Report on inclusion of chromium trioxide (CrO_3) in Annex XIV

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Table of contents

1 Differentiation between hard chromium plating and chromating/passivation

This report refers exclusively to hard chromium plating processes, whose final product forms a metallic layer of chromium. Metallic chromium is free of the chromium (VI) species, is not carcinogenic and has been classified by the International Agency for Research on Cancer (IARC) as not classifiable in Group 3[1]. Impairments to health resulting from metallic chromium and its alloys (e.g. ferrochromium) are unknown[2]. Thus hard chromium plating does not pose any risk whatsoever for final consumers. On the contrary, hard chromium plating has been in use in the foodstuffs industry for decades. Hard chromium plating is affected by this classification in precisely the same manner as decorative chromium plating, because chromium is deposited from electrolytes containing chromium (VI), not because it poses any threat to final consumers.

By contrast chromate coatings still contain chromium(VI), which cause repassivation reactions later when the coating is damaged. Such coatings containing chromium(VI) are strictly limited, for example, in automobiles in Europe today, and are hardly used at all any more for such applications. This article does not consider all coatings containing chromium(VI), as well the article does not consider decorative chromium coatings, deposited with maximum layer thickness of 1.5 µm, and whose deposited layers are completely free of chromium(VI), in the same manner as hard chromium plating.

2 Possibilities of contact with Cr VI during production in a hard chromium plating shop

When working in a hard chromium plating shop, there are a variety of possibilities for contact with chromium (VI): a) Skin contact, b) Inhalation and c) Ingestion. Case c) will not be discussed further here, because the hazards posed by chromium (VI) compounds are known to all employees so that they are not apt to swallow such substances inadvertently.

Skin contact is possible as a matter of principle during all types of disassembly work, when working on the baths and when replenishing chromium trioxide. However, work instructions as well as personal protective equipment have been issued for all such working areas, which when observed and used are capable of preventing skin contact. In the improbable event of skin contact (accident) emergency action is required to quickly remove the chromium from the skin and reduce the chromium (VI) still present, to decrease the hazard of absorption into the body and minimize any resulting toxic or carcinogenic effects.

The primary hazard is inhalation of chromium (VI) in the production environment. If the chromium (VI) concentrations are low, the secretions in the respiratory paths reduce it to chromium (III) thus detoxifying it. However high exposure concentrations can surpass the

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[1] B. Pesch et. al.: Berufliche Chrom (VI)-Exposition und Lungenkrebsrisiko. [Occupational exposure to chromium (VI) and risk of pulmonary carcinoma]. Arbeitsmed.Sozialmed.Umweltmed. 44, 6, 2009

[2] Merkblatt zur BK Nr. 1103: Erkrankungen durch Chrom. [Data sheet for BK No. 1103: Diseases caused by chromium]. http://www.dgaum.de/index.php/recht/berufskrankheiten-verordnung/merkblaetter/158-merkblatt1103chrom?format=pdf

reduction capacity of the lungs leading to cell damage from chromium (VI), which among other this can increase the risk of cancer[3].

Operation of the baths produces gas, which bubbles to the surface of the chromium electrolyte. When the gas bubbles burst, an aerosol develops, polluting the air with chromium (VI). This aerosol is removed and washed immediately after it occurs by suction units usually located at the edge of the bath reservoir. Various quantities of aerosol are emitted depending on the design of the system; for example, a cover over the surface of the bath significantly reduces the air pollution. With an insufficient suction the chromium aerosol can be released into the air surrounding the chromium baths, and can then be inhaled by the workers in the production shop. The primary toxic effect of chromium (VI) pollution for employees in surface treatment plants is therefore from inhalation into the lungs resulting in lung cancer. For this reason only this hazard aspect is considered below.

3 Statistical data on exposure measurements in annex XV report [5]

The argumentation in the annex XV report is based to a significant extent on the data from exposure measurements at the workplace made by the German State Accident Insurance. However when considered more closely, some points make the quality of the data dubious.

First various processes for metal refining are listed individually in the tables of measured values although the differences between these processes are not clear. Purely conceptionally, some process categories are included in others, for instance, hard chromium plating, sulphuric bath in hard chromium plating, although the figures contradict this.

The quality of the data is not reproducible. For example, mean values and standard deviations are specified for exposure values, which indicate that the values are not distributed normally. In nearly all categories the standard deviation intervals extend into the negative range.

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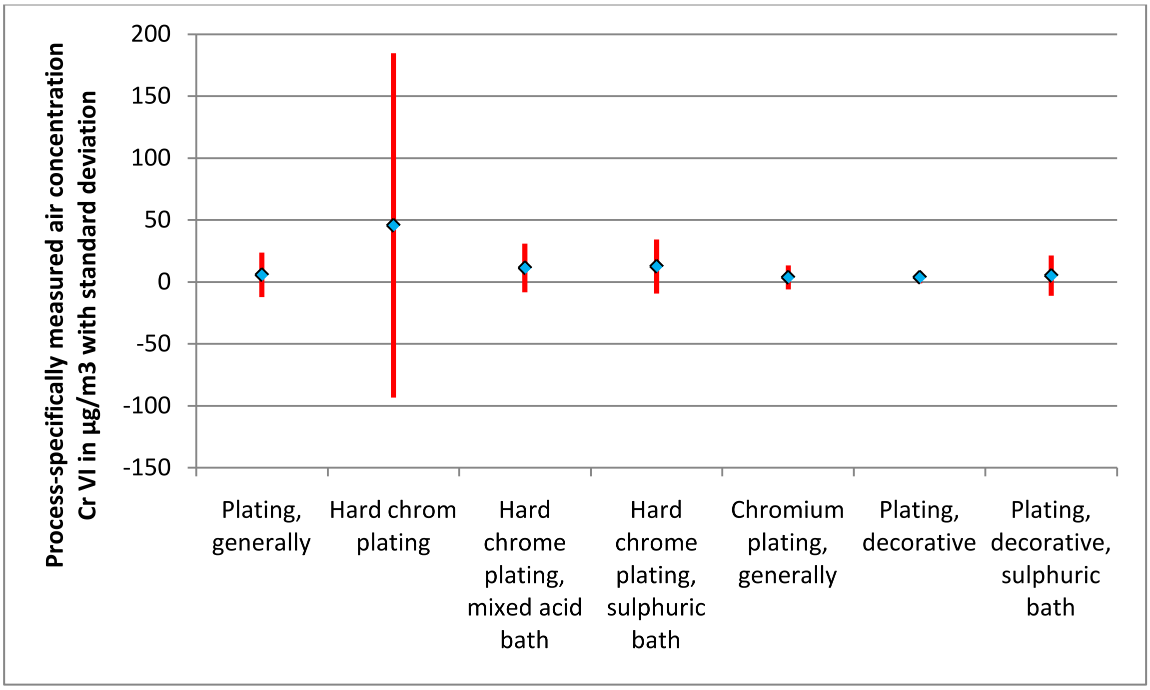
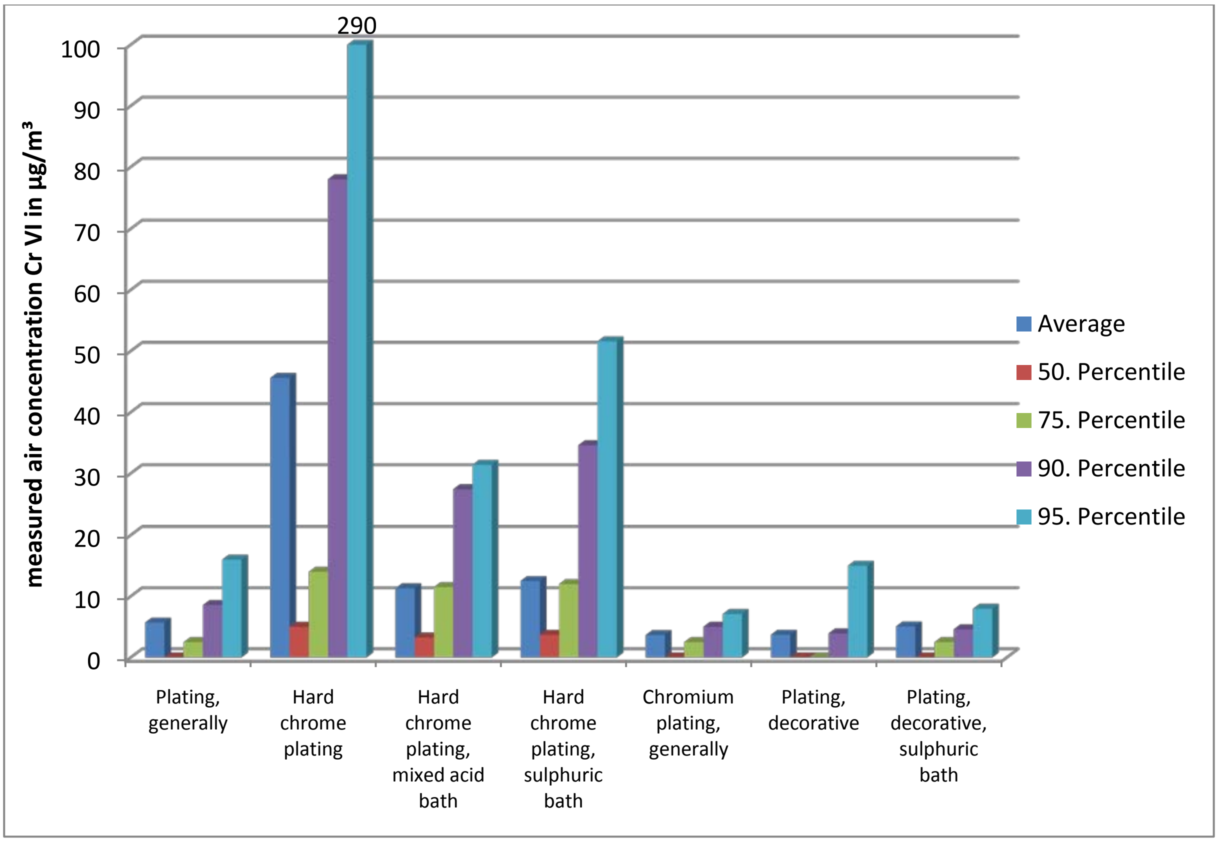
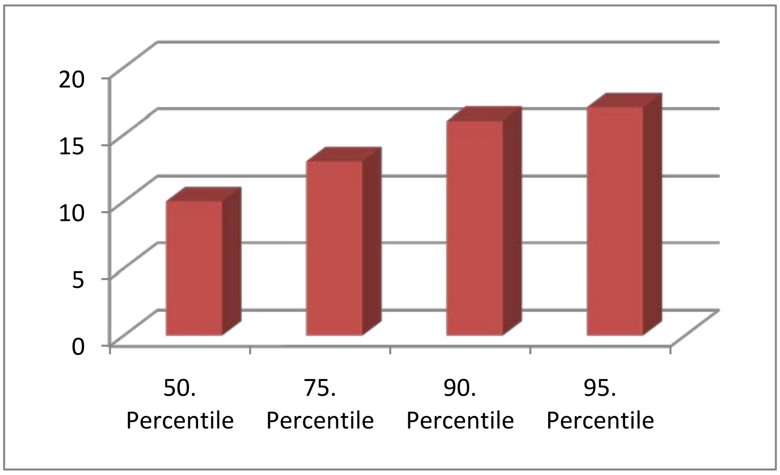
[3] Mesitschek, Fent: Chromexposition und Galvanikbetriebe. [Chromium exposure and galvanizing shops] Galvanotechnik 2010, 5, S. 1167-1180



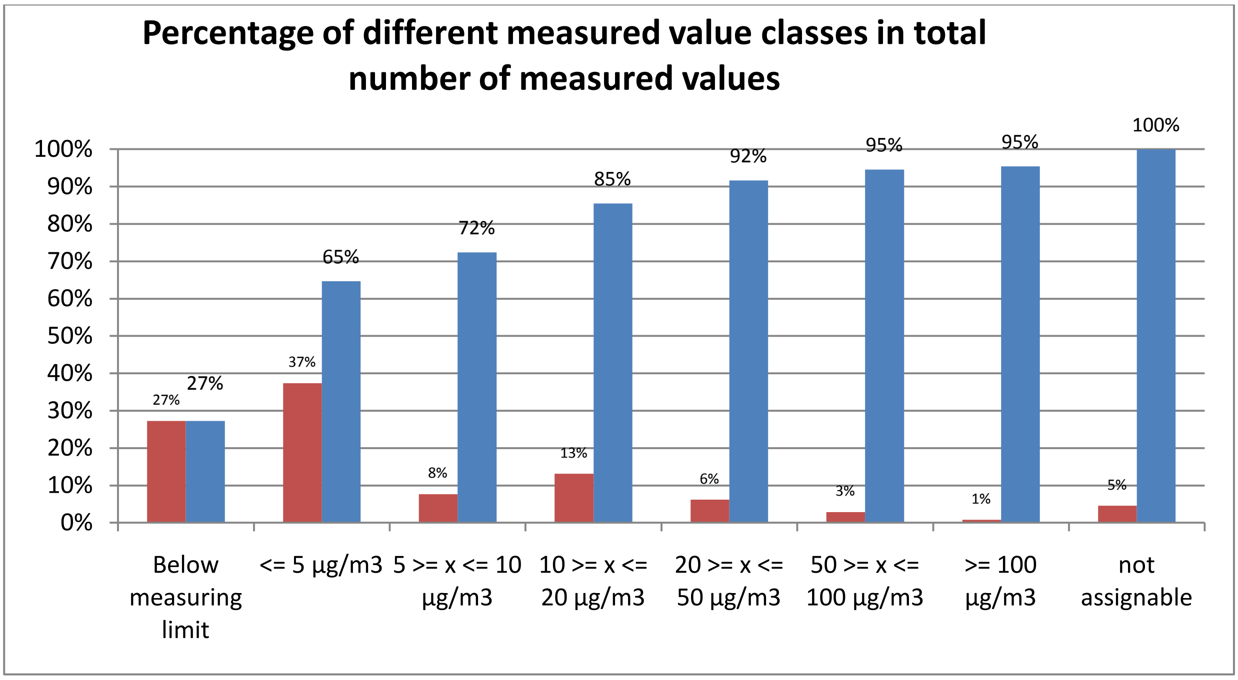
The percentiles specified also indicate that the measured values are not distributed normally. The diagram below shows the distribution of the specified percentiles for various process categories. For comparison a percentile distribution for a nearly normally distributed variable is shown below. The differences in the percentile value curves can be seen clearly. This means that normal distribution is not present with the data used, and thus it is necessary to ask what data was used here and why the distribution is so unusual. Correct interpretation of the measured values is possible only when this is known. However to conclude from this, that a very high level of chromium (VI) exposure exists, is neither permissible nor scientifically tenable.





Distribution of values in percentiles with nearly normal distribution of variables

Further evaluation shows that assumedly 65% of the measured values are below the limit of 5 µg/m³, even though precise determination is not possible from the information given. Nor is it clear, where the limit of quantification is located for the measured data in detail. In some categories various measured value limits are even consolidated in one category.



The red bars in the diagram above show the respective percentage of the measured values in relation to the overall measurement. The blue bars show the sum of the percentage up to the respective measurement interval. This means that for example the categories "below the measurement limit" and "<= 5 µg/m³" contain together already 65 % of all measurements.

All totalled, the validity of the data is very limited due to the uncertainties described and therefore cannot be used to generally describe or assess the situation in German hard chromium plating or plating shops.

4 Air concentrations of chromium (VI) and correlation with pulmonary carcinoma

The literature contains a large variety of research and studies on the hazards posed by chromium (VI) compounds. All these studies confirm the toxicity and carcinogenic properties of chromium (VI), however the risk posed by concrete exposure levels has not been quantified reliably to date. Various organisations such as the US Environmental Protection Agency, EPA, or the Scientific Committee on Occupational Exposure Limit Values [4] as well as others have come to highly differing assessments in various studies. The annex XV report on chromium trioxide[5] lists a variety of such values. An overview is given in the graph below, which specifies an increase in the risk of lung cancer between 1:100 and 1:10,000 for an air concentration of 1 µg/m³.

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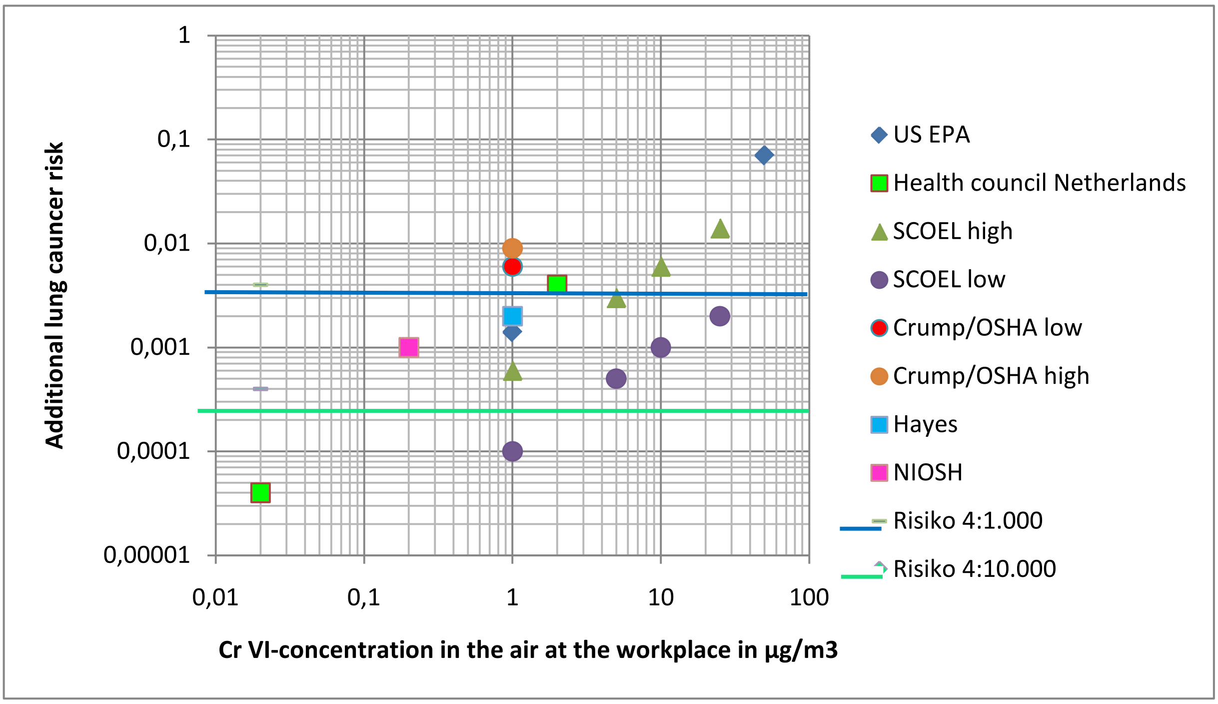
[4] The Scientific Committee on Occupational Exposure Limit Values (SCOEL) was set up by a Commission Decision (95/320/EC) with the mandate to advise the European Commission on occupational exposure limits for chemicals in the workplace.

[5] Annex XV report: PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1 OR 2, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN on Chromium trioxide, EC Number 215-607-8, Version August 2010



As a matter of principle, exposure to chromium (VI) requires differentiation between a momentary exposure value, for example in the air, and an exposure dose. The exposure value can change depending on the workplace or other factors and, as a rule, has an average value for an employee per shift or per work week. An exposure dose is a certain exposure value multiplied by the time this value is effective. Here, occupational medicine usually speaks of X µg/m³ x years. A dose of 1000 µg/m³ x years would therefore be reached after 20 years at an air concentration of 50 µg/m³.

Practically all epidemiological studies are based on measured exposure values and death rates of employees at two chromate production plants (not hard chromium planting plants) in the USA. These employee groups are referred to in the literature as the Painesville cohort and Baltimore cohort[1]. A very large number of chromium (VI) air measurements are present particularly for the Baltimore cohort and studies were performed regarding the cause of death of 2357 workers, who worked in the Baltimore chromate plant between 1950 and 1974. The data was collected the end of 1992. Comparison of the lung cancer mortality in this group of workers with that in the average population shows an increased risk of 1.80. The risk of a worker dying of lung cancer is 80% higher than in the normal population. However, in nearly all of these cases of lung cancer the subjects also smoked, because the percentage of smokers was also over 80% higher in this group. Moreover, the number of cases is too small, so that the statistical certainty for the magnitude of the additional risk is unclear. Moreover, only very high chromium (VI) exposure values were measured. Today the literature discusses limits for chromium (VI) concentrations in the air of less than 5 µg/m³; however the workers in the Baltimore cohort were subject to exposure values corresponding to a working time of 200 years at a limit of 5 µg/m³. It is not completely clear to what extent these high exposure values and the associated cancer risk can be scaled down to the low exposure values relevant today[6]. In the BGFA Information Bulletin dated 2008 Pesch noted: In consideration of the number of cases, the absence or insufficient information regarding smoking habits and the simultaneous co-exposure factors, the statistical uncertainty is substantial [6]. Particularly in cases of simultaneous exposure to cigarette smoke and chromium (VI) various studies come to the conclusion that the risk of lung cancer is increased in comparison to contact with chromium (VI) only (quoted from[1]).

A limit for chromium (VI) at workplaces does not exist currently in Germany. The old limit of 50 µg/m³, which was the result of previous technical capabilities, was abolished in 2006. Today only health-based limits are to be used; however such a limit has not been defined for chromium (VI) to date.

The US Occupational Safety and Health Administration (OSHA) defined a limit for chromium (VI) of 5 µg/m³ in 2006. An overview of other analyses is given in the table below, which specifies the air concentration limits for a lung cancer risk of 4 to 1,000 or 4 to 10,000 respectively. Practically all assessments are based on the data from the Baltimore and Painesville cohorts. However, the highly differing conclusions are possible depending on the assumptions made for the various marginal conditions and the statistical model used.

	Risk	Chromium concentrations in air in µg/m³ according to			
		US EPA	Health council Netherlands	SCOEL high	SCOEL low
Tolerable risk	4 : 1.000	2,86	2,00	6,83	50,15
Acceptable risk	4 : 10.000	0,29	0,20	0,35	3,82

However, it is necessary to note here that the chromium (VI) measurements commonly performed by the employer's liability insurance organizations in Germany today have a measuring limit of 5 µg/m³. Currently companies do not even know precisely what the maximum values are in their plants; they only know that they are below this measuring limit.

Various researchers have considered the question of the lifetime dose of chromium (VI) which would double the risk of lung cancer. Among others there are estimates of 300 µg/m³ x years to 1000 µg/m³ x years (quoted from[1]). At a chromium (VI) concentration of 5 µg/m³ at the workplace this corresponds to a working period of 60 and 200 years respectively. A realistic lifetime dose in a hard chromium plating plant today is between 50 and 250 µg/m³ x years, whereby a working time of 50 years and an air concentration of 1 or 5 µg/m³ were assumed. This again shows the major difference to the historical dose values of 1000 µg/m³ x years in the American studies.

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[6] Pesch et.al.: Chrom und seine Verbindungen am Arbeitsplatz. [Chromium and its compounds at the workplace] BGFA-Info 03/08

5 Occupational diseases

The annex XV report quotes the article by Pesch et.al.[6] published in 2008[7]. According to this a total of 222 chromium-related cases of occupational illnesses occurred between 1984 and 2006, of which 90% of the cases involved lung cancer. However this does not differentiate whether the cases of lung cancer resulted from the plating plant or from other hazardous industrial areas. A new evaluation[8] of the data from the German State Accident Insurance shows the following situation for the last 10 years:

Occupational disease documentation (BK-DOC) - Suspicion of occupational disease confirmed by the industry and civil service from 2001 to 2010: Occupational diseases caused by chromium and its compounds

				1103 Chromium
Lung cancer	No	Galvanizing plants	No	43
			Yes	33
	Yes	Galvanizing plants	No	103
			Yes	14
Together				193

DGUV Report Occupational disease statistics/ZIGUV D-53757 Sankt Augustin; compiled on 11th August 2011

Of the 193 confirmed cases of occupational disease in the period, only 14 cases or 7.25% were caused by the effects of chromium in the plating plant.

According to the estimate made by the author in the annex XV report, approximately 440,000 employees work in the surface treatment industry in Europe. Of these approximately one-tenth work with chromium (VI); amounting to approx. 44,000 employees in the EU. In Germany, the metal refining industry employees approximately 45,000 people[7]. Assuming that in Germany approx. one-tenth also work with chromium (VI), this means 4,500 employees for Germany. Above we have shown, that the cases of lung cancer involving workers working with chromium in plating plants averaged 1.4 cases per year during the last 10 years. For the 4,500 employees working with chromium (VI) this means the risk of contracting lung cancer is 0.00031 or 3.1 out of 10,000. By comparison the risk for the entire German population, of dying of lung cancer was 5.2 out of 10,000 in 2009[9].

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[7] Annex XV report[5] , P. 15

[8] Evaluation of cases of occupational disease in BK No. 1103 Chrom, Dr. M. Butz, 2011

[9] Statistisches Bundesamt Detuschland, Todesursachen in Deutschland, Fachserie 12 Reihe 4, http://www.destatis.de/jetspeed/portal/cms/Sites/destatis/Internet/DE/Content/Publikationen/Fachveroeffentlichungen/Gesundheit/Todesursachen/Todesursachen,templateId=renderPrint.psml, Zugriff 11.08.2011, 19.08 Uhr

6 Alternative processes

6.1 General characteristics of functional hard chromium plating

Functional hard chromium plating is distinguished by the following characteristics:[10]

- Layer thicknesses of 3 – 5000 µm [10]
- High hardness up to 1200 HV [11]
- High resistance to wear [10]
- Low friction and tribologically advantageous [10]
- Anti-adhesive [10]
- Machinable [10]
- Resistant to chemicals [10]
- Resistant to temperature [10]
- Recyclable and toxicologically harmless [10]

6.2 Overview of alternative processes specified in Annex XV

The literature mentions a large number of systems which could serve as possible substitute processes. Among these processes, however, only very few are feasible as a substitute. [12],[13],[14] Due to the complex interaction of coating characteristics, these cover only a small portion of the hard chromium plating spectrum - even when the total of all alternatives is considered.

The processes are listed below, which have the greatest potential as alternatives to hard chromium plating according to Annex XV

1. Thermal spraying with HVOF (**H**igh **V**elocity **O**xygen **F**uel)
2. Ni and Ni alloy coatings, as well as Ni coating systems
3. Co and Co alloy coatings

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[10] ZVO. ZVO position paper on the subject of decorative high gloss chrome plating and functional chrome coatings in the German galvanizing industry. 2003. http://www.zvo.org/fileadmin/zvo/download/ChromVITeil1eF.pdf (23.08.2011)

[11] Lausmann, A.; Unruh, J. N.: Die galvanische Verchromung.[Galvanic chrome plating]. Saulgau: Leuze Verlag, 2006

[12] Bielawski, M.: Alternative technologies and coatings for electroplated cadmium and hard chromium. Can. Aeronaut . Space J., Vol. 56, 2010, No. 3, pp. 67-80,

[13] Legg, K.: Clean Metal Finishing Alternatives. SERDP/ESTCP Metal Finishing Workshop. May 22, 23, 2006 http://www.asetsdefense.org/documents/Workshops/MFW-5-06/BackgroundReports/3-Metal_Finishing_Alternatives_Report.pdf (25.08.2011)

[14] TURI:Toxics Use Reduction Institute (TURI). University of Massachusetts Lowell, Five Chemicals Study.Chapter 6: Hexavalent Chromium, 2006 www.turi.org/library/turi_publications/five_chemicals_study/final_report/chapter_6_hexavalent_chromium (25.08.2011)

4. Vacuum process with PVD/CVD (**P**hysical/**C**hemical **V**apour **D**eposition)
5. Surface modification
6. Deposition of chromium (III)

Not included in the alternative processes at this point are the processes on a **Zinc basis,** the **sol-gel process and the hybrid polymers**, because they are specified in Annex XV as possible substitute processes for chromating and not for hard chromium plating. The difference between hard chromium plating, decorative chromium plating and chromating or passivation is described in Section 1.

No hazardous substance analyses whatsoever were performed for the alternatives specified in Annex XV report. The process provides for such analyses only during the authorization process. [15] This should be considered at an earlier time, due to the known hazard potentials of some of the alternatives specified such as, for example, development of fine, hard metal dust during thermal spraying.

6.3 Technical and hazardous substance analysis for specified alternative processes

The purpose of the following analysis is to determine the extent to which the process represents a substitute for hard chromium plating from a technical point of view as well as reveal the health risks posed by the substitute process.

6.3.1 Thermal spraying (TS)

TS is described most frequently in literature and said to be the primary alternative. Some characteristics of the HVOF layers particularly coincide with those of hard chromium plating[12].

In the HVOF process, powdered material is accelerated at high speed and temperature and sprayed on the component in a plastic state. The coating develops droplet by droplet.

Particularly WC-Co or Cr_3C_2-NiCr powder are used as substitutes for hard chromium[12]

However, there are significant limitations from a technical point of view:

Technical analysis

The points mentioned below indicate why thermal spraying can be used as a substitute for hard chromium plating to a limited extent only: [12],[13],[14]

- One of the major disadvantages of HVOF is that there are significant limitations for coating inner surfaces. It is not possible to coat diameters less than 200 mm.[16]
- The bond between the sprayed-on coating and the substrate is purely mechanical; by contrast, chromium platings adhere to the substrate according to

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[15] Annex XV Report P.40

[16] Bolleli, G.: Replacement of hard chromium plating by thermal spraying – problems, solutions, and possible future approaches . Surface Engineering. 2009. Vol.25, 4

the laws of solid-state physics. The mechanical bond of the TS coatings is potentially subject to poorer adhesion of the coating[17]

- Typically the coatings applied are porous and, if the coating thickness is too low, not impermeable, which can then lead to increased corrosion (the minimum layer thickness is 80 µm).[18] Therefore, TS cannot be accepted as a substitute, when coatings with thicknesses below the minimum are required to meet dimensional requirements.
- The TS application process results in rough coating surfaces. Depending on the application, this may require subsequent machining, which can be very costly when hard ceramic coatings such as WC-Co are used. Large quantities of hard metal dust are developed during the grinding process, in the same manner as when the metal powder is sprayed on when applying the coating.
- Small or complex components with undercuts are very difficult to coat, if they can be coated at all.
- HVOF coatings have a very low factor for elongation at fracture and are brittle.[14]

Hazardous substance analysis

Thermal spraying poses various hazard potentials, which make using it as a substitute for hard chromium plating appear contra-productive particularly in terms of employee protection:

- When the component is sprayed at high velocity with powder in a plastic state, only a portion of the sprayed material deposits as a coating. Up to 60 % overspray can be expected[19] Large quantities of the material, which is not deposited, are present in the form of hard metal dust, which also included A-fraction as well as E-fraction dusts.[20] (The A-fraction is the alveolar fraction and the E-fraction is the inhalable fraction of the dust.)
- When powders containing more than 5% chromium are used, it is possible to measure Cr(VI) in the exhaust air. [20],[21]
- Spraying hard metal powders also poses risks, particularly when WC-Co is used. Lasfargues considered primarily the fact that WC increases the effect of Co[22] . In

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[17] Legg, K. O.; Sartwell, B.: Alternatives to Functional Hexavalent Chromium Coatings: HVOF Thermal Spray. 2004. www.hazmat-alternatives.com.(21.10.2010)

[18] Kraus, J.: Heiße Flamme. [Hot Flame]. MM Das Industrie Magazin.[The Industrial Magazine]. 2004,35.

[19] Schwetzke, R. et al.: Wirtschaftlichkeitsbetrachtungen zum HVOF-Spritzen. [Economic considerations on HVOF spraying]. Kolloqium Hochgeschwindigkeits-Flammspritzen.7, 2006.

[20] BIA Report: Thermisches Spritzen. [Thermal spraying]. Gefahrstoffe, Messungen und Schutzmaßnahmen. [Hazardous substances, measurements and protective measures]. Berufsgenossenschaftliches Institut für Arbeitsschutz [German institute for occupational safety], 2004

[21] BGI 593: Schadstoffe beim Schweißen und bei verwandten Verfahren. [Harmful substances from welding and related processes]. BG Energie Textil Elektro, 2007.

the MAC list hard metal powder containing cobalt - tungsten-carbide is listed in Category 1.[23] IARC lists WC-Co powder in Category 2A.[23]

- ECHA identifies substances in Categories 1 and 2 as potential SVHC's for the REACh process.
- It is necessary to extract the overspray from spraying booths, and in some cases ensure that it is disposed of properly – because of its toxicity. [24]
- The low deposition rate and the high quantities of energy typically required for the process result in poor energy and material efficiency.

In conclusion, it can be said that, from a technical vantage point, TS, even though it might otherwise be suitable for a small range of applications, does not represent any real substitute for hard chromium plating due to its many health-endangering potentials, particularly because the familiar and technically controllable risks of hard chromium plating would be replaced by virtually unknown risks in handling carcinogenic fine dusts.

6.3.2 Nickel and nickel alloys

With nickel and nickel alloy coatings, particularly Ni-P and Ni-W alloys are specified as alternatives to hard chromium plating. [12],[13]

Deposition is accomplished electro-chemically or without electric current.

Technical analysis

Use of nickel and nickel alloys as alternatives is subject to a few technical limitations: [12,13]

- Unhardened nickel and nickel alloy coatings have a lower hardness (500-750 HV) than functional chromium plating. [13] This value is not sufficient for many applications.
- A heat treatment is required to increase the hardness of Ni-P alloys deposited without electric current. Here temperatures of approx. 400 °C are used [13], which lead to warping and violation of the component tolerances. [25] Subsequent treatment of thermally warped components is feasible only in the simple cases. Moreover, the temperature conducted into the components can lead to changes in the substrate, particularly on high strength steels and tempered steels, reducing the strength of the component in the final analysis. [13] Materials with low melting points are also excepted from hardening processes.

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[22] Lasfargues, G. et al.: Comparative Study of the Acute Toxicity of Pure Cobalt Powder and Cobalt-Tungsten Carbide Mixture in Rat. Toxicology and Applied Pharmacology. 1992, V 112.

[23] Vorh, H-W.: Toxikologie Band2: Toxikologie der Stoffe. [Toxicology Vol. 2: Toxicology of substances]. WILEY-VCH, 2010

[24] Smith, R. W.: Commentary: An Environmental Guideline for the Thermal Spray Industry. In:Journal of Thermal Spray Technology.Vol. 2 1993. S.307-310.

[25] Liebmann, G.: Ist bei verzugsempfindlichen Teilen eine Substitution der Einsatzhärtung durch Nitrieren möglich? [Can nitration hardening be substituted for case hardening on parts sensitive to distortion)]? http://www.haerterei.com/index/Aufsatz2.pdf (30.08.2011)

- In the unhardened state, the resistance to wear is lower.[13]
- In contrast to hard chromium platings, nickel or nickel alloy coatings are subject to higher adhesive wear.[26]
- Particularly when small-scale (nano-scale) particles are used to reinforce the coating by means of dispersion deposition, it is difficult to obtain uniform distribution of the particles in the coating. For this reason it is usually not possible to achieve homogeneous coating properties in most cases.[13]
- Multiple layer systems consisting of nickel, copper and its alloys cannot be considered as competition because the coatings obtained do not have the required hardness properties, even considering the latest developments [27]

Hazardous substance analysis

The literature increasingly mentions use of nano-particles to modify the coating properties - also for the purpose of more nearly approaching the characteristics of hard chromium plating. [28] Use of nano-particles is disputed:

- Use of nano-particles poses a major risk. A study by Sullivan & Frost performed in 2009 comes to the conclusion that the ratio of scenarios, which predict that the processes are "dangerous" or "unforeseeable" in comparison to "harmless" is 84:16[29], which, at the bottom line, means that the risk is incalculable.

Even if nickel and its alloys do represent a possible alternative for some applications, there are still significant limitations in the area of hardness and resistance to wear. To achieve higher values for hardness and wear-resistance, it is necessary to subject the alloy to a heat treatment. This results in new technical problems, caused by the effect of the high temperature of approx. 400 °C on the substrate material. [13]

6.3.3 Cobalt alloys and nano-crystalline cobalt alloys

Deposition of nano-crystalline Co-P alloys is considered to be a possible substitute for hard chromium plating. [30]

The alloy coatings can be hardened and inclusion of particles in the coating is possible.[31]

Various studies consider nCo-P as a supplement to TS for coating inner diameters. [12],[13]

The coating is deposited using the pulse current electroplating process or chemically. [31]

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[26] Riedel, W.: Funktionelle Chemische Vernickelung. [Functional chemical nickel plating]. Saulgau: Leuze Verlag, 1989

[27] Thoma Metallveredelung GmbH. Techniken [Techniques], NiL 35®. http://www.thoma-metallveredelung.de/?si_id=4,460&ly_id=1&lan=de (29.08.2011)

[28] Brooman, E.: Compliant electrodeposited and electroless nano-structured and nano-composite coatings to replace chromium coatings –Part1. Galvanotechnik. Bd. 96., 2005 Heft 12. S. 2843-2853

[29] Frost & Sullivan: Nanotechnology – Assessment of Health Safety and Environmental Factors, D1BD, 30. June.2009

[30] Annex XV Report P.44

Technical analysis

The following points significantly limit use of nCo-P coatings as an alternative to hard chromium plating: [13],[14],[31]

- In the unhardened state the nCo-P alloys are too soft (530-600HV) to compete directly with functional chromium plating.[31]
- Higher hardnesses (680HV)[31] are possible only with heat treatment, whereby this value is still considerably lower than the values achieved for technical chromium plating (> 900 HV).
- The resistance to wear is also lower. [14]
- The heat treatment can result in distortion of the component and changes in the properties of the substrate, which excludes use on many materials.

Hazardous substance analysis

The following points are critical in considering nano-crystalline Co-P coatings:

- Many cobalt compounds are on the REACh process candidate list in 2011. These also include cobalt dichloride and cobalt sulphate [32],[33]
- These compounds are contained in the electrolytes required for deposition of nCo-P alloys.[34]
- Other cobalt compounds are classified in Category 2 in the CMR list published by the [German] Federal bureau for labour protection and lobar medicine [Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (baua)] [35] and therefore also represent potential substances for inclusion in Annex XIV.

Both the technical problems specified as well as the high potential for hazardous substances contradict the use of nCo-P coatings as a substitute for hard chromium plating. From a technical

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[31] Facchini, D., Prado, R.A.: Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Alternative. ASETS Defense Workshop Sustainable Surface Engineering for Aerospace & Defense. 2009

[32] ECHA: SUPPORT DOCUMENT FOR IDENTIFICATION OF COBALT DICHLORIDE AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS CMR PROPERTIES. 2011 http://echa.europa.eu/doc/candidate_list/svhc_supdco_cobalt_dichloride_update_ec_231-589-4.pdf (24.08.20011)

[33] ECHA: SUPPORT DOCUMENT FOR IDENTIFICATION OF COBALT (II) SULPHATE AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS CMR PROPERTIES.2010 http://echa.europa.eu/doc/candidate_list/supdoc_cobalt_II_sulphate.pdf (24.08.2011)

[34] Bogenschütz, A.F.; George, U.: Galvanische Legierungsabscheidung und Analytik. [Galvanic alloy deposition and analysis]. Saulgau: Leuze Verlag, 1982

[35] baua: TRGS 905: Verzeichnis krebserzeugender, erbgutverändernder oder fortpflanzungsgefährdender Stoffe. [Index of carcinogenic, mutagenic or reproduction-endangering substances]. Bundesanstalt für Arbeitsschutz und Arbeitsmedizin [German Federal Institute for Occupational Safety and Health], 2008 http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/TRGS/pdf/TRGS-905.pdf?__blob=publicationFile&v=3 (25.08.2011)

point of view, it is not possible to achieve the decisive properties of hard chromium plating, specifically the hardness and excellent wear characteristics. To achieve higher hardness, heat treatment is required, which can lead to negative changes in the component, which in turn then exclude use for technical products. The positioning of the cobalt compounds used on the REACh candidate list excludes serious consideration of these as an alternative to hard chromium plating.

6.3.4 PVD/CVD Vacuum process

In the area of vacuum technology especially the PVD and CVD processes are mentioned as alternatives to hard chromium. Here titanium nitride (TiN), tungsten carbide (WC) and zirconium nitride (ZrN) are possible coating materials. [12]

Technical analysis

Due to the technical problems listed below, use of the vacuum process can only be considered to be a niche technology for replacement of hard chromium plating: [12],[14]

- The PVD and CVD processes usually allow coating thicknesses of only a few µm for wear resistance. [13] For this reason PVD/CVD are used primarily in combination with thin film technology.
- Some of the nitride or carbide coatings commonly used for wear resistance are brittle, when deposited in layers of greater than a few µm. [13]
- Due to the process technology, the component geometry is highly limited in terms of the size of the parts to be coated.[36]
- Since the achievable layer thicknesses are low, repair coatings are not possible, because these require deposition of greater quantities of material. [14]

Hazardous substance analysis

- The coating process does not expose employees to any toxic substances, because the coating process is accomplished under vacuum.
- However cleaning the coating chambers does pose a hazard from fine dust, when mechanically removing coating material which has deposited on the walls of the coating chamber. [14]
- Various substances such as carbon monoxide, sulphuric acid and various chloride compounds pose a high hazard potential for workers during the CVD process. [14]

The vacuum process cannot be considered to be an alternative to hard chromium plating, primarily from a technical stand point. Applications are imaginable, where it would be possible to change over to this alternative technology. However these are only niche areas. Use of

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[36] Flitney, B.: Alternatives to chrome for hydraulic actuators. Sealing Technology, 2007. http://www.sciencedirect.com/science?_ob=MImg&_imagekey=B6VJJ-4PYH29F-10-3&_cdi=6096&_user=3735032&_pii=S1350478907704609&_origin=&_coverDate=10%2F31%2F2007&_sk=979929989&view=c&wchp=dGLbVlW-zSkWB&md5=587d7fb12cbb3a04bc93f00fc13d85c4&ie=/sdarticle.pdf (29.08.2011)

PVD/CVD processes as a substitute for hard chromium plating is not feasible for use on large surfaces.

6.3.5 Surface modification

The surface modification processes mentioned in Annex XV are primarily nitration (nitriding) processes.

Nitriding can be accomplished using the plasma process or the tenifer treatment, whereby components are immersed in molten salt.

Technical analysis

The following technical limitations exist for surface modification processes: [12],[13],[14]

- During nitration, process temperatures of 520°C to 580 °C occur upon immersion in molten salt, while temperatures of 450°C to approx. 550 °C are common for plasma nitration. [37]
- The effect of the high temperature poses a hazard for the component tolerance. [25] Subsequent processing is virtually impossible, except on extremely simple component geometries and even then it is not always possible to restore the tolerances. Use of nitriding for heat-sensitive materials such as high strength steels, for instance, is not possible due to the enormous amount of heat transferred into the component. Moreover, depending on the material, a reduction in the strength can be expected as a result of the heat treatment.
- Since material is not deposited, repair coatings are not possible.
- The layers are very brittle, leading to flaking, cavitation and even fracture. This danger exists, above all, in the face of dynamic stress and surface pressure. [25]
- Surface modification processes are frequently mentioned in combination with other technologies.[12]

Hazardous substance analysis

- With some plasma/gas nitriding processes, oxides of nitrogen are specified as potential hazardous substances.[38]

Surface modification processes such as plasma nitration or the tenifer treatment do not deposit coatings. For this reason surface modification cannot be used in the area of repair work. A further barrier is the high temperature occurring during the process.

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[37] Grote, Karl-Heinrich. Dubbel: Taschenbuch für den Maschinenbau. [Machine construction manual]. 22., revised and expanded edition. Berlin; Heidelberg: Springer, 2007

[38] Brinke, T.; Krug, T.G.: Plasma-Assisted Nitriding Offers Production Flexibility. Industrial Heating, the international Journal of Thermal Technology, 2001. http://www.industrialheating.com/Articles/Feature_Article/d5b51d0dacbb7010VgnVCM100000f932a8c0____ (29.08.2011)

6.3.6 Deposition of trivalent chromium

Research has focused for some time on deposition of trivalent chromium electrolytes. [12]

In the area of decorative chromium plating, trivalent chromium electrolytes are already being used as a substitute for decorative chromium plating using hexavalent chromium electrolytes for some applications.

Technical analysis

- Processes for deposition of functional chromium coatings using trivalent chromium electrolytes are still in the development phase.
- Even after conclusion of the development work, deposition of hard chromium coatings from trivalent electrolytes will only be possible for special applications and for very simple component geometries due to the electro-chemical limits.[39]
- Use of the trivalent coating process presently in development will be possible only to a highly limited extent due to the component geometries.[39]

Hazardous substance analysis

- The author is not familiar with any hazard potentials.

6.4 Conclusion to the alternative processes

All significant points for technical and hazardous substance analysis are listed again and summarized below:

There are a variety of familiar alternatives for functional chromium plating using hexavalent electrolytes. These alternatives do not include one universal substitute process, capable of replacing hard chromium plating on a one to one basis.

The thermal spraying process, mentioned as the primary alternative, poses major health risks, preventing its use as an alternative to hard chromium plating. Moreover some of the technical inadequacies mentioned are criteria for exclusion.

Coatings and coating systems on a nickel or nickel alloy basis do not offer any real alternative to hard chromium plating, because the hardness and wear resistance in the unhardened state are lower than hard chromium, making them unacceptable as technical alternative.

Nano-crystalline cobalt-phosphorus alloys are deposited from cobalt sulphate and cobalt dichloride electrolytes. Both of these compounds are present in the SVHC list of substances to be included in REACh in 2011. Moreover the achievable mechanical properties are insufficient to meet the requirements placed on hard chromium platings.

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[39] Romankiewicz,K.: Abschlussbericht: Hochleistungschromoberflächen erzeugt durch ökologisch vorteilhafte Verfahren [High performance chrome surfaces produced using ecologically advantageous methods] BMWi project number: 0327349B. Fraunhofer Institut für Produktionstechnik und Automatisierung.2011

For technical reasons it is also necessary to consider the PVD/CVD process also mentioned as an alternative for niche applications only.

From a technical point of view the surface modification processes cannot be considered feasible particularly due to the high temperatures involved. Moreover, these processes do not deposit a coating, so that the entire repair range cannot be covered using surface modification.

Deposition using trivalent chromium electrolytes is still in the development phase and will be able to replace only a small portion of the hard chromium applications using hexavalent electrolytes.

If the functional hard chromium plating is to be replaced, it will be necessary to use processes, which do not have the same technical or mechanical properties and, in terms of health, do not offer any improvement in employee protection, because these introduce familiar as well as less well researched safety hazards. Other alternatives, on the other hand, are considered relatively harmless in terms of hazardous substances, however, from a technical vantage point, can only be considered as a substitute for niche applications.