/28/08
Penta zinc chromate 5 OH	C	12/19/11	Pb Chromate	C - R	01/13/10
Potassium Zinc chromate OH	C	12/19/11	Pb Sulfo-chromate	C - R	01/13/10
			K Chromate	C - M	06/18/10
			Na Chromate	C - M	06/18/10
			K Dichromate	C - M - R	06/18/10
			NH_4 Dichromate	C - M - R	06/18/10
			CrO_3	C - M	12/15/10
			Acids generated from CrO_3	C	12/15/10
			Sr Chromate	C	06/20/11

C : carcinogenic M: mutagenic R: toxic to reproduction

http://echa.europa.eu/web/guest/candidate-list-table

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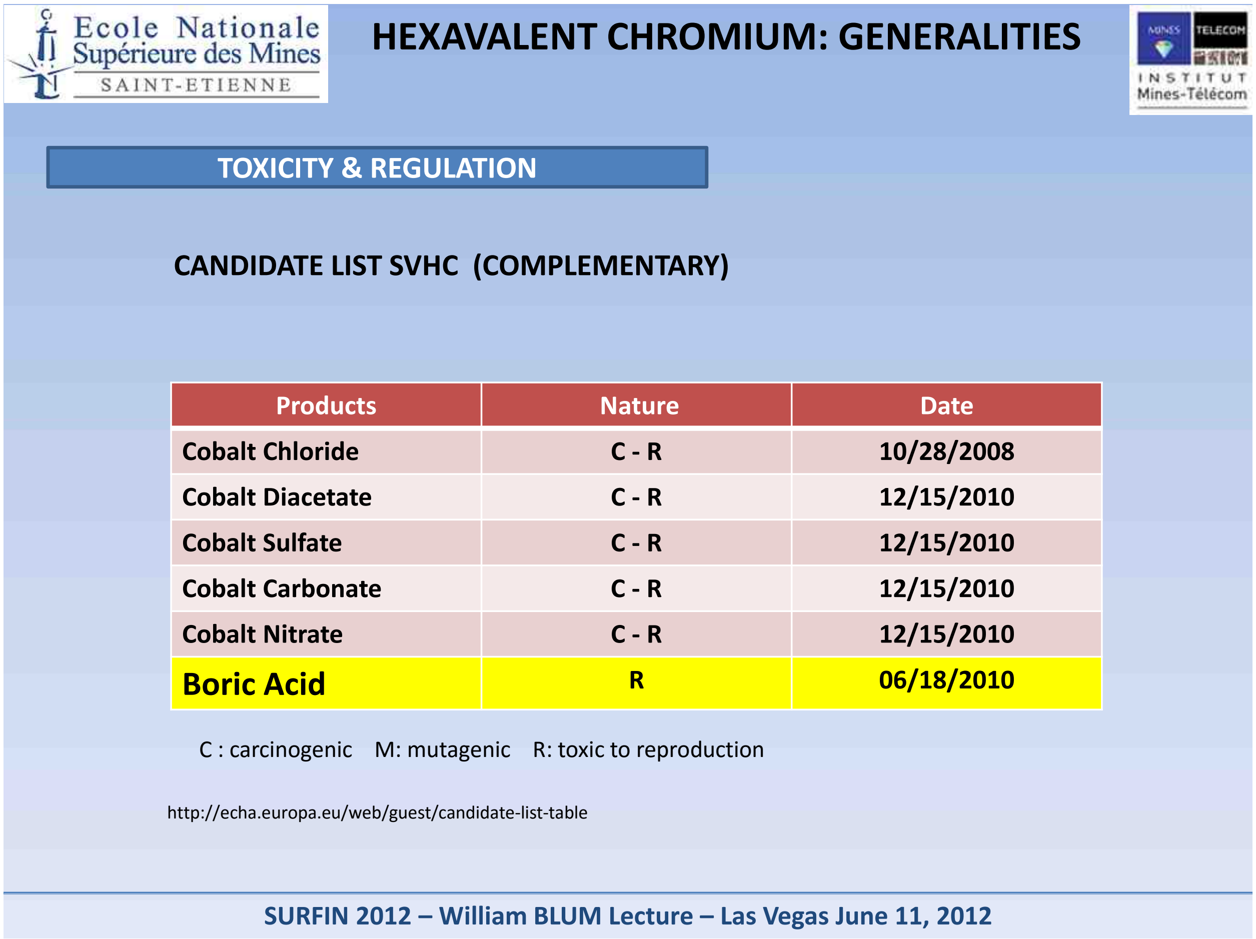
Beyond hexavalent chromium, a number of other substances involved in surface finishing technology (including electroless nickel additives) are candidates for the REACH list of SVHCs. Perhaps most profoundly, boric acid, a universally used chemical, is on the list.



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HEXAVALENT CHROMIUM: GENERALITIES

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CANDIDATE LIST SVHC (COMPLEMENTARY)

Products	Nature	Date
Cobalt Chloride	C - R	10/28/2008
Cobalt Diacetate	C - R	12/15/2010
Cobalt Sulfate	C - R	12/15/2010
Cobalt Carbonate	C - R	12/15/2010
Cobalt Nitrate	C - R	12/15/2010
Boric Acid	**R**	**06/18/2010**

C : carcinogenic   M: mutagenic   R: toxic to reproduction

http://echa.europa.eu/web/guest/candidate-list-table

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Given all of these regulatory challenges, hexavalent chromium-based surface finishing processes face an outright ban of their use. Faced with this situation, we must ask "What Else?" What else is available which provides equal or better performance in the many applications for which hexavalent chromium has been found to be very useful?

The remainder of this presentation offers an overview of a sample of some of the Cr(VI) replacement processes which have shown promise. It is neither a commercial catalogue, nor an exhaustive list. This is merely a sampling, and more detailed information is available from the metal finishing suppliers.

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What Else ?

Following presentation is not:

- ☐ **A commercial catalogue**
- ☐ **An exhaustive list of processes**
- ☐ **A modus operandi of different processes**

It is just an overview of some processes with some comments.

For more information, call your Supplier …

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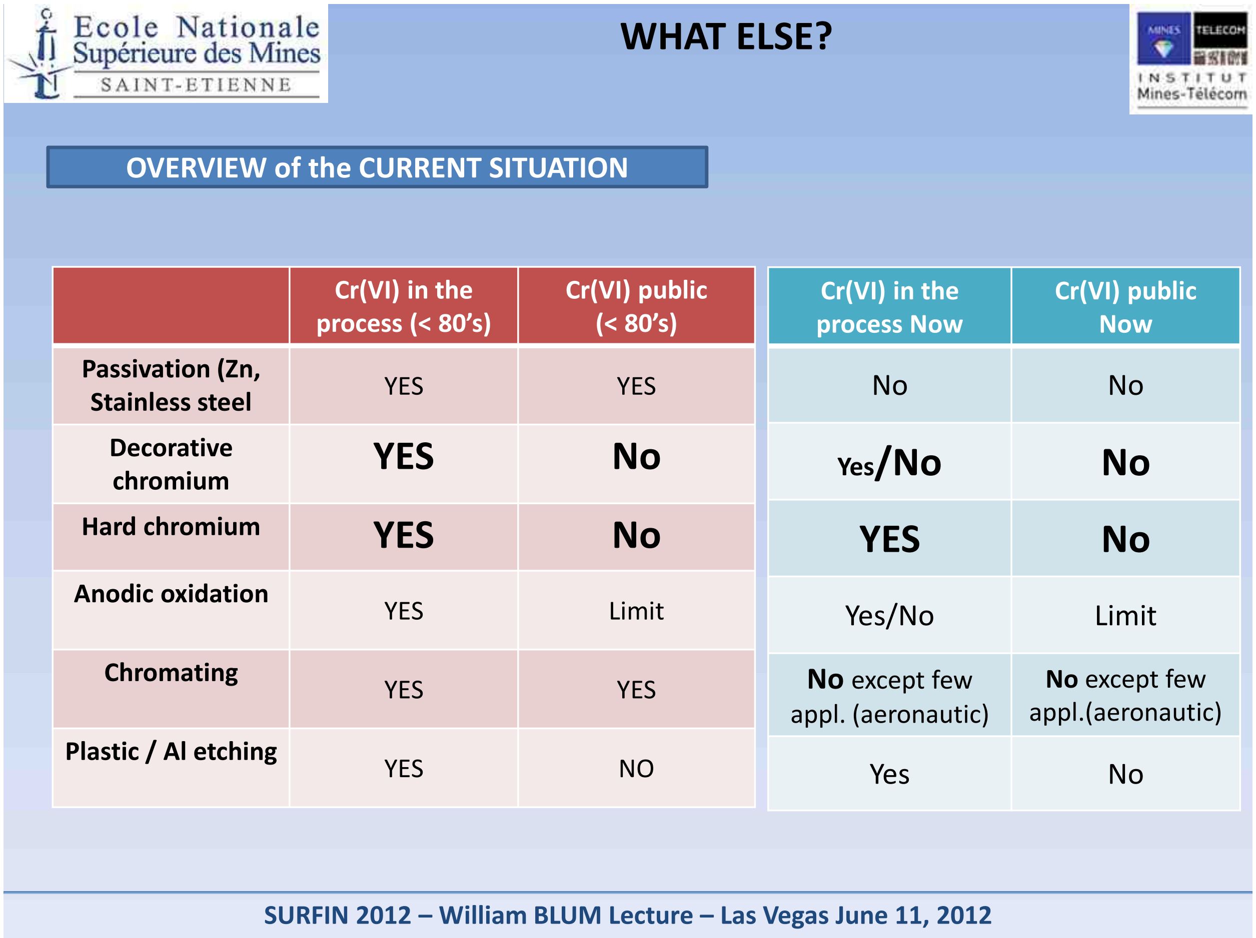
Before considering replacement processes, it is important to consider the current situation for Cr(VI) processes. After all, the drawbacks to hexavalent chromium chemistry have been known since the 1980s, and R&D efforts have already been devoted to reducing the risks posed by the use of Cr(VI). Further, the situation must be viewed in terms of (1) whether hexavalent chromium is present in the process and (2) whether the public is exposed to hexavalent chromium in the final product. An obvious example of the second perspective is with electroplated chromium, whether decorative or hard chromium. Clearly, chromium metal is deposited from a process solution containing Cr(VI). But the end result is plated chromium metal; the final form that reaches the public has no Cr(VI) chemicals present.

The table below considers six of the major Cr(VI) processes in this light. Since the 1980s, when Cr(VI) was used in all processes, it can be seen that Cr(VI) has been weaned, to a greater or lesser extent, from passivation, anodizing and chromating technology. And in most cases, the public's exposure to Cr(VI) in the final products has been virtually eliminated, with a few exceptions. Though somewhat reduced, the concerns remain in the manufacturing processes.



WHAT ELSE?

OVERVIEW of the CURRENT SITUATION

	Cr(VI) in the process (< 80's)	Cr(VI) public (< 80's)	Cr(VI) in the process Now	Cr(VI) public Now
Passivation (Zn, Stainless steel	YES	YES	No	No
Decorative chromium	**YES**	**No**	**Yes/No**	**No**
Hard chromium	**YES**	**No**	**YES**	**No**
Anodic oxidation	YES	Limit	Yes/No	Limit
Chromating	YES	YES	**No** except few appl. (aeronautic)	**No** except few appl.(aeronautic)
Plastic / Al etching	YES	NO	Yes	No

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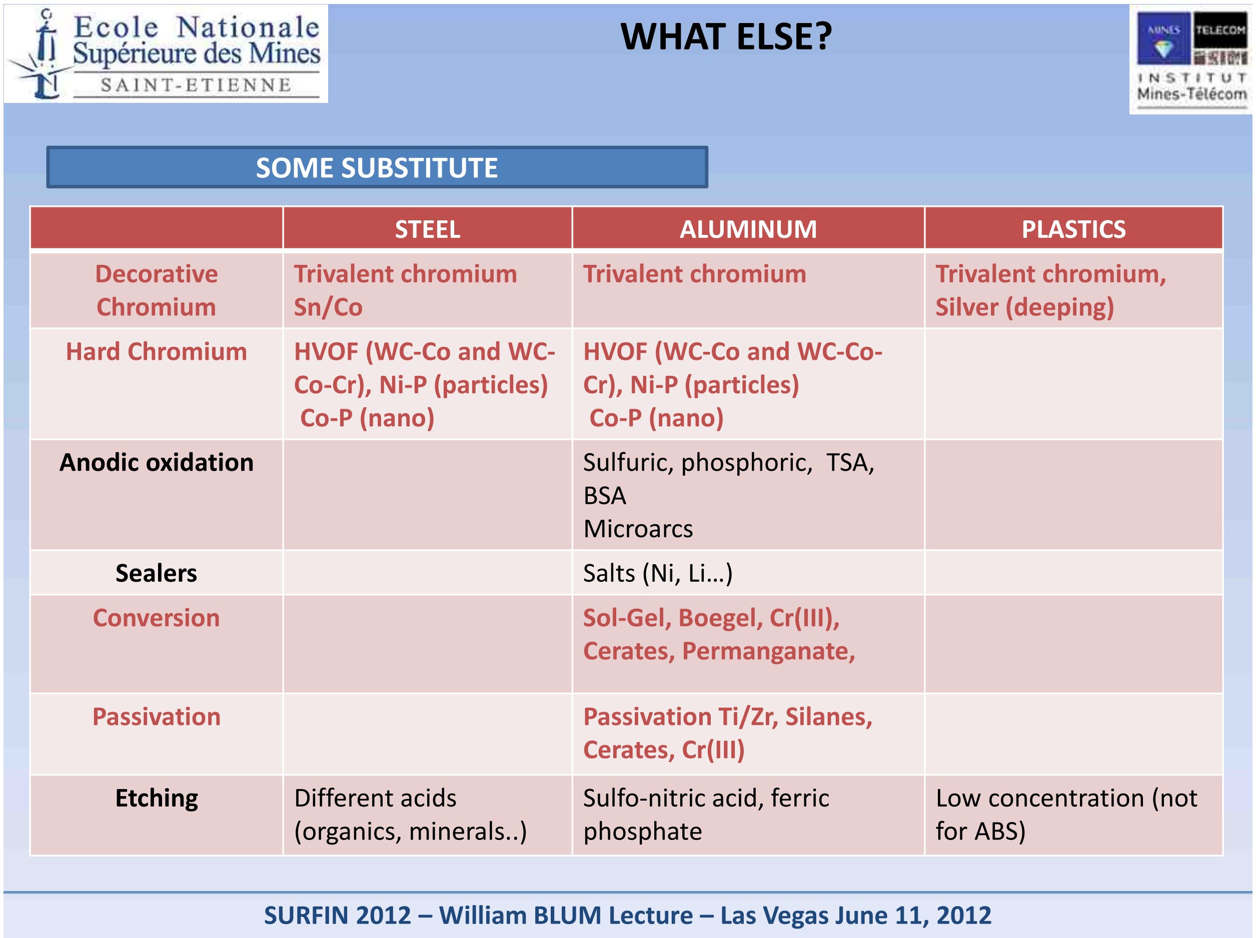
The table below shows a number of processes which have shown promise in replacing Cr(VI)-based surface finishing processes. Steel, aluminum and plastic substrates are considered. For decorative plating, trivalent chromium [Cr(III)]-based processes have shown considerable promise. For hard chromium, entirely different technologies have been developed, where the higher thicknesses of wear-resistant coatings can be obtained. Overall, it appears that many substitute candidates exist for aluminum substrates. In plated plastics, the replacement of Cr(VI) in the etchant remains problematic. For many plastics, an etch with a reduced Cr(VI) concentration is adequate. However, for the workhorse ABS resin, a full concentration Cr(VI) etch is still most effective.



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SOME SUBSTITUTE

	STEEL	ALUMINUM	PLASTICS
Decorative Chromium	Trivalent chromium Sn/Co	Trivalent chromium	Trivalent chromium, Silver (deeping)
Hard Chromium	HVOF (WC-Co and WC-Co-Cr), Ni-P (particles) Co-P (nano)	HVOF (WC-Co and WC-Co-Cr), Ni-P (particles) Co-P (nano)	
Anodic oxidation		Sulfuric, phosphoric, TSA, BSA Microarcs	
Sealers		Salts (Ni, Li…)	
Conversion		Sol-Gel, Boegel, Cr(III), Cerates, Permanganate,	
Passivation		Passivation Ti/Zr, Silanes, Cerates, Cr(III)	
Etching	Different acids (organics, minerals..)	Sulfo-nitric acid, ferric phosphate	Low concentration (not for ABS)

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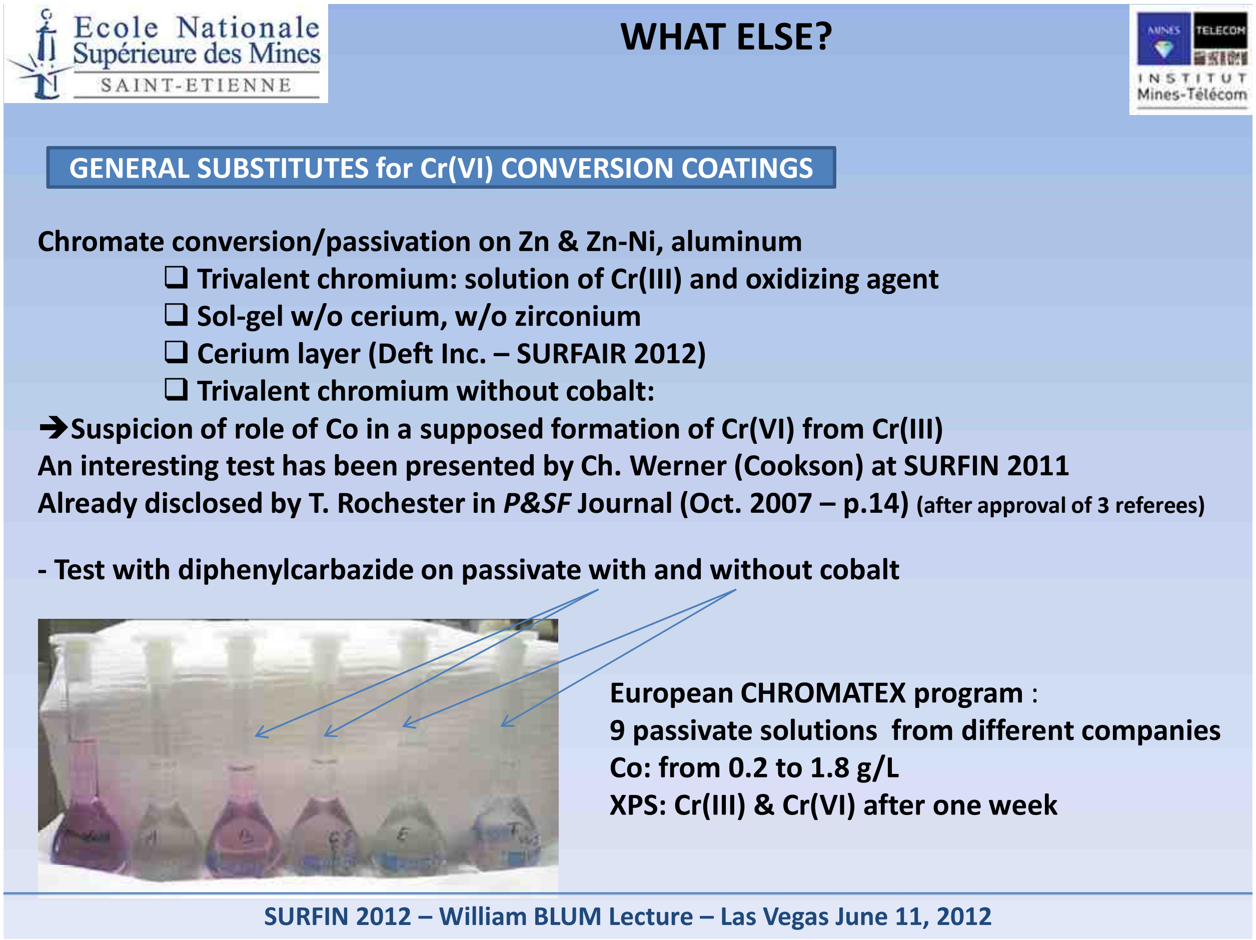
Considerable effort has been devoted to research and development in substitutes for Cr(VI) post-plate conversion coatings, particularly on zinc and zinc-nickel coatings and aluminum. Trivalent chromium-based processes have seen success. A sol-gel process has shown promise, as has a cerium layer, reported by Deft, Inc. (Irvine, CA).

One concern with the trivalent chromium passivate has arisen regarding the use of cobalt as an additive in promoting the layer formation process. There has been some evidence that the cobalt ion can play a role in oxidizing Cr(III) to Cr(VI) in the final layer. Indeed, Rochester [*P&SF*, 94 (10), 14 (2007)] observed such a reaction with a diphenylcarbazide test. This issue is particularly important in that the potential of general public exposure to Cr(VI) would be a concern.



WHAT ELSE?

GENERAL SUBSTITUTES for Cr(VI) CONVERSION COATINGS

Chromate conversion/passivation on Zn & Zn-Ni, aluminum

- ☐ **Trivalent chromium: solution of Cr(III) and oxidizing agent**
- ☐ **Sol-gel w/o cerium, w/o zirconium**
- ☐ **Cerium layer (Deft Inc. – SURFAIR 2012)**
- ☐ **Trivalent chromium without cobalt:**

➔Suspicion of role of Co in a supposed formation of Cr(VI) from Cr(III)
An interesting test has been presented by Ch. Werner (Cookson) at SURFIN 2011
Already disclosed by T. Rochester in *P&SF* Journal (Oct. 2007 – p.14) **(after approval of 3 referees)**

- Test with diphenylcarbazide on passivate with and without cobalt

European CHROMATEX program :
9 passivate solutions from different companies
Co: from 0.2 to 1.8 g/L
XPS: Cr(III) & Cr(VI) after one week

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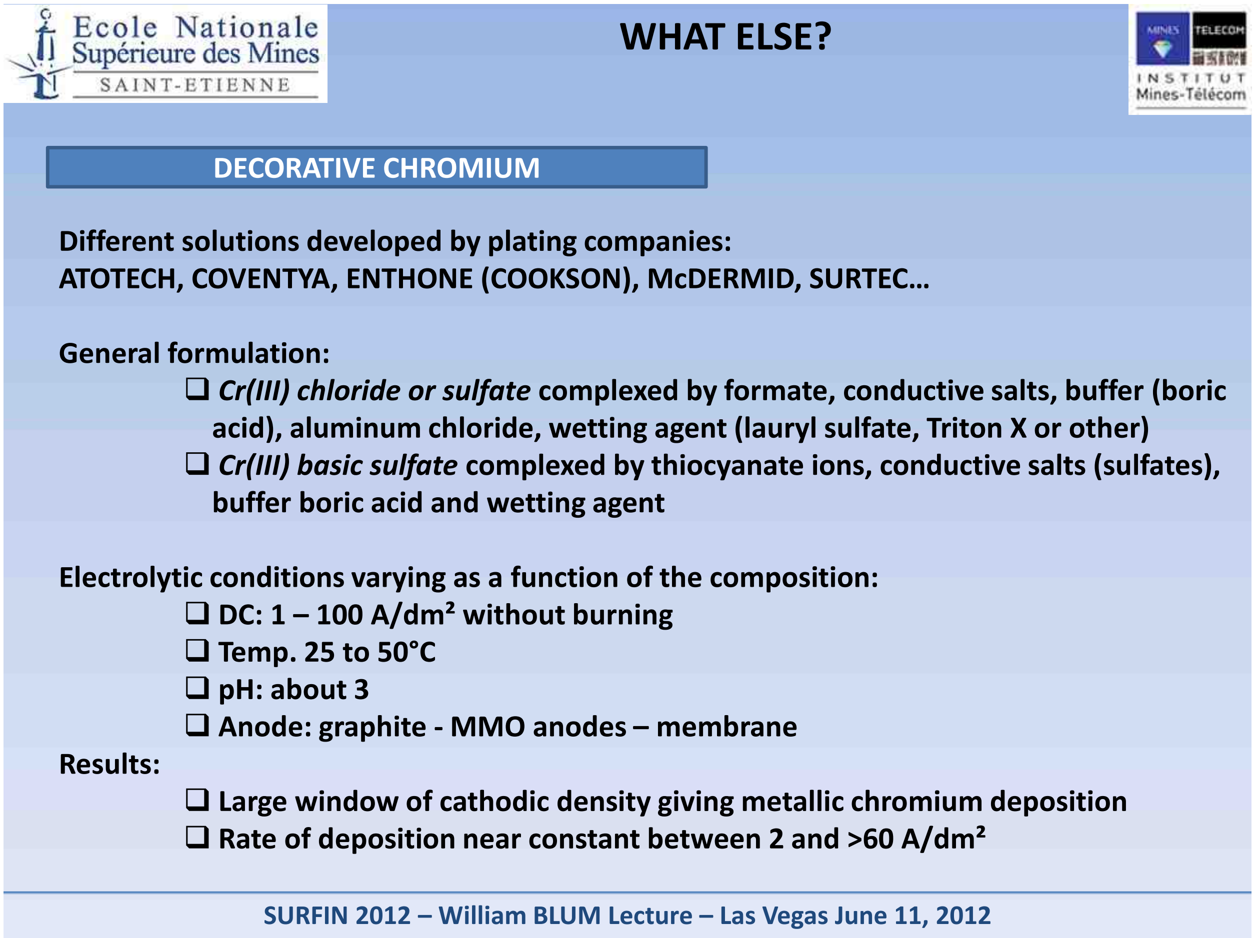
Cr(VI) replacements for decorative chromium have been developed by many of the plating suppliers. After decades of work, trivalent chromium has seen considerable success in meeting the exacting manufacturing standards for appearance and corrosion performance. Several chemistries have been developed, each having specific characteristics for a given application. Most important, the processes allow operation over a wide range of current densities.



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DECORATIVE CHROMIUM

Different solutions developed by plating companies:
ATOTECH, COVENTYA, ENTHONE (COOKSON), McDERMID, SURTEC…

General formulation:

- ***Cr(III) chloride or sulfate*** **complexed by formate, conductive salts, buffer (boric acid), aluminum chloride, wetting agent (lauryl sulfate, Triton X or other)**
- ***Cr(III) basic sulfate*** **complexed by thiocyanate ions, conductive salts (sulfates), buffer boric acid and wetting agent**

Electrolytic conditions varying as a function of the composition:

- **DC: 1 – 100 A/dm² without burning**
- **Temp. 25 to 50°C**
- **pH: about 3**
- **Anode: graphite - MMO anodes – membrane**

Results:

- **Large window of cathodic density giving metallic chromium deposition**
- **Rate of deposition near constant between 2 and >60 A/dm²**

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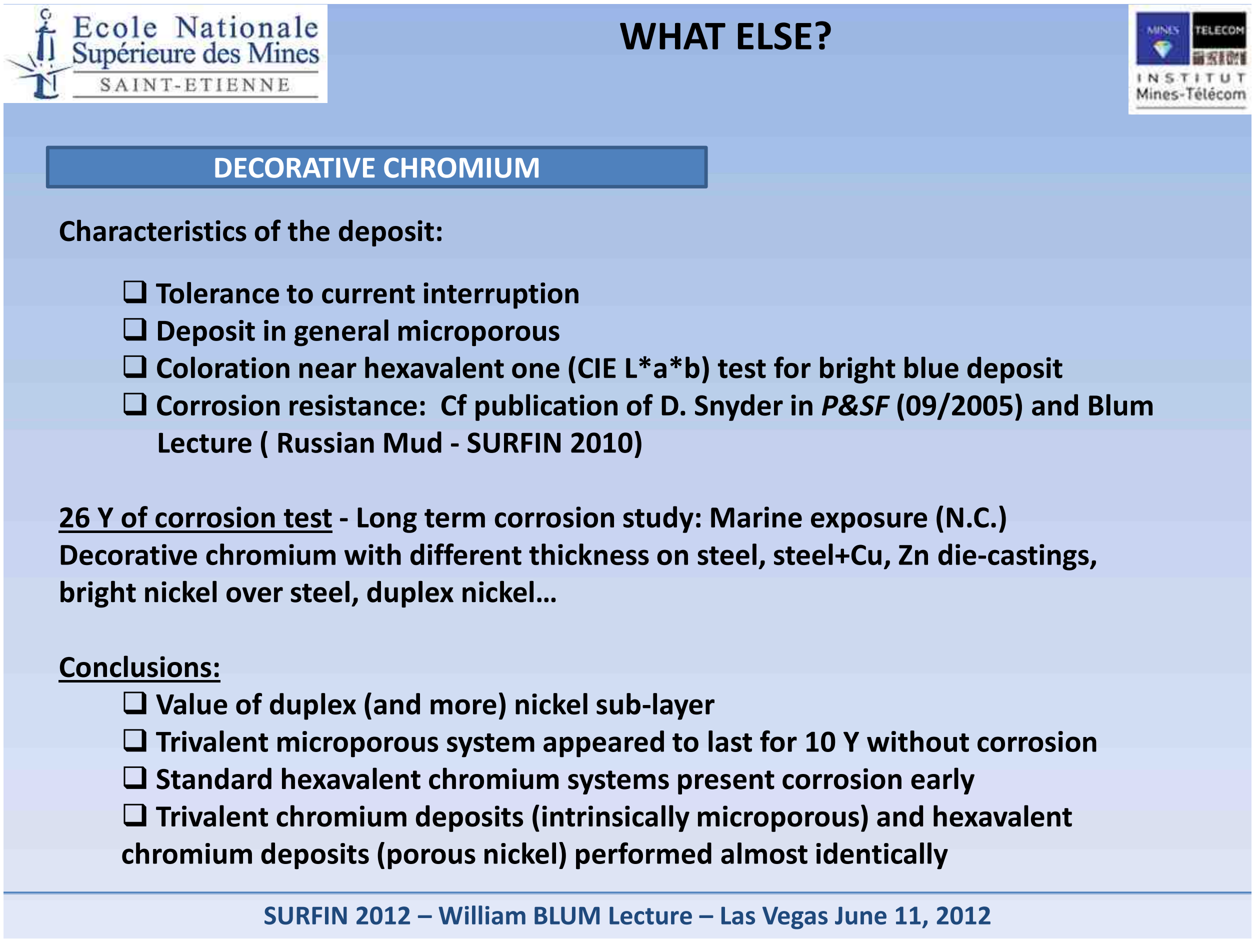
Indeed there are many advantages that trivalent chromium deposits have over their hexavalent counterparts. In operation, the depositing layer has a tolerance to current interruption, something that was lacking in Cr(VI) systems. In general, the deposit structure is microporous, a desirable situation for chromium over nickel. The deposit color produced by current Cr(III) technology approaches that for hexavalent chromium, something that has been steadily improving over the decades.

The corrosion performance has been shown to be equal or better than hexavalent-based deposits. There is a long history of trivalent chromium development , including long-term results going back 26 years. A considerable body of work, including the valuable contributions of Don Snyder, have spanned this period of time. A large variety of substrate and Cr(III) multilayer systems have been studied.

Among the important conclusions of this work, the importance of using multiple layer nickel systems (duplex or higher) under trivalent chromium was critical to performance (as it was under hexavalent chromium). In field tests, the trivalent microporous chromium showed no corrosion after ten years, while standard Cr(VI) exhibited corrosion earlier. Finally, Cr(III) layer performance was equal to that of Cr(VI) over microporous (or deliberately microcracked) nickel, a rather robust multilayer system.



WHAT ELSE?

DECORATIVE CHROMIUM

Characteristics of the deposit:

- ☐ **Tolerance to current interruption**
- ☐ **Deposit in general microporous**
- ☐ **Coloration near hexavalent one (CIE L*a*b) test for bright blue deposit**
- ☐ **Corrosion resistance: Cf publication of D. Snyder in *P&SF* (09/2005) and Blum Lecture (Russian Mud - SURFIN 2010)**

26 Y of corrosion test - Long term corrosion study: Marine exposure (N.C.) Decorative chromium with different thickness on steel, steel+Cu, Zn die-castings, bright nickel over steel, duplex nickel…

Conclusions:

- ☐ **Value of duplex (and more) nickel sub-layer**
- ☐ **Trivalent microporous system appeared to last for 10 Y without corrosion**
- ☐ **Standard hexavalent chromium systems present corrosion early**
- ☐ **Trivalent chromium deposits (intrinsically microporous) and hexavalent chromium deposits (porous nickel) performed almost identically**

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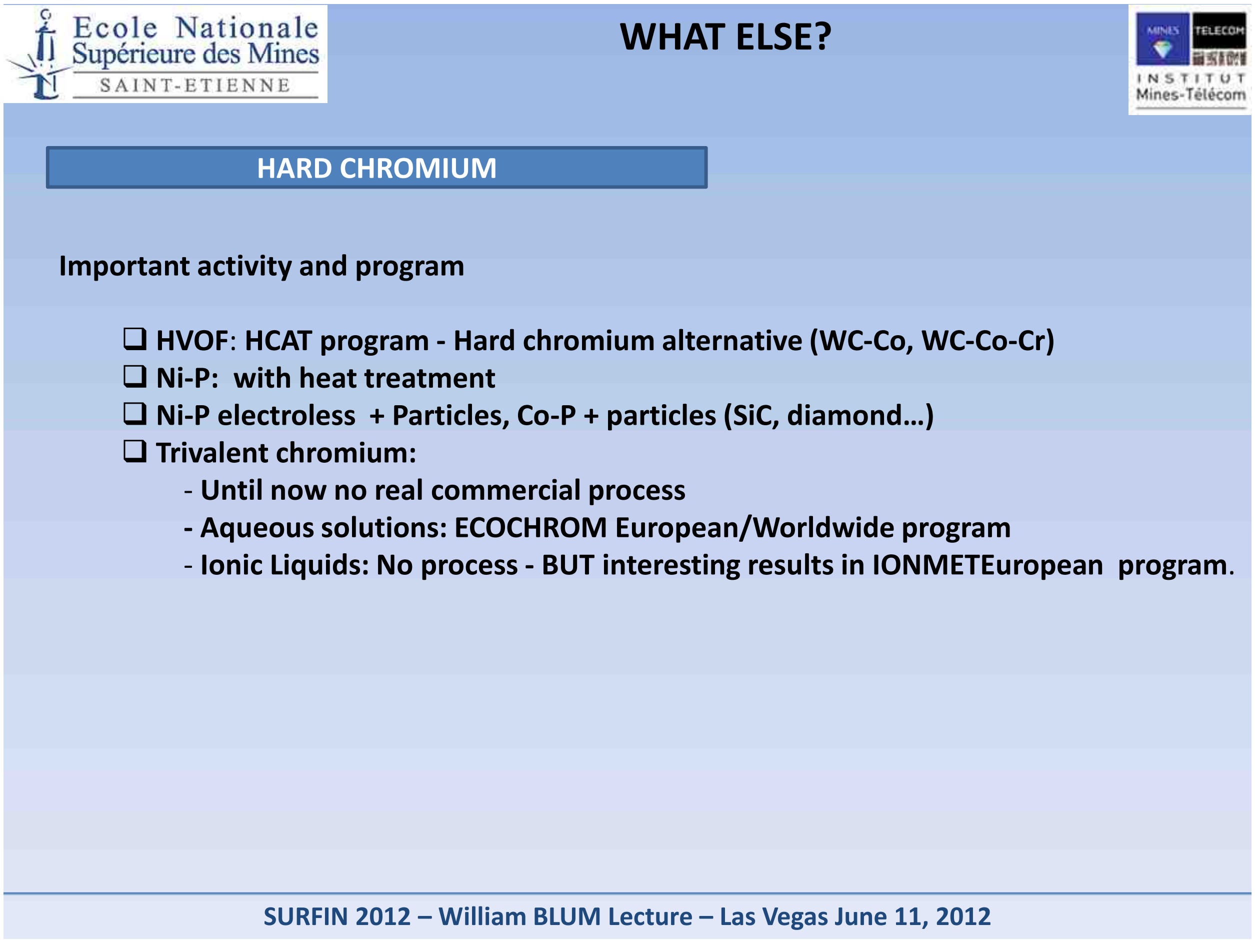
The current status of trivalent deposits for hard chromium applications is not as advanced. Applying the higher thicknesses of hard chromium applications from decorative Cr(III) chemistry is problematic, at this point. At present, there is no actual commercial process. Nonetheless, efforts to develop a viable process are underway in many quarters, from both aqueous solutions and ionic liquids. Pulse waveforms have been used by Taylor, et al. with promising results, and other programs in Europe and other venues are ongoing.

Nonetheless, several hard chromium substitutes have been developed which provide the characteristics required for hard chromium plating. These include thermal spraying, in particular the high velocity oxy-fuel (HVOF) technology with WC-Co and WC-Co-Cr materials; heat treated electroless Ni-P and electroless Ni-P and Co-P with codeposited particles, such as silicon carbide, diamonds and the like.



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WHAT ELSE?

HARD CHROMIUM

Important activity and program

- ❑ **HVOF: HCAT program - Hard chromium alternative (WC-Co, WC-Co-Cr)**
- ❑ **Ni-P: with heat treatment**
- ❑ **Ni-P electroless + Particles, Co-P + particles (SiC, diamond…)**
- ❑ **Trivalent chromium:**
  - **Until now no real commercial process**
  - **Aqueous solutions: ECOCHROM European/Worldwide program**
  - **Ionic Liquids: No process - BUT interesting results in IONMETEuropean program.**

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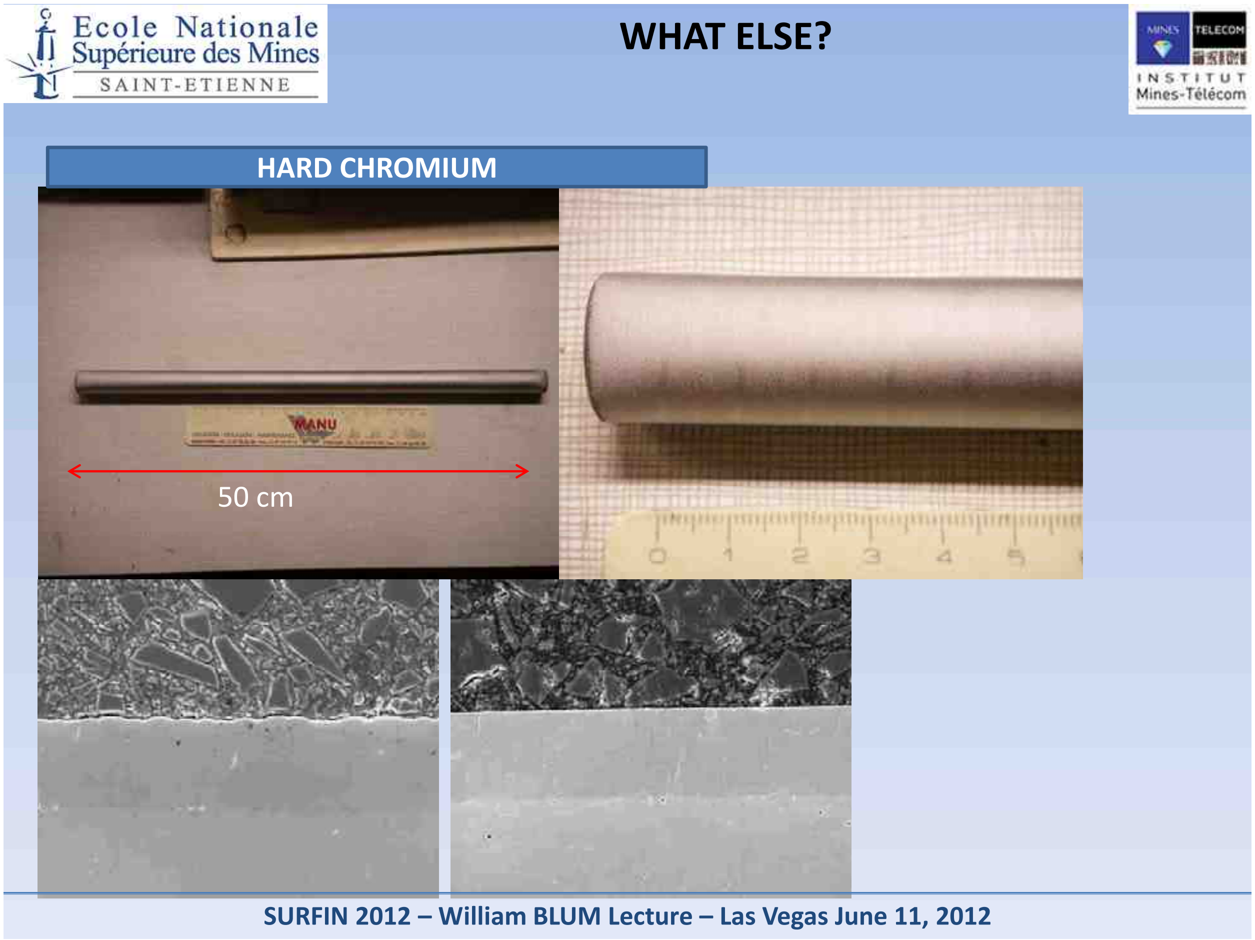
This slide shows the appearance and structure of a hard chromium deposit obtained from an aqueous trivalent chromium bath that has been developed in the ENSM-SE laboratory during the ECOCHROM - European Programme. The upper left picture represents a hard trivalent chromium deposit produced on a steel bar [length: 50 cm (20”), diameter: 2 cm (0.8”)] in a 300-L tank. The upper right photo shows the lower part of the bar, and in the lower part of the slide, the pictures give an aspect of the cross section of the chromium deposit (L) without and (R) with mechanical polishing. The thickness of the chromium deposit is about 50 -55 µm (20 µ-in.).



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HARD CHROMIUM

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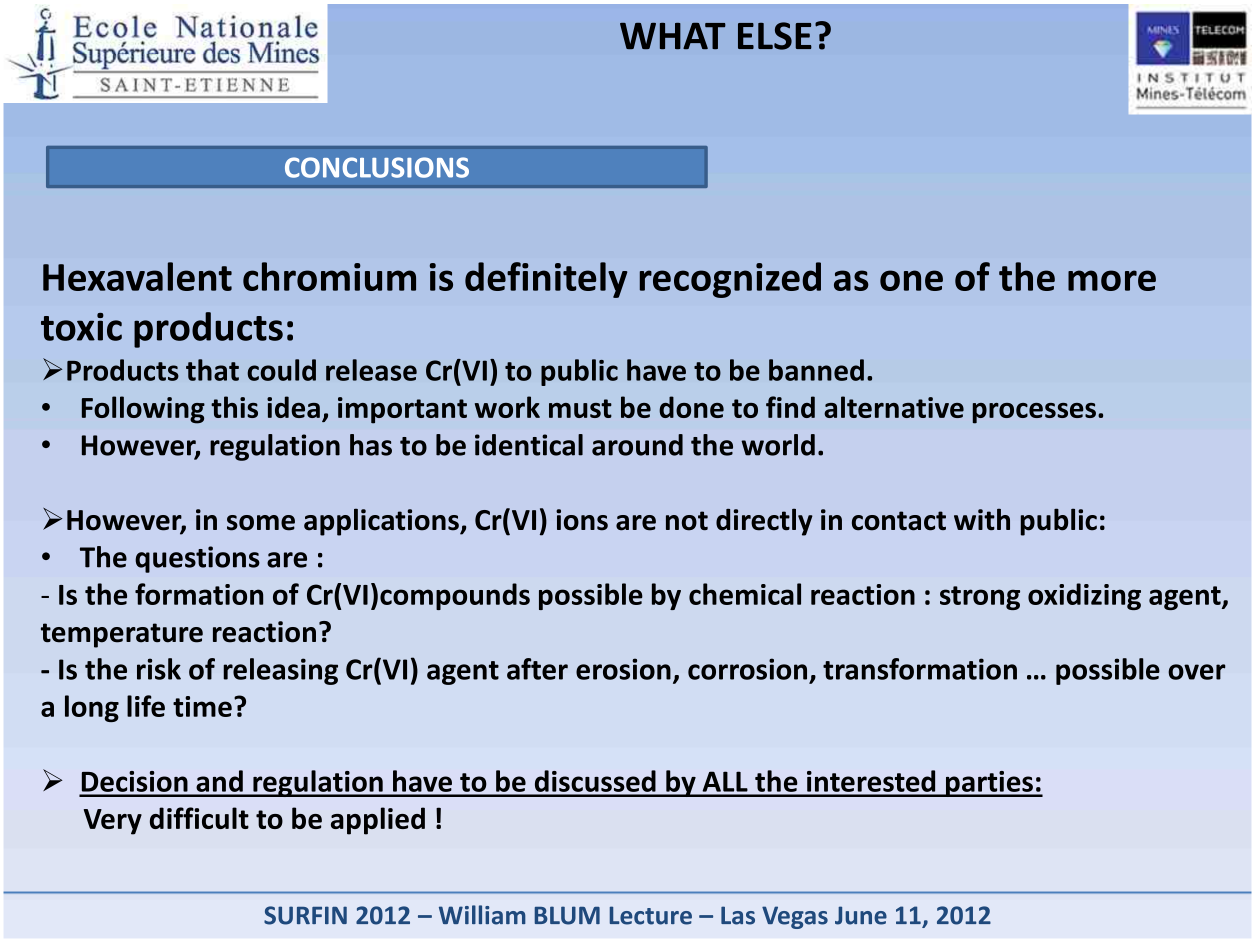
Dr. Benaben concluded his lecture by noting that Cr(VI) is clearly one of the more toxic chemistries in industry these days. He stressed that, separate from the use of Cr(VI) in manufacturing, any end products that could result in releasing Cr(VI) to the general public must be banned. With this in mind, alternative processes and technologies must be found where the public could be at risk. He also stressed the need for any regulation to be identical around the world. The alternative would be a confusing and unworkable hodgepodge of conflicting regulations from nation to nation.

He noted that using Cr(VI) processes in product manufacture do not necessarily expose the general public to the toxic chemistry. Chromium plated articles are one such example. Nonetheless, there are issues. The matter of Cr(VI) formation over time in trivalent passivates was one concern. Long term Cr(VI) release would be another.

A very important part of his message dealt with communication. The decisions on regulation in these areas must be openly discussed by all interested parties, including industry, regulators and environmental interests. But as Dr. Benaben noted, this is "very difficult to be applied." Nonetheless, the need for such open communication is paramount.



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CONCLUSIONS

Hexavalent chromium is definitely recognized as one of the more toxic products:

➢ **Products that could release Cr(VI) to public have to be banned.**
- **Following this idea, important work must be done to find alternative processes.**
- **However, regulation has to be identical around the world.**

➢ **However, in some applications, Cr(VI) ions are not directly in contact with public:**
- **The questions are :**

- Is the formation of Cr(VI)compounds possible by chemical reaction : strong oxidizing agent, temperature reaction?
- Is the risk of releasing Cr(VI) agent after erosion, corrosion, transformation … possible over a long life time?

➢ **<u>Decision and regulation have to be discussed by ALL the interested parties:</u>**
Very difficult to be applied !

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AND MANY THANKS to NASF

Dr. Patrick Benaben (center) receives the NASF Scientific Achievement Award plaque after his selection was announced at SUR/FIN 2011 in Rosemont, Illinois. With him are Executive Vice-President Christian Richter (left) and NASF President Tony Revier (right).

About Dr. Patrick Benaben:

Dr. Patrick Benaben is Full Professor at École Nationale Supérieure des Mines de St-Étienne (ENSM-SE)(France) which is a French Engineers High School (Training of Engineers and PhD). He is Research Director enabled by the French Ministry of Research and Universities. He is currently in charge of one of the Research Departments in the “Centre de Microélectronique de Provence” at ENSM-SE in Gardanne (Provence). His research is focused on new electrolytic processes, more precisely on the use of ionic liquids in hard chromium plating and on such materials as high ordered alumina obtained by anodic oxidation. He has authored or co-authored about 100 papers and is inventor or co-inventor of ten international patents. Dr. Benaben is the French representative on the European Board of the European Academy of Surface Technology (www.east-site.net) and a member of the French Surface Treatment Organization. He has organized several International Colloquia on Chromium Plating in Saint-Étienne (France) and is President of the SURMAT Colloquium. He has been a member of NASF (AESF) since 1990 and has served six years as 1st Vice-President of the AESF International Branch. He has been awarded both the Silver and Gold medals for outstanding papers published in *Plating & Surface Finishing* respectively at SUR-FIN Boston (1990) and SUR-FIN Chicago (2000). He is a member of the NASF Hard Chromium Committee. In 2011, he was selected to be the 50th recipient of the AESF/NASF William Blum Scientific Achievement Award, the association’s highest honor.