Cr(VI)-Free Post-Treatment Processes for Zinc & Zinc Alloys

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The ability of a chromate layer to protect the zinc coating from corrosion is strongly dependent on the thickness of the passivate layer. As a result, yellow chromate coatings are more protective than blue passivate coatings. A new Cr(III) containing passivate solution has been developed that is able to build up a thicker conversion coating than conventional blue passivates. The corrosion protection achieved is even better than for conventional yellow chromate coatings when annealed. This passivate can be applied on zinc, zinc-iron and zinc-nickel deposits. A Cr(VI)-free black passivate has also been developed for zinc-iron. The corrosion protection of the passivated coating can even be improved by deposition of an inorganically based top coat on the passivate layer. The top coat penetrates into the passivate layer, stabilizes it and seals any cracks and pores. At the same time, it increases the surface strength and meets the highest automotive industry corrosion standards.

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Introduction

Since first patented 1936 by E.J. Wilhelm [1] it took some 20 years that chromate films became essential as passivation of electrolytically applied zinc coatings. Nowadays we have to search for a zinc plated part without chromate on top. Jelinek estimated 1982, that 60% of the applied chromate films were blue, 20 to 25% yellow, the rest olive or black [2], changes in the spreading all over the different industries are assumed to be minor.

The advantages of the passivation by chromates are well known and obvious: they are available, even in different colours, easy to apply and fully integrated in the different zinc processes, they are cheap and offer good adhesion for waxes, topcoats or organic coatings.

The acknowledged best corrosion protection is gained by the thicker chromate films containing hexavalent chromium, Cr(VI), which unfortunately became suspicious to cause cancer.

For this reason the European Community started to focus on Cr(VI) in mid of 1997. In order to minimise the impact of end-of-life vehicles on the environment the different national measures concerning end-of-life vehicles should be harmonized. Even from the first proposal it was turned out, "that preventive measures be applied from the conception phase of the vehicle onwards and take the form, in particular, of reduction and control of hazardous substances in vehicles, in order to prevent their release into the environment, to facilitate recycling and to avoid the disposal of hazardous waste. In particular the use of lead, mercury, cadmium and hexavalent chromium should be prohibited. These heavy metals should only be used in certain applications according to a list, which will be regularly reviewed. This will help

to ensure that certain materials and components do not become shredder residues, and are not incinerated or disposed of in landfills".

Since the final act of the "Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of-life vehicles" [3] it is clear, that

- 1. the Directive covers "vehicles and end-of-life vehicles, including their components and materials, as well as spare and replacement parts, without prejudice to safety standards, air emissions and noise control", that
- the date from which on the "Member States shall ensure that materials and components of vehicles put on the market do not contain the 4 above mentioned elements will be 1 July 2003" [3], Article 4(2) (a), and that
- 3. for hexavalent chromium in "corrosion preventative coating on numerous key vehicle components" as long "maximum 2 g per vehicle" are permissible [3], Annex II, line 12, at least as long as the "use is unavoidable".

The Commission emphasizes, that it will "on a regular basis, according to technical and scientific progress, amend Annex II".

So far the original text from the directive, which acts as a driving force for both automotive and galvanic industry to accelerate the development of Cr(VI) free corrosion protective systems.

Both automotive industries and the customers strongly demand that the directive shall affect neither the costs nor the quality of the corrosion protection [4,5].

This paper shall review the different protective properties of chromate films, will have a glance on alternative conversion layers, explain the difficulties of a reliable quantitative determination of Cr(VI) in chromate films and finally present a very promising Cr(VI) free corrosion protection system.

State of the art

Chromate conversion coatings are produced by dipping a zinc coated substrate into a chromate solution containing oxidizing acid. The outer zinc layer is dissolved by oxidation to Zn^{2+} and chromate is reduced to trivalent chromium [6-8]. A gel like chromate conversion coating is produced by precipitation of trivalent chromium compounds with incorporation of Zn^{2+} , water and hexavalent chromium compounds.

The ability of a chromate conversion coating to protect the zinc coating from corrosion is often claimed to depend on its Cr(VI) content, but is rather related to the thickness of the chromate layer [9]. Generally, thickness and Cr(VI) content increase simultaneously, thus both influences are difficult to separate.

Blue chromate conversion coatings have a layer thickness of up to 80 nm (see fig. 1). The conversion coating exhibits no crack formation as a result of the small layer thickness. In practice a corrosion protection of 20 - 40 h to first appearance of white rust (zinc oxide formation) in the neutral salt spray test (NSS) according to DIN 50021-SS is achieved. The amount of hexavalent chromium has been identified between 10 - 30 mg/m², when deposited from a chromic acid solution [2].

Yellow chromate conversion coatings are more protective than blue chromate coatings. They have a higher layer thickness, between 250 and 500 nm, as well as a higher content of Cr(VI), between $80 - 220 \text{ mg/m}^2$. Common salt spray results for yellow chromates on zinc coatings are between 200 and 300 h to white rust. The incorporation of hexavalent chromium into the conversion coating is evident from its yellow colour. Crack formation can be observed.

Olive chromate conversion coatings exhibit a layer thickness of 1 to 1.5 μ m, resulting in an increased corrosion protection against white rust of 400 – 500 h NSS. The crack formation is pronounced as a result of the increased layer thickness. The amount of hexavalent chromium is between 300 – 360 mg/m².

Black chromate conversion coatings can only be produced by incorporation of black pigments. To produce a black chromate coating on pure zinc, the pigment used is typically silver, which is supplied by the chromate solution. The incorporation of silver into the chromate coating leads to a decrease of the corrosion protection of the conversion coating. Although the layer thickness of a black chromate conversion coating is similar to a yellow or olive chromate coating, between $0.25 - 1 \mu m$, the corrosion protection against white rust achieved in practice is only 20 - 40 h, similar to a blue chromate conversion coating on zinc.

The corrosion protection contribution of a black chromate conversion coating is improved by treating a zinc alloy instead of zinc. A silver free chromate solution can be used in this case. Common zinc alloys are ZnFe, ZnCo and ZnNi, producing respectively iron, cobalt and nickel oxides as black pigments, when dissolving the upper layers of the zinc alloy by forming the chromate coating. The black chromate conversion coating on zinc alloys can achieve a corrosion protection of 250 – 350 h to first appearance of white rust in the NSS test. This result is comparable to the corrosion protection of yellow or olive chromate coatings of the same layer thickness. Crack formation is observed. The amount of hexavalent chromium is between $80 - 400 \text{ mg/m}^2$ depending on the coating thickness of the chromate.

	Thickness An jam	Corrosion Resistance in Nours (DIN 50021 NSS)	(CrVI) mg/m²
Bue -	5.025 - 5.05	29 - 60	10+20
Yellow	0.25 - 0.50	300 - 500	80 - 320
oll 1		(300+360
III SHOWAN	6.25 - 1	¥0 - 60	80-400

Fig. 1 Properties of chromate conversion coatings

Alternative coatings

The striking performance of chromates as low-cost decorative and protective finishes always impeded the development of alternative conversion coatings, although the toxicity of hexavalent chromium compounds is known ever since. However, a couple of research institutes investigated a whole plethora of chromium-free alternatives, mainly based on other transition metal oxides or phosphates.

Molybdate, cerate, and permanganate-based coatings were characterized on Zn/Ni [10], as well as molybdate/phosphate [11], tungstate or zirconate based passivates on zinc. A review on the subject was given by Wilcox and Wharton [12], concluding that, regarding the protective properties and versatility, no alternative can compete with the chromate system up to now.

The most advanced "Cr(VI)-free" coating at present is the Cr(III)-based passivate [9,13], which will be considered in detail in the following sections.

Although technically often classified as a Cr(VI)-free coating, the Cr(III)-based passivate is – from an electrochemical point of view – expected to contain a finite concentration of Cr(VI).

Determination of Cr(VI) in passivates

A prerequisite for the control of the total Cr(VI) content in vehicles is a reliable procedure for its analytical determination in passivate layers. While the analysis of Cr(VI) in aqueous solution is straightforward, this is not the case for the gel-like passivates.

The quantification of Cr(VI) in solution is generally performed via reaction with diphenylcarbazide. Diphenylcarbazide is oxidized by Cr(VI) in acidic solution to diphenylcarbazon, the Cr(VI) being reduced to Cr(III). The diphenylcarbazon forms a red complex with Cr(III), which can be quantified spectroscopically in the UV/VIS range (e.g. [14]).

Alternatively, a direct quantification of the chromate concentration in solution is possible via ion chromatography [15]. Both techniques, the spectroscopic and the chromatographic, were crosschecked for these investigations and found to agree within an error budget of less than 5%.

Regarding the analysis of passivates, an analyte solution has to be prepared from the coating prior to analysis. This is the crucial part of the analytical procedure since no generally accepted method is available for this purpose up to now. Dissolution of the passivate in 250 g/l NaOH at room temperature was proposed by General Motors [16], whereas the association of the german automotive industry (VDA) proposes leaching for 5 minutes in boiling deionized water [17], and VOLVO in Sweden has established a test after leaching in synthetic sweat solution at 40°C [18]. The less aggressive approaches are intended to validate the risk of contamination upon physical contact (risk of allergies) with passivated parts, whereas the more aggressive are aimed at determining the total content of the layer.

Preliminary measurements indicated that leaching in highly caustic solutions gives erratic values since Cr(III) oxidation by atmospheric oxygen is fast in these solutions. Leaching in neutral environment, on the other hand, is not aggressive enough for a quantitative determination, with the VOLVO approach (synthetic sweat, 40°C) giving systematically lower values for Cr(VI) than the VDA approach (5 min. boiling water).

For the present investigations, an optimised procedure was developed on the base of the proposal from General Motors [16]. The samples were leached for 1 hour in 0.1 M NaOH (4 g/l) at room temperature. Comparative measurements were performed according to the VDA proposal (5 min. in boiling water). In both cases, a visible residual film remains on the surface.

Comparative measurements were performed on zinc layers deposited from acidic and alkaline solution. No differences were observed between acid and alkaline zinc.

Irrespective of the applied procedure, two questions have to be addressed:

- 1. Is there any Cr(VI) left on the sample surface (and thus escapes detection)?
- 2. Is the Cr(VI) content affected by the analytical procedure?

Analytic Results

As a reference sample, a standard yellow chromate coating on zinc was analysed. A Cr(VI) content of 50 mg/m² was determined after leaching in 0.1 M NaOH, somewhat lower than the text book values of 80-220 mg/m² [2]. Leaching in boiling water gave a slightly lower value of 40 mg/m², indicating that some Cr(VI) remains in the coating with this procedure.

Some of the leached samples were immersed a second time for 1 h in 0.1 M NaOH in order to

estimate the efficiency of the applied procedures. For those samples, which had already been leached in NaOH before, the Cr(VI) content in the analyte was hardly above the detection limit of 0.01 mg/m^2 . For those previously leached in water, higher values around 10 mg/m² were found in the second step. These results indicate that leaching for 1 h in 0.1 M NaOH extracts the Cr(VI) more or less quantitatively (>95%), while with hot water only around 50-80% of the Cr(VI) are extracted.

For the newly developed Cr(III) based passivate, the Cr(VI) content of the passivating solution is below the detection limit of $10^{-3} \mu g/l$. Nevertheless, on the passivated surfaces a small but finite amount of Cr(VI) was found.

Analysis of a freshly deposited passivate within 1 h after preparation yielded a Cr(VI) content of 0.2 ± 0.05 mg/m². The Cr(VI) concentration in the passivate increases with time upon storage under ambient conditions and saturates at 2.5 ± 0.5 mg/m² within one week, as determined by leaching of stored samples in NaOH. For leaching with hot water, around a factor of 2 lower values were determined for the Cr(VI) content. These values summarize the results from roughly 20 independent samples, which were investigated within 6 weeks.

Since on freshly deposited samples the Cr(VI) content was found 1 order of magnitude smaller than on stored samples one can conclude that Cr(III) oxidation in the course of analyte preparation is negligible.

The influence of temperature was screened by analysing samples after storage at either 120° or 160° C. The Cr(VI) content of heated samples was 20 to 50% lower than for samples stored at room temperature.

In order to assess the influence of a top coat on the Cr(VI) content of the passivate, comparative measurements were performed on passivates sealed with a SiO₂-based top coat. Leaching in NaOH gave essentially the same values as for the samples without top coat. Upon leaching with boiling water, however, no Cr(VI) could be detected at all, and even after thorough scratching of the top coat with a knife-edge the value was hardly above the detection limit of 0.01 mg/m².

The possibility of systematic experimental errors was checked by analysing dilute alkaline solutions of Cr(III). The solutions were found to be stable against extended exposure to air. However, in the presence of metallic zinc in the electrolyte, a Cr(VI) content increasing with time was determined analytically.

Discussion of the Analytical Results

Since the Cr(III) based passivate was developed in order to eliminate Cr(VI) from passivated parts, the determined Cr(VI) content in the layer, although very small, is certainly a drawback. An understanding of the mechanism of Cr(VI) build-up is mandatory for judging the compatibility of the Cr(III) based passivate with future regulations.

It is a trivial assumption that Cr(VI) can only be formed by oxidation of Cr(III) compounds. Further on, it is obvious that oxygen from air is the only relevant oxidizing agent within the given system. Thus one may arrive at a first hypothesis assuming simply oxidation of Cr(III) to Cr(VI) by atmospheric oxygen. This hypothesis is, however, in disagreement with some of the experimental results.

Firstly, one would expect the reaction rate to increase with increasing temperature and hence give a higher Cr(VI) concentration for heated samples, in contrast to the experimental results. This discrepancy indicates that moisture may play an important role in the oxidation process, with higher temperature involving lower humidity. Secondly, one would expect that Cr(III) is also oxidized by dissolved oxygen in aqueous solution, again in contrast to the experimental result. This indicates that oxygen is not the active species for the oxidation reaction.

In the presence of metallic zinc, the oxidation of Cr(III) to Cr(VI) proceeds in aqueous solution. Obviously, zinc promotes the oxidation reaction. It is known that the reduction of oxygen at zinc involves the formation of hydrogen peroxide species as intermediates [19]. Thus it seems a reasonable assumption that the oxidation of Cr(III) to Cr(VI) is due to the hydrogen peroxide, which is formed by oxygen reduction at the zinc surface.

With an explanation for the process in aqueous solution at hand, it is straightforward to assume that basically the same mechanism operates within the passivate layer. It is well known that an adsorbed water film is present on the surface under ambient conditions. It is also known that, at a small rate, oxygen is reduced at the passivated surface, else it would never corrode. Hence one may conclude that build-up of a small concentration of hydrogen peroxide occurs within the adsorbed water layer. The hydrogen peroxide is reduced to OH⁻ either by oxidizing Zn metal, or by oxidizing Cr(III) to Cr(VI), thus giving rise to a Cr(VI) concentration increasing with time. The Cr(VI), supposedly in the form of CrO_4^{2-} , may diffuse to the zinc surface and again be reduced there, improving the surface passivation as known from the self-healing of conventional chromate coatings.

The generation and consumption of hydrogen peroxide as well as of CrO_4^{2-} within the passivate apparently approach a steady state within a few days, with a steady state concentration of Cr(VI) of roughly 2.5 mg/m².

At a first glance, the proposed mechanism for Cr(III) oxidation in the passivate seems in

contradiction to the results from the top-coat protected passivate. Since on this sample Cr(VI) can not be extracted with boiling water, indicating that the top-coat is highly hydrophobic, one may conclude that water is unlikely to play an essential role in the oxidation mechanism. On the other hand, even though the top-coat may be impermeable to liquid water, it may nevertheless be transmissive to water vapour. On the base of this assumption, the top-coat does not significantly inhibit the formation of Cr(VI), but immobilizes the Cr(VI) against dragout.

Trivalent chromium-based passivates

The interest of this investigation was to develop a substitute for chromate conversion coatings. Therefore it has to be inexpensive, easy to handle, applicable in existing conventional plating lines, and as low in Cr(VI) content as possible.

Obviously the easiest path is to change a hexavalent chromate solution into a trivalent chromium solution. Blue passivate coatings produced from a trivalent solution are well known, but also their minor corrosion protection. New chromium (III) containing passivate solutions have been developed. By addition of special ingredients the chromium solution has been stabilized. When using these passivate solutions, which are also containing a higher concentration of chromium (III) compared to conventional blue passivates, at increased bath temperature (see fig. 2), it is possible to build up a conversion coating of an increased layer thickness.

The layer thickness of a black silver free passivate coating on zinc iron alloy, which is presently field-tested, is demonstrated in a SEM micrograph of a cross section (see fig. 3).

The layer thickness was identified to be in the same range as for conventional black chromates on

ZnFe. The black colour of the passivate is formed by the iron pigments dissolved from the zinc iron coating.

	Indescant	Black	
🐱 Temperature	140 (130 - 180) *F		
• pH • on alta zinc • on alkallor zinc	2 (1.7 - 2.2) 1.7 - 2.0 2.0 - 2.2 pH adjusted with NaHCO, or HNO,	1.F (1.5 - 1.9) pH adjusted with HCt or NaOH	
Immersion time	60 (30 - 90) s		
🖌 Bath ngitation	mechanical or slight air agitation		
Crittl-Concentration	1.34 (1 + 1.34) oz/gal	2.6t oz/gal	

Fig. 2 Operating conditions of Cr(VI)-free passivation processes



Fig. 3 SEM/EDX analysis of cross section from black passivate on zinc/iron

When increasing the layer thickness of a blue passivate in the range of a yellow chromate, an iridescent passivate is produced, which can be applied on zinc and zinc alloys. Although the layer thickness is the same for a yellow chromate and an iridescent passivate, the colour of the coating is different, because no hexavalent chromium is incorporated from the solution into the passivate coating. The iridescent colour is produced on all zinc substrates, pure or alloyed.

As the ability of a chromate conversion coating to protect the zinc coating from corrosion is

strongly depending on the thickness of the chromate layer, the same relationship can be observed with passivates of different layer thickness. Fig. 4 demonstrates the first appearance of white rust on zinc-plated panels, which were passivated in a beaker under optimal deposition conditions, in the neutral salt spray test according to DIN 50021-SS.



Fig. 4 Comparison of corrosion resistance of passivates and chromate on zinc (lab-scale)

The as-deposited blue passivate has only basic corrosion protection of up to 72 hours, whereas the achieves vellow chromate good corrosion protection. When tempering the panels the blue passivate and the yellow chromate tend to dehydrate and the conversion coating looses its protection properties. Blue passivates build up cracks and yellow chromates are widening the cracks, thus zinc is corroding in the cracks. When the iridescent passivate is deposited on zinc the corrosion protection is comparable to the yellow chromate coating, which is resulting from the same layer thickness produced, but on the other hand the tendency of the iridescent passivate to dehydrate is not as dramatically observed. Therefore the corrosion protection of an iridescent passivate is more stable, even when heat treated.

The morphology of a black passivate on ZnFe is demonstrated in fig. 5. Crack formation is observed as usual for black chromates, but there is no crack widening when tempering the coating.



Fig. 5 Surface morphology of black passivate on Zn/Fe (SEM)

The corrosion protection of the passivated zinc or zinc alloy deposit can be further improved by covering with a chromium free top coat containing colloidal silicon dioxide. The top coat penetrates into the passivate layer, stabilizes it and seals any cracks. Fig. 6 shows the first appearance of white rust according to DIN 50021-SS of the same blue and iridescent passivates and yellow chromate on zinc plated panels shown in fig. 4, which were deposited in a beaker under optimal conditions, when applying a top coat. It can be seen that by using a top coat the corrosion protection is highly improved.



Fig. 6 Comparison of corrosion resistance of passivates and chromate with top-coats on zinc (lab-scale)

Even the conventional blue passivate shows significant corrosion protection, which can be

achieved also when heat treated. No white corrosion products were produced on the top coated yellow chromated and the top coated iridescent passivated zinc deposit until the corrosion test was stopped after 648 hours. At the same time the top coat improves the wear resistance and leads to a homogeneous colour of the coating. The iridescent effect of the passivate is minimized.

practice, when using the iridescent In passivate in combination with or without the top coat in conventional existing plating lines, the corrosion results achieved are depending on the application. In rack plating (see Fig. 7) the corrosion protection of an iridescent passivate on zinc can reach the same values as achieved in the beaker test. Also when the top coat is used on a blue or the iridescent passivate the corrosion results are similar to those exhibited in Fig. 6. with or without heat treatment. Another behaviour can be observed for plating mass articles in a barrel application line (see Fig. 7). The iridescent passivate itself achieves 192 hours to first appearance to white rust. A conventional blue passsivate, even covered with a top coat, looses its corrosion protection when plated in a barrel application line. The plated parts investigated here were deposited with zinc in a barrel and afterwards transferred in a basket for passivation and top coating. Also under this gentle plating condition the corrosion protection is negligible.

By top coating the iridescent passivate the corrosion protection can be improved to 288 hours to first appearance of white rust. The reason for this difference in corrosion protection is the layer thickness of the passivate coating. The top coat has to be fixed on the zinc surface by a passivate or chromate conversion coating. It is applied in a dipping process from an aqueous solution and penetrates into the passivate. By increasing the passivate thickness the top coat has the possibility for better penetration and therefore the adhesion on the zinc layer is by far superior.



Fig. 7 Corrosion resistance of passivates with/without top coat obtained in production

For the automotive industry the heat resistance of corrosion protection coatings is of special interest, as zinc plated parts may be used also close to the engine. Fig. 8 gives an overview of top coated iridescent passivated parts from the automotive industry, which were plated with zinc iron alloy. There is no difference in the corrosion protection performance of parts with or without heat treatment. Even after a thermal shock of 24 hours at 320° F the resistance to white rust was 720 hours, whereas red rust corrosion products were only observed after 1560 hours in the salt spray test.



Fig. 8 Corrosion resistance of iridescent passivate with topcoat on Zn/Fe

Table 1	Applicability of Cr(III)-based passivate systems				
	Zn Coatings				
Iridescent Passivate	Acid Zinc	Cyanide-free Alkaline Zinc	Cyanide-free Alkaline Zinc/Iron	Cyanide-free Alkaline Zinc/Nickel	
Iridescent Passivate with Top Coat	Acid Zinc	Cyanide-free Alkaline Zinc	Cyanide-free Alkaline Zinc/Iron	Cyanide-free Alkaline Zinc/Nickel	
Black Passivate with Top Coat			Cyanide-free Alkaline Zinc/Iron		

Table 1 summarizes all Cr(III)-based corrosion protection coatings obtained from Cr(VI)free solution. These are commercialized today and used in many job shops in Europe in conventional plating lines. The consumption of the passivate solution is mostly depending on the drag out. As the trivalent passivate solution is more concentrated than conventional blue passivates the drag out is increased. The cost of the passivation process is slightly higher than for conventional chromates due to increased concentration and bath temperature, but can be reduced by recirculation of the rinse water

Conclusions

The development of ecologically acceptable corrosion protection systems is still in progress. Regarding the avoidance of Cr(VI) in passivates, plenty of promising initial laboratory results have already been reported for a variety of alternative systems. Regarding technical applicability and performance, however, the Cr(III)-based passivates are presently the only alternative to conventional chromates.

Iridescent as well as black Cr(III)-based passivates offer the same corrosion protection as conventional chromates, at least for rack plating, and have the additional advantage of improved heat resistance compared to the latter. They are, however, not totally free of Cr(VI), but build up a small concentration of about 2.5 mg/m^2 of Cr(VI) within a few days.

Considering the present target value of 2 g Cr(VI) per vehicle in total, around 800 m² of passivated metal surface may be used for construction of a single car before this limit is exceeded. Since estimates of the total passivated area within a usual passenger car amount to roughly 7-10 m², one may assume that even the largest truck will contain much less than 2 g of Cr(VI), if Cr(III) based passivates are applied on all of its parts.

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