# Substitution of Cr (VI) - containing chromate coatings by the European automobile industry

**Birgit Sonntag**
Atotech Deutschland GmbH, Erasmusstraße 20, D 10553 Berlin, Germany
Email : Birgit.Sonntag@atotech.com

and

**Venkatesh Sundaram**
Atotech India Ltd., 66 KM – Stone, NH – 8, Delhi – Jaipur Highway, Sidhrawali Village, District Gurgaon – 123413, India. Email: vsundaram@atotechindia.com

## Abstract

Hexavalent chromium is carcinogenous and its use in automobiles has been restricted by the ELV directive of the European Union. The IMDS system tracks the use of potentially hazardous and recyclable material in automobiles. A method for determination of Cr(VI) in components is discussed. Properties of Cr(VI) based post treatments and Cr(VI) free thin and thick passivation films are discussed. Thick passivation affords corrosion protection surpassing that of traditional yellow chromates after heat treatment. Sealers incorporating nanoparticles and zinc alloys such as ZnNi and ZnFe can be used to further increase the corrosion protection afforded by Cr(VI)-alternative processes, corroborated by the results of the VDA round robin test 2.

## Keywords

Automobile industry, chromium, chromate, End-of-Life-vehicle directive (ELV), International Material Data System (IMDS), nanoparticles, neutral salt spray test (NSS), passivate, sealer, *Verband der Automobilindustrie* (VDA), zinc, zinc alloys, zinc – iron, zinc - nickel

## Introduction

Directive 2000/53/EG of the Parliament of the European Union [1], commonly known as the End – of – Life – Vehicle Directive (ELV), restricts the use of Cr (VI), mercury, lead and cadmium in automobiles from 1st July, 2003. For corrosion preventative coatings Cr(VI) has to be removed from 1st July, 2007 [2]. Numerous automobile components have historically been plated with zinc or its alloys using Cr(VI) based post treatments and effective substitution of such processes has become a matter of great importance to the automobile industry and in turn, the electroplating industry. In order to ensure that the automotive industry is Cr(VI) free by the year 2007, the plating industry needs to implement Cr(VI) - free processes right now. Most plating shops in Europe supplying to the automobile industry are currently operating with Cr(VI) containing and Cr(VI) free processes side by side.

It is helpful to understand why Cr (VI) is toxic and its use hence restricted by the above legislation, as opposed to Cr (III) and Cr (0). Since thousands of components are used in automobiles, a system to track their chemical composition and potential hazards, among other information, has been developed jointly by many automobile manufacturers. This system, known as the IMDS, is explained. The German automobile industry has undertaken various studies and other activities to help its members implement the directive of the Parliament of the EU, some of which are discussed. The properties of various types of Cr (VI) substitute passivation processes, such as blue and iridescent, are dealt with, followed by a discussion on sealers which help provide better corrosion resistance.

**Toxic nature of Cr (VI) and the ELV directive**

The ELV regulations seek to deal with the problem of waste generated by automobiles at the end of their service lives. This waste hitherto has contained several substances which could be easily leached by aqueous solutions into the ground, causing a lot of long – term damage to the environment. In particular, the ELV legislation forbids the use of lead, cadmium, mercury and hexavalent chromium in automobile components.

As is well known, chromium exists in three principal oxidation states: metallic (elementary) chromium with oxidation state 0, trivalent chromium with oxidation state 3, and hexavalent chromium with oxidation state 6. It may be noted that Cr (III), has a low toxicity and, in fact, is an essential nutrient whose use is not forbidden by the ELV legislation. The use of metallic chromium, which is commonly found on piston rings and shock absorbers in automobiles, is also not forbidden, even though the chromium plating is currently carried out using processes containing Cr (VI).

Cr (VI) is absorbed by mammals either through oral or dermatological routes. It is toxic on account of its high oxidation potential and a structural similarity of chromate with sulfate, allowing the chromate to penetrate sulfate channels in cell membranes. The lethal oral dose is 50-60mg/kg body weight. A possible scheme discussing the manner in which Cr (VI) acts on the cells leading to cancer is given in Figure 1 below.

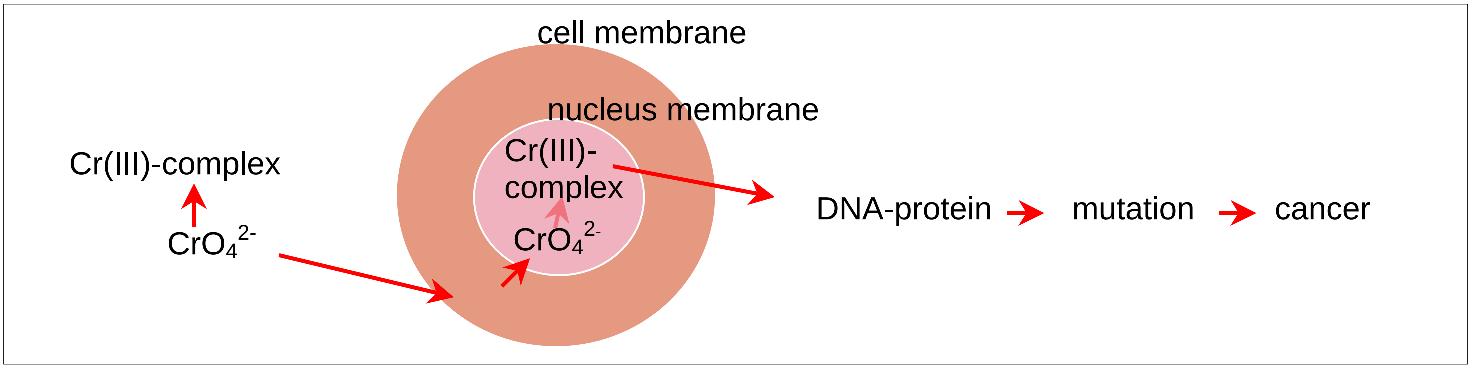



Figure 1: Schematic showing possible route leading to cancer induction by Cr (VI) in mammals

Thus Cr (VI) is a very harmful species and it is in the general interest to limit and progressively prohibit its use. Cr(VI) in its eminently water – leachable form is the main constituent of various kinds of conversion coatings widely used on zinc and zinc alloy coatings to increase their service lives. These coatings are used on a large number of automobile components, including fasteners, brake calipers, tubes and many others. The risk of handling Cr (VI) is often not realised by people using or assembling chromated parts, like fasteners; it is not uncommon for workers to even put screws in the mouth while using their hands!

**Suppliers to the automobile industry and the International Material Data System**

A typical automobile has zinc plated components with an area totaling 40 $m^2$ on a rough average. This translates to a leachable hexavalent chromium content of up to 10 grams per automobile. Considering the sheer number of automobiles, which are scrapped each year through the world, it is clear that the amount of toxic hexavalent chromium, which can be potentially released into the environment by this route, is truly colossal. Since the Cr(VI) elimination in cars becomes effective 1st July 2007, it means that in the supply chain to the automotive industry the elimination of Cr(VI) occurs step by step and is already in progress. The first supplier in this chain is the chemistry supplier, followed by the plating industry, the Tier 2 / Tier 1 system supplier and the automotive industry itself. Chemical processes have to be made available by the chemistry supplier, which have to be operated correctly by the applicator and have to fulfill the specifications of the required application of the Tier 2/ Tier1.

Since there are literally thousands of components, which are used in an automobile, the task of identifying hazardous substances is immense. An evaluation of all the materials used in automobiles has been addressed by introducing a data base called IMDS (International Material Data System). This data base not only permits easy identification of all hazardous materials, but also identifies valuable material for recycling. These are of great interest to the automotive manufacturers since they have, in addition to controlling the use of hazardous substances, also to establish waste reduction strategies.

IMDS is an electronic system for tracking the chemical composition of materials in automotive components [3]. The IMD System is a joint project between major automobile manufacturers (BMW, Fiat, Ford, Fuji Heavy Industries, Daimler Chrysler, Mazda, Mitsubishi, Nissan, Opel /GM, Porsche, Suzuki, Toyota, Volvo, VW/ Audi). Founded in 1999, it has grown with the participation from Japanese and American automobile companies recently. On the basis of IMDS all chemical elements present in the car are reported and restricted elements like Cr(VI) can be easily identified. The IMDS data base build up is hierarchical. For example, a screw, is made from a base material defined in the IMDS database by the screw manufacturer. It is coated by an applicator of zinc processes with a material, which needs to be defined in the IMDS database, based on the composition, density and thickness. The supplier of the process chemicals, which go into the making of the layer, has to help out with this information. All information has been provided for currently available processes and IMDS data sheets have been created accordingly. Typically, a material is described by the following data:

- IMDS number
- Material Name
- Ingredients (basic substances in wt % and CAS number)
- Density
- Recycle Information

Each classification is assigned with a specific IMDS Number. For example,

- 213570 is the number assigned to : e-plate Zinc
- 899586 is the number assigned to Chromate film black Zn
- 900896 is the number assigned to Passivation thick layer Zn /ZnFe/ZnNi
- 974606 is the number assigned to inorganic sealer

It is important to know that Cr(VI) containing conversion coatings are named “chromate” in the IMDS whereas Cr(VI) free conversion coatings are named “passivation”. It was needed to distinguish between these two finishes and this nomenclature has been chosen and is used within the industry.
The IMDS system thus helps quick identification of material type as well as its inherent hazards if any, as well as possibilities for recycling and reduction of natural resource wastage on an industry wide basis.

**Determination of Cr(VI) in conversion coatings**

In order to control the absence of Cr(VI) on automotive components a Cr(VI) determination method had to be developed [4]. This analysis method is based on the photometric determination of Cr(VI) by means of diphenylcarbazide after an extraction performed on the part. The characteristic purple – pink colour formed by solutions containing Cr(VI) intensify and turn towards redder shades with increasing Cr(VI) content. The method has been validated by corroboration tests with members of the German association of car manufacturers (*Verband der Automobilindustrie* - VDA), the German association of chemistry suppliers and applicators (*Zentralverband Oberflaechentechnik e.V.*_- ZVO) as well as workers of other international automotive manufacturers. The determination limit is 1 $mg/m^2$ (Fig.2). Parts under this limit are considered to be Cr(VI) free. Work is ongoing to make this analytical method a European standard. Then an internationally recognized analysis method for the qualitative determination of Cr(VI) according to the demands of the European Union automobile guideline will be available.

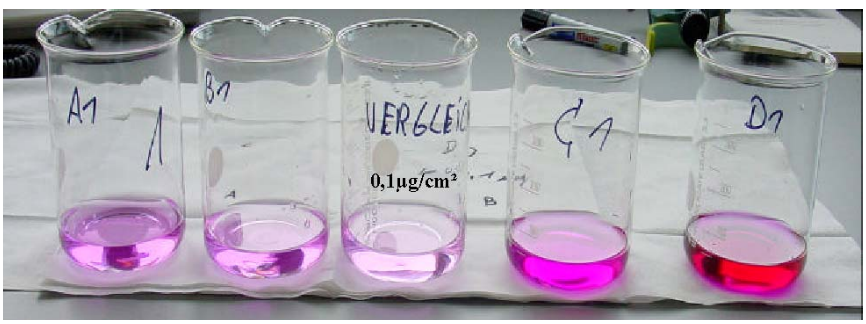



Figure 2: Photo of solutions containing Cr(VI). In the centre is the reference sample corresponding to 0.1 µg/cm² (1 mg/m²) Cr(VI). Darker colours correspond to Cr(VI) containing coatings, brighter colours to Cr(VI)-free coatings. (picture courtesy Bosch)

**Properties of Cr (VI) chromates and the advent of substitutes based on Cr (III)**

Hexavalent chromium containing conversion processes are primarily used in automobile components plated with zinc or zinc alloys since they increase the corrosion resistance which is usually measured by Neutral Salt Spray (NSS) tests. Commonly used hexavalent Cr conversion coatings are usually characterized by their colours – blue, yellow, olive and black. Their properties are summarized in Table 1 (1).

| Type | Film Thickness in µm | NSS Corrosion Resistance hours (DIN 50021) | Cr(VI) content mg / $m^2$ |
|---|---|---|---|
| Blue | 0.025 – 0.08 | 20 - 80 | 10 – 30 |
| Yellow | 0.25 – 0.50 | 200 - 300 | 80 – 220 |
| Olive | 1.0 – 1.5 | 400 - 500 | 300 – 360 |
| Black | 0.25 – 1.0 | 20 - 60 | 80 – 400 |

Table 1 : properties of commonly used hexavalent chromium containing conversion coatings on zinc [5]

The quality of the corrosion protection afforded by a particular type of zinc conversion coating is often thought to be a mere function of the Cr (VI) content. However, a perusal of Table 1 will show that the corrosion protection also increases with higher film thickness. As the Cr (VI) content too increases with film thickness, it is not easy to separate the effect of these two factors on corrosion protection afforded by the chromate film in the case of Cr (VI) – based conversion coatings.

A comparison of conventional chromate conversion processes employing Cr (VI) and alternative processes based on Cr (III) is made in Table 2 below. Conventional yellow chromate processes (e.g. "CorroYellow") provide more corrosion protection than blue passivation. It has a higher thickness (approximately 0.3 µm) as also a higher chromium content (in the region of 70 to 90 mg/$m^2$). The Cr (VI) content in yellow chromate films is high since the solutions from which they are obtained have a high concentration of Cr (VI). The conversion layer itself is based on amorphous trivalent chromium components. Cr(VI) is incorporated in the conversion layer from the Cr(VI) process solution, which gives this chromate coating the yellow appearance and the often discussed self-healing effect. In practice, it can provide corrosion protection of up to 200 hours before the advent of white rust when tested in NSS as per DIN 50021 –SS.

| Process | Cr(VI content (g/l)) in process bath | Estimated film thickness (µm) | Total Cr (mg/ $m^2$) | Cr (III), (mg/ $m^2$) | Cr (VI), (mg/ $m^2$) |
|---|---|---|---|---|---|
| Corro Triblue | 0 | 0.1 | 30 - 35 | 30 - 35 | < 1 |
| CorroTriblue Ultra | 0 | 0.2 | 35 - 40 | 35 - 40 | < 1 |
| EcoTri | 0 | 0.3 | 70 - 80 | 70 - 80 | < 1 |
| CorroYellow | 1.3 | 0.3 | 140 - 150 | 60 - 80 | 70 – 90 |
| CorroBlack | 10.5 | 0.8 | 300 - 400 | 200 - 300 | 90 – 110 |

Black chromate films are usually obtained by incorporating pigmenting agents, usually silver. This reduces the corrosion protection afforded by them. Even though the film thickness is higher than that obtained with yellow chromate, it provides corrosion protection only in the region of 24 – 72 hours in the NSS as per DIN 50021 – SS. The Cr (VI) content of the film is in the region of 90 to 110 mg / $m^2$.

Thus the metal finishing industry now have the task of coming up with substitutes which meet the needs of the automobile industry for corrosion protection, service life and other properties in efficient and cost effective ways. In fact, conversion coatings based on Cr (III) have been worked on long before the increased environmental concern which has prompted directives like the ELV regulation to be enacted [6]. Many, if not all the advantages afforded by Cr (VI) containing processes could be obtained with these processes too. However, these have not widely been adopted as mainstream processes, on account of factors such as costs of materials and their qualification, aesthetics (final appearance), additional processing steps, energy requirements, and lack of familiarity. The ELV regulations have given a fillip to an immense international effort by automobile manufacturers, Original Equipment Manufacturers (OEMs), applicators, suppliers and other institutions to characterize and evaluate a long list of Cr (VI) substitutes.

Blue passivate coatings (e.g. CorroTriblue), available on the market already long before the ELV, only build up a thin conversion coating over zinc and therefore only provide limited corrosion protection. There is no difference between the corrosion protection afforded by blue passivates processed from trivalent and from hexavalent chromium process baths. The trivalent chromium based processes, which provided acceptable aesthetics, have been in use for long time already in the plating industry because the change from Cr(VI) to Cr(III) could be handled without additional investment in the plating line and the cost of the coating is very similar. Figure 3 shows a scanning electron micrograph of a blue passivate coating.

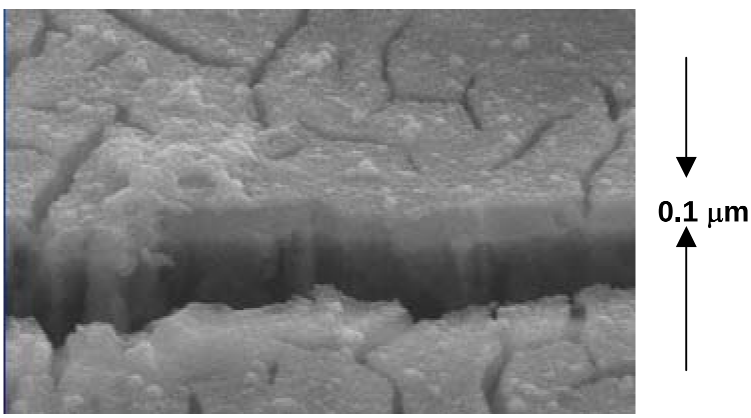



Figure 3: Blue passivation (thin film passivation) as characterized by scanning electron microscopy

There are new passivation processes available that provide higher corrosion resistance compared to general blue passivates. By incorporation of silicon dioxide nano particles, the thickness of the conversion coating is increased and the corrosion protection improved.

It is also possible to increase the layer thickness by working with highly concentrated trivalent chromium solutions that are processed at elevated temperatures up to 70 °C. Layer thicknesses up to 0.3 μm can be produced, as demonstrated in Figure 4. These coatings have an iridescent colour and provide a corrosion protection similar to a traditional Cr (VI) – containing yellow chromate coating. In cases where the components are subjected to conditions of elevated temperatures (> 100 °C) before the corrosion testing the corrosion performance is even better compared to a traditional Cr (VI) – containing yellow chromate. General chromate conversion coatings based on Cr (VI) dehydrate easily, the cracks are widened and white corrosion products are formed immediately.

While incorporating such new Cr(VI) free processes in the plating line the applicator needs to control the process parameters a lot more frequently than with traditional Cr (VI) containing yellow chromates. The concentration of the passivate bath, the pH of the solution, the bath temperature and the immersion time need to be confined within a narrow, specified working window to ensure consistently high performance of the coatings. It is also recommended to analyze the contaminations like the increase of zinc and iron in the passivate solution. The higher process cost compared to yellow chromates can be reduced by use of ion exchanger technology, which eliminates zinc and iron from the solution and prolongs the bath life. This technology also ensures that the process bath is maintained in the stable condition required for high performance coating.

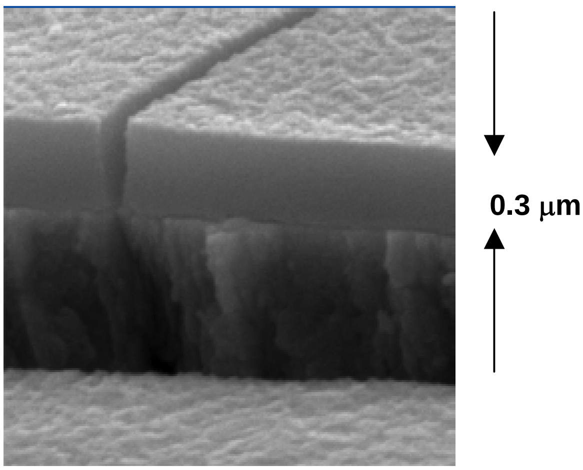



Figure 4: Thick film (iridiscent) passivation characterized by scanning electron microscopy

To further improve the corrosion protection, a sealer can be used over the passivate coating. The best performance could be obtained by using sealers that consists of nano-particulate silicon dioxide particles (Figure 5).

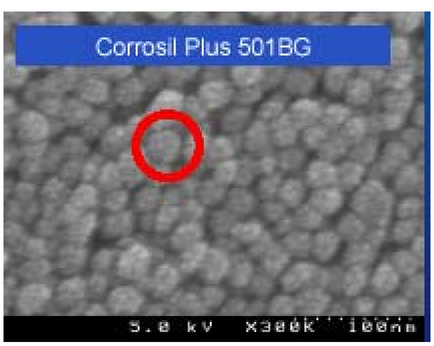



**Figure 5: Scanning electron micrograph of a sealer coating indicating the presence of nano-particles.**

The formation of black passivate films is even more complicated than the formation of transparent, blue or iridescent conversion coatings because besides forming the film itself, it is also necessary to homogeneously distribute black pigments within the coating. Black passivates have been developed for pure zinc, zinc-iron and zinc-nickel alloy coatings and have been tested in production conditions in the plating industry. Figure 6. shows a scanning electron micrograph of a black passivate over ZnFe. It has been realized that the desired corrosion protection can only be achieved by the use of sealers over the black passivate coating. Currently a lot of testing is done in the field to qualify these coatings for the automotive industry.

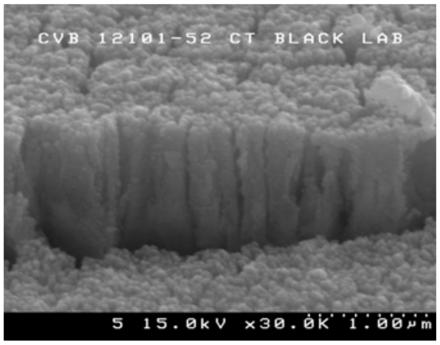



Figure 6: Black passivation as characterized by scanning electron microscopy

**Characterization of Cr(VI) alternatives by the association of the German automotive industry (VDA)**

The VDA, association of the German automotive industry, has created a working team for the substitution of Cr(VI), members of which are Audi, BMW, Bosch, Daimler Chrysler, Ford, INA, Opel, Porsche and VW. Two round robin tests have been undertaken to validate currently available Cr(VI) free processes. Corrosion was tested by NSS according to DIN 50 021-SS. Parts were tested with and without heat treatment 24 hours for 120°C before the corrosion testing. The figures presented in this section have been presented at the Stuttgarter Automobiltag by VDA representatives [7]. It has been reported that thick film passivates provide better corrosion protection than thin film passivates on zinc coatings (Figure 7, Table 3).

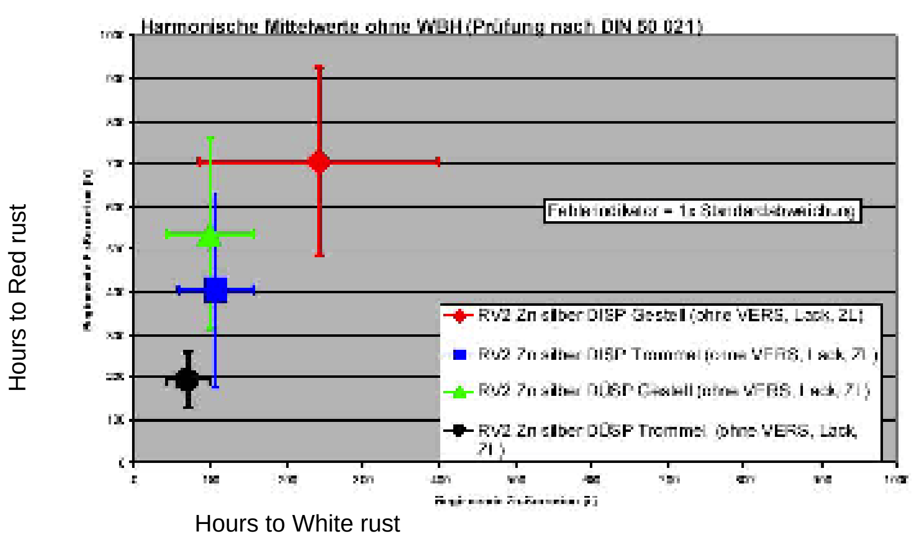


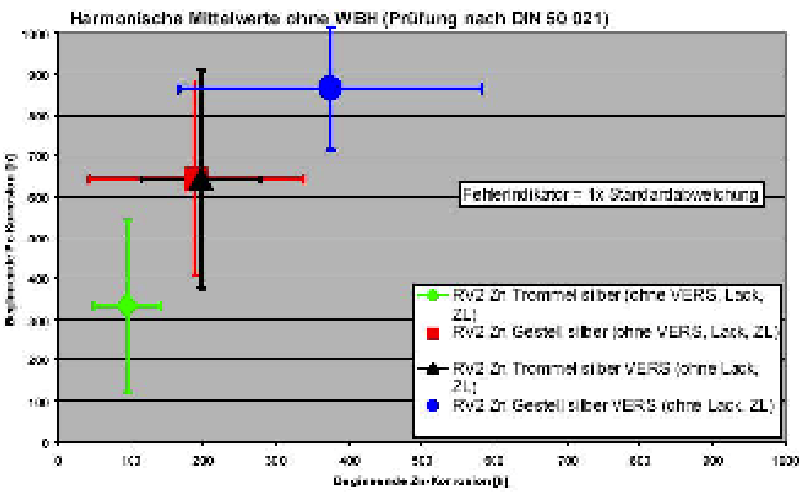

Figure 7: Corrosion Results of VDA Round Robin test 2 without heat treatment (red, diamond: thick film passivate in rack application; blue, square: thick film passivate in barrel application; green, triangle: thin film passivate in rack application; black, circle: thin film passivate in barrel application)

| Type of coating | Hours for the onset of white rust (Zn corrosion) | Hours for the onset of red rust (Iron corrosion) |
|---|---|---|
| Zinc, barrel plating, thin passivate, no sealant or lacquer | 50 - 100 | 125 – 275 |
| Zinc, barrel plated, thick passivate, no sealant or lacquer | 75 - 150 | 175 - 625 |
| Zinc, rack plated, thin passivate, no sealant or lacquer | 50 – 150 | 310 - 750 |
| Zinc, rack plated, thick passivate, no sealant or lacquer | 80 - 400 | 485 - 930 |

Table 3: Corrosion Results of VDA Round Robin test 2 without heat treatment tabulated

The corrosion protection can further be improved by usage of a sealer coating (Figure 8, Table 4)

Hours to Red rust




Hours to White rust

Figure 8: Corrosion Results of VDA Round Robin test 2 without heat treatment (blue, circle: with sealer in rack application; black, triangle: with sealer in barrel application; green, diamond: without sealer in barrel application; red, square: without sealer in rack application)

| Type of coating | Hours for the onset of white rust (Zn corrosion) | Hours for the onset of red rust (Iron corrosion) |
|---|---|---|
| Zinc, barrel plating, no sealant, no lacquer | 50 - 130 | 120 – 550 |
| Zinc, barrel plated, thick passivate, with sealant but no lacquer | 125 - 275 | 375 - 910 |
| Zinc, rack plated, no sealant or lacquer | 50 – 350 | 405 - 875 |
| Zinc, rack plated, with sealant but no lacquer | 170 - 580 | 710 - 1000 |

Table 4: Corrosion Results of VDA Round Robin test 2 without heat treatment tabulated for sealants

The corrosion protection can also be improved by using zinc alloy coatings instead of pure zinc coatings (Fig. 9, table 4). Zinc alloys are commonly used for applications in the car that have certain specific requirements. Zn-Fe coatings are used when high corrosion protection is required to be combined with high ductility (e.g. crimping or bending of component part after plating). Zn-Ni coatings are used when high corrosion protection needs to be combined with the ability to withstand higher temperatures (e.g. near the engine or brakes) or when the part is in contact to aluminium.

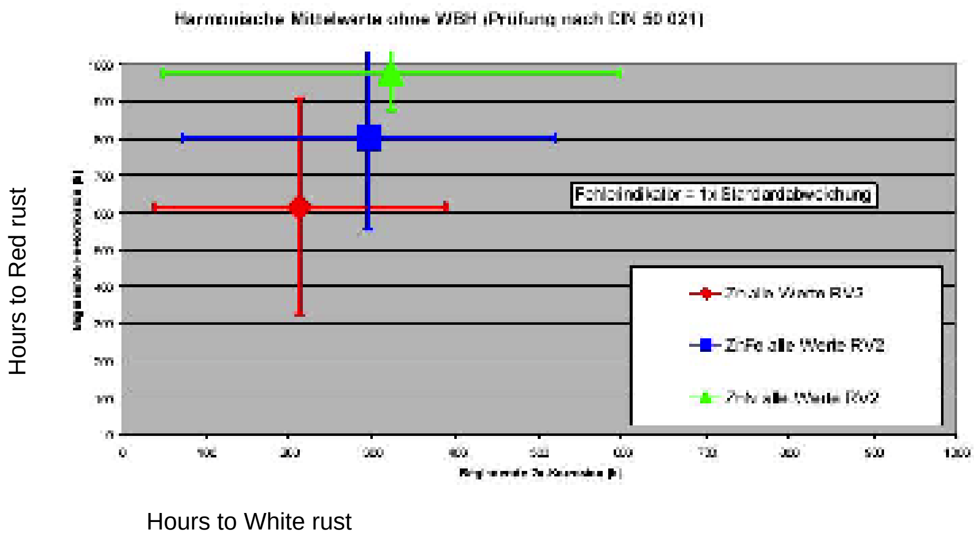



Figure 9: Corrosion Results of VDA Round Robin test 2 without heat treatment (green, triangle: Zn-Ni; blue, square: Zn-Fe; red, diamond: pure Zn)

| Type of coating | Hours for the onset of white rust (Zn corrosion) | Hours for the onset of red rust (Iron corrosion) |
|---|---|---|
| Zinc | 50 - 400 | 320 - 910 |
| Zinc - iron | 75 - 510 | 550 – 1000+ |
| Zinc - nickel | 65 - 600 | 870 – 1000 + |

Table 5: Corrosion Results of VDA Round Robin test 2 without heat treatment tabulated for zinc alloys

These round – robin tests conducted by the *Verband der Automobilindustrie* have helped to establish the applicability of various Cr (VI) alternatives on production scales in an empirical and practical manner. As can be seen from Figures 7, 8 and 9, in all categories, the corrosion protection results were highly distributed over a wide range. The requirement of the automotive industry, however, is to always obtain coatings with as high a level of corrosion protection as has been obtained by the top third of the coatings from the round robin test 2. This would require plating establishments to a higher level of control over the plating and associated procedures, and will increase the work of checking and maintaining bath conditions and process parameters on a regular basis. The plating process has to be continuously improved in order to fulfill the requirements of and become accepted by the European automotive industry. For black coatings only few systems were submitted to the VDA round robin test 2 and it could therefore not be shown that the plating industry is ready to move from Cr(VI) to Cr(III) for black finishes.

Challenges thus still obviously exist for the chemistry suppliers to develop new Cr(VI) free processes to fulfill the requirements of various kinds of different automotive applications. On the other hand the plating shops have to learn a lot about how to run Cr(VI) free processes under conditions of regular production. All Tier 1 or 2 suppliers have to qualify the alternative coatings for the different requirements of automotive parts. The coating in each case has to be chosen according to the substrate material, the shape of the component and the use of the component in the automobile. It is expected that a lot of different coating combinations will be the answers.

**Conclusions**

Chromium (VI) is a toxic substance and products which are capable of releasing it into the environment need to be substituted by alternatives at the earliest. As one of the largest users of leachable - Cr(VI) for corrosion protection, the automobile industry has been compelled by legislation in the European Union to do so without delay.

The International Material Data System (IMDS) has made it possible to track the hazardous nature as well as potential for recycling of various components used in the automobile industry. Suppliers of processes for coatings contribute to this system by providing information on the composition of the coatings produced with their processes. Cr (VI) can be detected using a photometric method based on diphenylcarbazide after extraction. Components which have Cr (VI) contents less than 1 mg / $m^2$ of component area as determined by this method can be described as Cr (VI) – free.

Traditional chromate conversion coatings based on Cr (VI) provide corrosion resistance in the region of 20 – 500 hours to white rust in the neutral salt spray test (DIN 50021-SS). Blue passivate conversion coatings based on Cr (III) can provide similar corrosion protection as those based on Cr(VI) and have been in use for some time now. While other substitutes have been worked on long before the ELV legislation was contemplated, considerations such as cost, aesthetics (appearance), processing steps, lack of familiarity and established standards had not allowed these to become mainstream processes. Conversion coatings based on Cr (III) with higher film thicknesses and consequently providing higher corrosion resistance can be obtained from more concentrated solutions, operated at higher temperatures and longer immersion times. Such coatings in fact perform even better than coatings obtained from Cr (VI) based processes after heat treatment. However, greater process control is required to obtain consistent results with such Cr (III) based processes. Corrosion protection can be further enhanced with the use of sealants incorporating nano – particles.

Round robin tests conducted by the VDA have established that (i) thick film passivates provide better corrosion protection than thin film passivates based on Cr (III), (ii) that this performance can be further improved by using sealers and (iii) that more corrosion protection can also be obtained by using alloys such as zinc – iron and zinc – nickel. Thus the fact that substitution of Cr (VI) in automobile components is possible with similar or better characteristics has been placed on a firm footing backed by considerable empirical evidence. There are still challenges both for suppliers of chemistry as well as for the platers who apply the coatings, which need to be accepted and met.

## Acknowledgements

The authors would like to thank their colleagues Dr Roland Vogel and Dr Claudia Andrle of Atotech Deutschland GmbH and Craig Bishop, of Atotech USA Inc. for helpful suggestions.

## References:

[1] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of-life vehicles, Official Journal of the European Communities **L269** (21.10.2000).
[2] Commission Decision of 27 June 2002 amending Annex II of Directive 2000/53/EC of the European Parliament and of the Council on end-of-life vehicles, C(2002)2238
[3] http://www.mdsystem.comT/
[4] C. Andrle, C. Bauspiess, 2004, ZVO report **3,** 25
[5] T.W. Jelinek: "Galvanisches Verzinken", 1982, Leuze Verlag, Saulgau
[6] C. V. Bishop, D. M. Burdt, K. R. Romer, 1980, Galvanotechnik **71**, 1199
[7] A. Hasse, H.-D. Hesse, Presentation at Stuttgarter Automobiltag, November 2003, Germany