DEUTSCHER SCHRAUBENVERBAND E.V.
Informations-Centrum Schrauben

GERMAN FASTENERS ASSOCIATION
Fastener Information Centre

Status-Report
Changeover to Hexavalent-chromium-free Coatings *)

May 2003

*) This status report was prepared by members of the German Fasteners Association (Deutschen Schraubenverbandes e.V.)
Contact:
Dipl.-Phys. Frank Naumann
Tel.: ++49-(O)2331 -9588-45
e-mail: fnaumann@dsv.wsu.de

CONTENTS

1. Starting Situation

According to Appendix II of the EU End-of-Life Vehicle Directive (status June 2002), as from 1 July 2007 coatings containing hexavalent chromium may no longer be used for corrosion prevention in motor vehicles. In the EU Directive on Waste Electrical and Electronic Equipment, the use of hexavalent chromium is also forbidden as from 1 January 2006. The dates quoted in the legislation require immediate action by manufacturers of coating materials, by coating plants, by fastener manufacturers and by vehicle manufacturers.

The greatest challenge in substituting hexavalent-chromium-free coatings for many of the coatings containing hexavalent chromium used hitherto and which have proved their value in practice, is providing equivalent corrosion protection whilst simultaneously fulfilling other essential requirements for mechanical fasteners.

When converting from conventional coatings containing hexavalent chromium to those without, three different systems must be considered:

- hexavalent-chromium-free electroplating systems
- hexavalent-chromium-free water-based zinc-flake systems.
- hexavalent-chromium-free solvent-based zinc-flake systems.

With electroplating systems, passivation using hexavalent chromium must be replaced by suitable alternatives without loss of corrosion protection. As regards water-based zinc-flake systems, the Dacromet© system, used widely in Germany and Europe and which contains hexavalent chromium, must be replaced by a hexavalent-chromium-free system. The hexavalent-chromium-free solvent-based zinc-flake system most widely used hitherto in Germany and Europe has been the Delta Tone© system, mostly in combination with the Delta Seal© surface-sealing system. Here no change is required. The strategy here is product improvements to this system together with the use of further solvent-based systems using the same plant and technology.

Today, a large number of new hexavalent-chromium-free electroplating systems, a new hexavalent-chromium-free water-based zinc-flake system and product improvements for solvent-based zinc-flake systems, together with some new systems of this latter type, are all available. Many of these systems are in the pre-production test phase. Several systems are already in series production.

For a large-scale changeover from systems using hexavalent chromium to hexavalent-chromium-free systems in all areas of the automotive industry to take place, a number of problems still have to be solved:

- Clear definition of systems, requirements and strategies, so that sufficient planning security is achieved and the necessary investments in all areas can be made.
- Harmonisation of test requirements and standards with the characteristics and special features of the new systems.
- Creation of sufficient coating capacity adapted to the new systems. This is particularly important for electroplating systems.
- Adaptation of existing coating plants to the technical requirements and special features of the new systems, where required.
- Improvement of the process stability and process security of new products and equipment, taking the special features of the new systems into consideration.
- Clarification of uncertainties with regard to the costs of hexavalent-chromium-free coatings in comparison with conventional coatings containing hexavalent chromium, including further costs in connection with the alterations.

- Preparation of exit strategies for all companies which at least until 2007 have to provide both hexavalent-chromium-free coatings and coatings containing hexavalent chromium.

These tasks must be tackled by manufacturers of coating systems, coating plants, fastener manufacturers and automotive companies, all acting together.
At present some vehicle manufacturers and suppliers are taking a cautious wait-and-see position as regards the conversion to hexavalent-chromium-free coatings. This attitude is reinforced by the following aspects:

- The introduction of hexavalent-chromium-free systems in standards and delivery specifications is often accompanied by an increase in corrosion protection requirements.
- The process security of hexavalent-chromium-free coatings has not yet reached the level of conventional systems containing hexavalent chromium, in particular as concerns corrosion protection.
- Hexavalent-chromium-free coating systems are often markedly more expensive than conventional coatings containing hexavalent chromium, not least because of the increased requirements.
- The introduction of new systems with insufficient quality levels as compared with coatings containing hexavalent chromium in combination with higher costs is, in spite of legislative demands, not plausible.

The tasks resulting from these aspects consist mainly of making sustained improvements in the processes, process security and quality of the new hexavalent-chromium-free systems. High reliability and the necessary confidence in these systems will favour and advance their speedy introduction on a broad front.
The members of the German Fastener Association and the coating plants who are working together with them have accepted this challenge and, together with the German automotive industry, are making every effort to convert to hexavalent-chromium-free systems systematically and within the shortest possible time.

2. Purpose

In this report, the members of the German Fastener Association, together with their partners in the surface-coating branch, have made it their task regularly, speedily and comprehensively to portray and assess the current status of activities concerned with the change to hexavalent-chromium-free coatings and to develop and implement constructive suggestions for a smooth changeover. The following aspects should especially be taken into consideration:

1. Corrosion protection and functional characteristics
2. Processes, process-security and quality
3. Standardardization
4. Status of introduction
5. Costs
6. Suggestions for further action

These aspects will now be discussed in detail.

3. Status

The bases of comparison used below for the status of conversion to hexavalent-chromium-free coatings are conventional zinc or zinc alloy electroplating with passivation containing hexavalent chromium and water-based zinc-flake systems containing hexavalent chromium (here Dacromet 320© or Dacromet 500©).
Solvent-based zinc-flake systems which are already free of hexavalent chromium (e.g. Delta Tone© + Delta Seal©), improvements of these systems and hexavalent-chromium-free zinc-flake systems from other manufacturers which can be used with the same equipment technology enjoy a special status. The characteristics and special features of these systems will be referred to below as necessary.

3.1 Corrosion Protection and Functional characteristics

When choosing a suitable hexavalent-chromium-free surface coating system for mechanical fasteners, not only the necessary corrosion protection and functional characteristics, but also the type and size of the fastener in question must be taken into account. Thus, for small parts using the dip/spin process, special equipment or equipment settings are often required to give consistent and even coating thicknesses and to hold thread tolerances whilst giving a high degree of corrosion protection. With increasing size, the weight of each individual part leads to an increasing danger of surface and other mechanical damage. Parts M14 and larger often require special methods (coating on racks). These dimension-related problems are dealt with later.

3.2 Corrosion Protection

Electroplating systems. For electroplating systems hexavalent-chromium-free passivation is used in place of passivation containing hexavalent chromium. Besides having a film thickness which is more difficult to adjust than with chromate-based systems, the main disadvantage is the lack of the so-called self-healing effect. Damage to the passivation resulting from handling or transport no longer heal, leading to a considerable decrease in resistance to zinc corrosion. The result is that resistance to rusting is also reduced for the same thickness of coating.

To compensate for the greater sensitivity to damage caused by the lack of a self-healing effect, extra sealers are often used on electroplating having hexavalent-chromium-free passivation. Practice shows that zinc corrosion resistance can often only be maintained in series production by using such sealers. Also, by using suitable additives, sealers can also be used to achieve the required coefficient of friction. Furthermore, corrosion resistance can be further increased by pigmentation and thus, apart from optical considerations (for example silver or black), further properties such as electrical insulation or the avoidance of contact corrosion can be achieved.

Zinc-flake systems. Hexavalent-chromium-free zinc-flake coatings, as opposed to zinc-flake coatings containing hexavalent chromium, also show no self-healing effect. Practical experience from the past shows that this disadvantage can be compensated for by using greater film thicknesses for hexavalent-chromium-free coatings. This experience has been incorporated in the relevant standards (e.g. DIN EN ISO 10683).

Well-known manufacturers of hexavalent-chromium-free coating systems envisage, or at least recommend, the use of supplementary inorganic or organic topcoats. Such coatings assume, as a result of their specific characteristics, the function of a sealer and result in a major increase in corrosion protection. Furthermore, when provided with integrated lubricant additives, they can be used to achieve specified coefficients of friction.

3.2.1 Functional characteristics

Optical appearance

Silver-coloured coatings. Silver-coloured hexavalent-chromium-free electroplated coatings are achievable in practice but with certain limitations. When zinc or zinc alloy plating is used with only a so-called "thick-film" passivation, this can lead to varying iridescence because of light refraction. With plain zinc plating this iridescence changes with increasing thickness of the passivation film from reddish-gold via blue and greenish-blue to reddish-green. With zinc-iron alloys a grey-brown colour often occurs and with zinc-nickel alloys the iridescence is often a strong dark blue to green-yellow with marked greying. When extra surface sealers are used, these iridescent effects largely disappear in favour of the metallic appearance of the base metallic plating. As opposed to plain zinc, the brownish or greyish appearance of zinc alloy platings is normally visible from a considerable distance.

For silver-coloured hexavalent-chromium-free zinc-flake coatings there are in practice no limitations. All currently known hexavalent-chromium-free zinc-flake coating systems have an attractive silver appearance, whether the basic coating or with an organic or inorganic topcoat.

Black coatings. For black hexavalent-chromium-free coatings greater limitations on corrosion protection must currently be accepted. For hexavalent-chromium-free zinc and zinc alloy electroplated coatings, the oxidising effect of chromates plays a central role in creating corrosion resistance. Because trivalent chromium compounds cannot take over this role, optically attractive black hexavalent-chromium-free coatings have relatively limited resistance to zinc corrosion. Therefore to obtain a uniform black colour and acceptable resistance to zinc corrosion for zinc alloy coatings (ZnFe and ZnNi), usually a combination of transparent passivated or phosphated zinc alloy with a black-pigmented sealer is used. Black zinc coatings are not being further pursued on a large scale at present.

In individual cases it has now been found possible to create black-pigmented passivation on zinc alloy plating which is optically acceptable and has an adequate resistance to corrosion of the coating. Here a black pigmentation of the sealer is not required.

For zinc-flake coatings a uniform black colouring can only be achieved using a suitable and sufficiently thick topcoat. Variants with an intermediate sealer, which provide a dark colouring and also increase the adhesion of the black surface layer, are currently at the test phase.

Holding of thread tolerances

Providing equivalent corrosion protection for mechanical fasteners using hexavalent-chromium-free electroplating usually means increasing the thickness of the plating, depending on the requirements also in combination with a sealer or topcoat, which is mostly applied by the dip/spin process. This can sometimes affect the holding of tolerances considerably, depending on the size of the fastener. Small metric fasteners (= M8) and parts with internal threads are particularly affected here.

Fasteners with metric external thread which are intended for electroplating are nowadays normally manufactured to the tolerance class 6g, whilst similar fasteners which are to receive zinc-flake coatings are, because of the increased coating thickness, usually manufactured to tolerance class 6f or 6e. The choice of tolerance class has repercussions on the maximum possible coating thickness. **Table 1** shows examples of metric external threads with the average practicable coating thicknesses for tolerance classes 6g and 6e for which the threads of the finished product are within tolerance to gauge. These values have already taken into consideration the fact that local build-up (up to twice the thickness) may occur during the coating process.

Because compliance with the required life of the corrosion protection largely depends on the layer thickness of the coating or coating system, the necessary coating thickness must be taken into consideration when choosing thread tolerances.

Table 1: Average practicable coating thickness for fasteners with metric threads M3 - M24 in tolerance classes 6g and 6e (approx. Values)

<table>
<tr><th>pitch</th><th colspan="2">diameter</th><th>6g</th><th>6e</th></tr>
<tr><th>P</th><th>standard thread</th><th>fine thread</th><th>s_{ave} in µm</th><th>s_{ave} in µm</th></tr>
<tr><td>0.5</td><td>M3</td><td rowspan="2"></td><td rowspan="6">12</td><td rowspan="6">18</td></tr>
<tr><td>0.7</td><td>M4</td></tr>
<tr><td>0.75</td><td></td><td>M6</td></tr>
<tr><td>0.8</td><td>M5</td><td></td></tr>
<tr><td>1</td><td>M6</td><td>M8</td></tr>
<tr><td>1.25</td><td>M8</td><td>M10</td></tr>
<tr><td>1.5</td><td>M10</td><td>M12
M14
M16
M18</td><td rowspan="3">18</td><td rowspan="3">24</td></tr>
<tr><td>1.75</td><td>M12</td><td></td></tr>
<tr><td>2</td><td>M14
M16</td><td>M20
M22
M24</td></tr>
<tr><td>2.5</td><td>M18
M20
M22</td><td rowspan="2"></td><td rowspan="2">24</td><td rowspan="2">30</td></tr>
<tr><td>3</td><td>M24</td></tr>
</table>

For the coating of internal threads with zinc-flake coatings, taking into consideration local build-up, the tolerance class 6G is normally chosen. In future this will also have to be taken into consideration for electroplated internal threads with additional sealers.

Internal drive features can also be affected by build-up of coating material so that they no longer are to gauge. In general the danger and the degree of possible impairment of tolerance to gauge depends on the hardness of the sealer or topcoat. In particular inorganic coatings containing silicate layers can be problematical in this respect because such coatings cannot be "pushed aside" during the screw assembly process or by the insertion of a drive tool.

It must be further noted that all layers which are additional to those required for coatings containing hexavalent chromium are associated with additional mechanical handling processes. Here the effect of possible mechanical damage on gauging, especially of metric external threads, must always be taken into consideration and checked for. This problem increases with increasing size and weight of the fasteners concerned.

Abrasion resistance

Abrasion of surface coatings during handling (tipping, mechanical sorting and automatic feeding) or transport processes has a negative effect on their corrosion properties, causes problems with automatic assembly equipment and affects the reliability of sensitive (e.g. electronic) components.

The abrasion resistance of surface coatings can be influenced both positively and negatively by additional sealers and topcoats. These additions must be tested in each case.

Temperature resistance

Initial experience shows that in practice electroplating with hexavalent-chromium-free passivation has a higher temperature resistance than with passivation containing hexavalent chromium.

This positive characteristic can be made use of, for example with a view to realising increased resistance to zinc corrosion in components subjected to higher temperatures.

Coefficient of friction

With traditional electroplating with passivation containing hexavalent chromium and with zinc-flake coatings containing hexavalent chromium (Dacromet 320© or Dacromet 500©) the required coefficient of friction (e.g. VDA 235-101: µtotal = 0.09 - 0.14) is normally achieved by using an additional lubricant (e.g. Torq'n'Tension©, gleitmo 605©), applied by a dip/spin process. This also applies to hexavalent-chromium-free solvent-based zinc-flake coatings when used without a topcoat.

With hexavalent-chromium-free coatings, the required coefficient of friction can be achieved by using lubricants integrated into the sealer or topcoat. Here additional lubrication is not necessary. It is to be expected that lubricants defined in terms of composition and quantity will lead to a reduction in variance in coefficient of friction. With integrated lubricants, the use of the hitherto customary greenish or bluish coloration of the added lubricant can be dispensed with, thus improving the optical appearance of the coating and avoiding problematical wear of the coloration.

Practical experience has however shown that, where sealers and/or topcoats are used, local build-up of coating - especially on threads - can lead to increased variance in coefficient of friction when testing in accordance with DIN 946. Therefore when converting to hexavalent-chromium-free coatings, especially in the initial phase, it will be necessary to pay increased attention to the determination of coefficients of friction. It will be necessary to test and supervise the screw assembly and process parameters for individual cases. When required the application technology may have to be adapted to give a more even coating.

With coatings on thread-forming fasteners for screwing into plastics, no lubricant additives should be used in sealers or topcoats. On the other hand other thread-forming fasteners must have lower coefficients of friction than those laid down in, for example, VDA 235-101, in order to guarantee lower application torque.

Compatibility with pre-coated adhesive and prevailing torque patches

A series of test results has shown that an impairment of the adherence of such features is possible for hexavalent-chromium-free coatings where integrated lubricants are used to ensure the correct coefficient of friction. In each case it will be necessary to check whether the requirements of DIN 267-27 (Fasteners with adhesive coatings) and DIN 267-28 (Fasteners with prevailing torque patches) are still met.

Fasteners with adhesive patches are mainly used where threaded fasteners must be secured against unscrewing when subject to high dynamic loads, especially those at right angles to the axis of the part. Here the highest possible pretension which cab be reliably applied is required. This allows the sole use of fasteners whose coefficient of friction has been optimised with suitable lubricants. As it is known that lubricants on or in coatings can have a negative effect on the ratio between loosening and application torque laid down in DIN 267-27, in the course of the revision of this standard the lowest required ratio was reduced from 1 to 0.9 so as to reach an optimal compromise between the highest possible tightening torque and an adequate margin of safety against loosening.

Paintability

Paintability can also be negatively affected by sealers, topcoats and lubricants (whether integrated or applied additionally). Thus when changing over to new or altered systems this property should also be checked in each case. If required, for example for automotive body-in-white applications, it may be necessary either to refrain from using integrated lubricants or to fully dispense with the use of sealers or topcoats.

Electrical conductivity and weldabilit

The use of sealers and topcoats on electroplating or zinc-flake coatings considerably reduces their electrical conductivity. This can be put to use for particular combinations of metals (e.g. components made of aluminium or magnesium alloys) so as to reduce the danger of contact corrosion; on the other hand such fasteners are not normally suitable for earthing connections. Because of their low conductivity, fasteners with such coatings are generally not weldable.

Influence of temperature on loosening behaviour

Organic components or particular lubricants (e.g. PTFE) in passivation films, sealers or topcoats can seriously affect frictional and loosening behaviour at higher temperatures up to 150°C. Lower loosening torque at higher temperatures could under unfavourable circumstances (e.g. threaded fasteners subject to lateral dynamic forces) lead to spontaneous loosening of an assembly.

Requirements for safety and loosening behaviour at 150°C together with a suitable test procedure are currently being determined in a VDA test sheet.

3.3 Processes, Process-Security, Quality

When converting from coatings containing hexavalent chromium to hexavalent-chromium-free coating systems, the whole process chain, from manufacturer of the coating via coating plant, fastener manufacturer and transport to assembly by the end user, must be investigated and supervised in relation to process security and uniform quality. With improved process control, however, there are also opportunities for optimising processes in coating (online supervision, analysis etc.) and handling (more careful transport, reduction in fall heights, etc.) and as a result also for improving quality.
The most important aspects will be explained in detail below.

Chemicals

Constancy in quality of supplies of the starting chemicals is an important basis for constancy in quality of the corrosion protection produced. This must first be tried and tested when new chemicals for hexavalent-chromium-free passivation and sealers or for hexavalent-chromium-free zinc-flake coatings with their accompanying topcoats are brought into use.

For a number of new systems there is little experience with the long-term stability of the chemicals involved or of the factors influencing this. In particular the influence of impurities and of bath carry-over is of importance. Concrete experience concerning this can only be made on the basis of continuous production over a longer period of time.

Both for electroplating and for zinc-flake coating plants the question of the choice of the most suitable system for the particular plant must be raised. In this connection the following aspects must be taken into consideration:

- In the choice of chemicals/systems - insofar as the coating plant is not itself the developer - questions of licensing play a role. During the development phase for newly licensed systems, intensive personal and technical guidance from the specialist firm supplying the coating material is indispensable.
- Each factory must make its own choice of systems based on its own experience, existing or planned plant and equipment, existing or planned capacity and not least the range of products to be coated. Systems cannot be changed at will for equipment and capacity reasons.
- After establishing all the important requirements, coating companies must be allowed the responsibility of choosing their own equipment. It is - especially for plating facilities - not possible to cover all the special wishes of the various automotive companies for different systems or combinations of systems.

Adaptation of equipment technology and process control

Electroplating systems. For electroplating systems two routes can be taken for the change from chromate passivation to hexavalent-chromium-free passivation:

- Application of normal hexavalent-chromium-free transparent so-called "thin-film" passivation. For adequate protection against zinc corrosion an additional sealer must always be applied as well.
- Replacement of chromate passivation by so-called "thick-film" passivation. The aim of the suppliers of such passivation systems is to achieve a similar protection against zinc corrosion as with chromate passivation. At present however for fasteners additional sealers are at least to be recommended and are probably necessary.

The changes in process and equipment technology required for the changeover are described below together with the necessary measures to be taken:

- In order to ensure a sufficient film thickness of the passivation, "thick-film" passivation must normally be carried out at a temperature above approx. 50°C (ideally 60-80°C). The temperature here must be carefully controlled. In particular the maintenance of the working temperature of the bath is of decisive importance. It must be ensured that no excessive cooling occurs as a result of putting cold, in particular heavy, items into the bath in such a way that process security is no longer upheld. Critical parts may perhaps need to be pre-warmed before "thick-film" passivation. To avoid energy losses in heating the passivation bath, suitable insulation must be installed. Ideally heat-exchangers should be used.
- The concentration of trivalent chromium needed for process security in "thick-film" passivation is normally about five times that of the concentration of hexavalent chromium in a conventional yellow passivation: the necessary contact time is at approx. 60 seconds about three times as long as for yellow passivation.
- An accumulation of cations such as Zn, Fe, Ni or Al in the passivation bath can seriously reduce the life of the bath and thus the process security as far as corrosion protection is concerned. The concentration of these impurities must therefore be controlled in a suitable manner.
- Because of the much higher costs of running a trivalent chromium-based bath in comparison to one containing hexavalent chromium, in the medium and long term an attempt should be made not to dispose of the bath on, for example, reaching specific limiting values for Zn and Fe contamination but to operate on a continuous basis. Here a system of on-line analysis for the continuous monitoring of the chemical composition of the passivation bath must be installed, together with on-demand dosing equipment for particular chemicals, filtration equipment for the removal of Zn and an ion-exchange unit to remove Fe and/or other metallic impurities.
- Increased effort must be taken with the rinsing and drying technology. For continuous operation reuse of the rinse water would be advantageous. This allows a more effective recycling of the bath but on the other hand has the effect that Zn, Fe and other metallic impurities accumulate more quickly. On-line analysis and continuous removal of impurities would also be required here.
- Because of the high concentration of trivalent chromium, it will be necessary to investigate whether the waste-water treatment facilities must be altered. For example the enlargement of neutralisation tanks or the use of alternative precipitation agents may be necessary to meet the legal limits for trivalent chromium.
- The hardening period of "thick-film" passivation can be as much as 48 hours. This should be heeded, especially with respect to quality and to the cost situation, especially when sealers needing a dry surface for their proper application are subsequently to be applied. Such aspects make necessary a separation of passivation and sealing, as well as of the quality control facilities and measures, in terms of both time and equipment. In cases where the sealer can be applied to the passivation "wet-on-wet", a decoupling of the equipment is not absolutely necessary. Here pre-drying, sealing and hardening can all take place in centrifuge baskets.

- Follow-up treatments such as sealing can not yet normally be carried out in the barrels used for electroplating, especially for small and mass-produced parts. For the treatment of such parts they are normally put into other containers (e.g. dip and centrifuging baskets) with as much care as possible. For the future, container systems must be developed which can be used equally well in both types of equipment (electroplating and follow-up treatments). The aspects mentioned make clear that to assure process security and maintain quality many parameters must be continuously monitored. Furthermore, practical experience has shown that with such systems these parameters have to be held considerably more closely than with chromate passivation. This means that not inconsiderable expense needs to be incurred for on-line analysis and control as well as for the assurance of the whole process.

Zinc-flake systems. For new hexavalent-chromium-free zinc-flake coatings the following aspects are of particular importance:

- To obtain sufficient process security and to fulfill various other requirements, the new zinc-flake systems normally require an additional topcoat as in the past (e.g. the system Delta Tone© + Delta Seal GZ©). Whilst the improvement of existing solvent-based hexavalent-chromium-free systems requires only the testing of new chemicals for large-scale use and no investments in major equipment changes, for water-based systems which have hitherto contained hexavalent chromium (Dacromet 320© and Dacromet 500©) additional investment in plant and equipment will have to be made to implement the changeover to hexavalent-chromium-free variants. In the first instance this means additional dip/spin equipment for the topcoat and additional oven capacity for drying and baking. In this connection must be mentioned that at approx. 180 - 200°C the drying temperatures of conventional topcoats (e.g. PLUS L© on Geomet©) is lower than the baking temperature of Dacromet© or Geomet© of approx. 300°C. In order to make a changeover from Dacromet© to Geomet© + topcoat (e.g. PLUS L©) as economical as possible, for example a corrosion resistance in a salt spray test to DIN 50021-SS of 720 hours which is currently achieved by triple Dacromet© coating, would mean for the hexavalent-chromium-free variant coating with Geomet© twice followed by a single coating of PLUS L©. With comparable coating thicknesses this means that the topcoat must compensate for the reduction of cathodic protection from three to two layers.
- The chemicals for Dacromet© and those for Geomet© are completely incompatible. This means that a plant for series production can normally be used for only one of these systems.
- Coating plants for hexavalent-chromium-free solvent-based zinc-flake systems (e.g. Delta Tone© + Delta Seal©, Delta Protekt KL 100© + Delta Protekt VH 301© or new systems from Magni and Kunz) and for water-based zinc-flake systems (e.g. Geomet© + PLUS L©) are normally not interchangeable (e.g. for reasons of explosion protection or different oven lengths). Exceptionally, a plant laid out for a solvent-based system can be used for water-based systems.

When extending plants using solvent-based products, often a series of environmentally relevant aspects and additional approval processes must be taken into account.

Both hexavalent-chromium-free electroplating with sealers and zinc-flake coatings with topcoats are very sensitive to mechanical damage during the whole process chain, in particular because of their lack of a self-healing effect. Therefore, when changing over to hexavalent-chromium-free systems, measures to ensure more careful handling of fasteners during the whole coating process (special design and materials for barrels and containers, making barrel movement more gentle, wet-loading, reduction of fall-height) must be considered now. This is of course equally valid for transport and handling and for automatic sorting and feeding processes at fastener manufacturers and at OEMs.

A meaningful assessment and an effective optimisation of the whole hexavalent-chromium-free coating process can only be undertaken when sufficient quantities of fasteners for a continuous series production

coating process over a sufficiently long period of time become available. For some systems several years experience exists. For a large number of other systems such experience is still lacking.
Table 2 below gives an overview of the current status of experience with various hexavalent-chromium-free electroplating and zinc-flake coating systems in comparison with systems containing hexavalent chromium.

Table 2: Experience with fasteners with hexavalent-chromium-free coatings compared with the coatings containing hexavalent chromium previously used

Zn or Zn-alloy, chromate passivated (reference system)	- appearance and resistance to zinc corrosion also subject to variance - the systems have not been tested very much in the past - low temperature resistance of the chromate passivation
Zn + "thin-film" passivation	- several years production experience - specially suitable for small diameters - sensitive to fall height - corrosion resistance strongly dependant on geometry of part and design of edges and corners - higher temperature resistance through sealer
Zn + "thick-film" passivation (+ transparent sealer) [1])	- still partial lack of experience with fasteners - rinsing and drying techniques often not optimised - sensitive to fall height - note hardening time for passivation (up to 48h) - corrosion resistance strongly dependant on geometry of part and design of edges and corners and on the process security of the "thick-film" passivation - higher temperature resistance of the passivation
ZnFe, phosphate-coated + black-pigmented sealer [1])	- limited plant availability for ZnFe - sticking together of flat and smaller parts - small parts not true to gauge - internal drive features fill up - VDA requirement "240h DIN 50021-SS without visual alteration" cannot be maintained in series production
ZnFe, black passivated (+ transparent sealer) [1])	- limited plant availability for ZnFe - VDA requirement "240h DIN 50021-SS without visual alteration" cannot be maintained in series production
ZnNi + "thick-film" passivation (+transparent sealer) [1])	- limited plant availability for ZnNi - still partial lack of experience with fasteners - rinsing and drying techniques often not optimised - sensitive to fall height - note hardening time for passivation (up to 48h) - corrosion resistance strongly dependant on geometry of part and design of edges and corners and on the process security of the "thick-film" passivation - higher temperature resistance of the passivation
ZnNi black passivated (+ transparent sealer) [1])	- Limited equipment availability for ZnNi - VDA requirement "240h DIN 50021-SS without visual alteration" cannot be maintained in series production
ZnNi. Passivated + black topcoat (KTL) [1])	- Limited equipment availability for ZnNi - Sticking together of flat and smaller parts - VDA requirement "240h DIN 50021-SS without visual alteration" cannot be maintained in series production

[1]) With electroplated coatings with sealers - especially with pigmented sealers - and topcoats (KTL) there is limited applicability to smaller diameters (especially 2.5 and 3 mm). Using a special process technique the process security can be improved. However equipment availability is very low at present.

Table 2 (continuation): Experience with fasteners with hexavalent-chromium-free coatings compared with the coatings containing hexavalent chromium previously used

	System	Remarks
Zinc-flake systems	Dacromet 320/500© [2]) (reference system)	- currently the most widely-used zinc-flake system - limited suitability for diameters <6mm - by avoidance of a topcoat, lower coating thicknesses or higher corrosion protection possible
	Zinc-flake systems silver-coloured [2])	- several years series production experience Delta Tone© + Delta Seal© - new system Delta Protekt KL 100© partially in series production, mostly in combination with topcoat Delta Seal GZ© - the systems Delta Protekt KL 100© + Delta Protekt VH 301© at trials stage; process parameters must be optimised - new systems Geomet© + PLUS L© partly at trials stage, partly already in series production; process parameters must be optimised - systems of other suppliers (Magni, Kunz) at trials stage - general problems with small sizes (sticking, build-up, out of tolerance) - corrosion resistance strongly dependant on geometry of part, size and handling methods
	Zinc-flake systems black [2])	- at present only Delta Tone© + Delta Seal© in production - for good appearance usually 2 coats of Delta Seal GZ sw© necessary - occasional use of other topcoats (e.g. KTL) - problems especially with small sizes (sticking, build-up, out of tolerance) - VDA requirement "240h DIN 50021-SS without visual alteration" cannot be maintained in series production

[2]) Zinc-flake coatings are - especially when additional topcoats are used - generally critical for diameters =6mm. The process security for small sizes can be improved using special equipment technology in connection with a layer structure suitable for such parts. Plant availability is however at present very low.

3.4 Standardardization

The main aim of VDA test sheets for the various types of surface protection for fasteners is the reduction of the number of these types, a reduction in the variety of standardised parts and quality improvement. This aim should be retained during the changeover to hexavalent-chromium-free coatings .

In this section firstly the experience acquired so far with hexavalent-chromium-free coatings is summarised. Then recommendations for currently realistic corrosion protection requirements are made from the joint point of view of both coating plants and fastener manufacturers.

3.3.1 Technical Aspects of Standardardization

The following fundamental aspects should be particularly taken into consideration during standardisation and when deciding on requirements:

- When the functional characteristics of new hexavalent-chromium-free systems vary considerably from those of the coatings containing hexavalent chromium previously used, the designations used in standards should allow clear differentiation of old and new systems. Here such aspects as traceability and product liability as well as system relevant parameters (e.g. parameters for the assembly of fasteners in production) are of special importance.
- In standards and test sheets realistic requirements must be laid down with respect to the corrosion resistance which can be achieved under production conditions (including tipping, sorting and handling processes). Standards and test sheets are not a suitable way of asserting pressure on the producers of coating materials. An unwanted side-effect in the case of unrealistically high

requirements is that expensive complaints occur. In contrast, with realistic requirements, the changeover to hexavalent-chromium-free coatings can be made more smoothly, equipment can be run continuously, experience can be collected and processes and equipment can be optimised. After a start-up and optimisation phase, the requirements can then be reassessed and adjusted if necessary.

- In standards and specifications for suppliers no particular products or combinations of products should be specified. Especially during the introductory phase for hexavalent-chromium-free coatings, at first realistic requirements should be laid down, against which the new systems can be measured. Then, in ring tests involving coating material producers, fastener manufacturers and automotive companies, systems which appear likely to meet the requirements should be validated and approved. For example, it would involve many electroplating companies in very great trouble and expense, if it were technically possible at all, to use several "thick-film" passivation systems from different suppliers at the same time, even more so when combined with a variety of sealers. Equally zinc-flake coating companies cannot use a multiplicity of systems in one item of plant.

3.3.2 Validation Tests and Production Testing

When laying down tests and test requirements in standards or test sheets a clear differentiation should be made between validation tests and testing during production.

- ***Validation tests*** are once-off acceptance tests. With them the product and system characteristics of new coating systems are tested to particular requirements. A corresponding VDA test sheet is in preparation.
- ***Production testing*** serves primarily process control. Here only one production testing method for each validated coating system should be defined, covering all the particular specialities of the process. The call for the limitation to one testing method results particularly from the fact that the testing requirements for hexavalent-chromium-free coating systems in the coming years will increase enormously through the changeover and initial-sample phases and the testing capacity of coating plants and fastener manufacturers will be at capacity. A corresponding VDA test sheet for the establishment of the requirements for production testing is in preparation.

3.3.3 Number of Different Hexavalent-chromium-free Coating Systems and their Corrosion Protection Requirements

Number of different Hexavalent-chromium-free Coating Systems

With a view to economy and practicality, and taking into account practical experience with fasteners, a large-scale type-reduction of hexavalent-chromium-free coatings to those contained in Table 3 should be made. The choice of the systems named in the table has been co-ordinated with that of the VDA working group *Mechanische Verbindungselemente* (mechanical fasteners).

Table 3: Hexavalent-chromium-free systems for fasteners (co-ordinated with the VDA working group "Mechanical Fasteners)

VDA-No.	System	Corrosion characteristics and examples of application
20	Zn electroplating, transparent passivated	Corrosion protection low (to medium); mainly internal use
25	ZnNi electroplating, transparent passivated	Corrosion protection high; if necessary for exposed positions
30	ZnFe electroplating, black passivated	Corrosion protection medium; not for exposed positions
35	ZnNi electroplating, black passivated	Corrosion protection medium; not for exposed positions
40	Zinc-flake coating, silver-colour	Corrosion protection high; if necessary for exposed positions
42	Zinc-flake coating with organic/inorganic topcoat, silver colour	Corrosion protection very high
50	Zinc-flake coating with organic/inorganic topcoat, black	Corrosion protection medium; not for exposed positions

Corrosion protection requirements

When laying down corrosion protection requirements the following points of view should be taken into consideration:

- The salt spray test to DIN 50021-SS as a widespread standard "quick" test will continue to be in the specification for hexavalent-chromium-free coatings and will remain one of the central corrosion tests.
- The effective corrosion resistance (i.e. the protection remaining at the end of the whole process chain, but before assembly) of fasteners using hexavalent-chromium-free systems is more affected by damage sustained during the part's "prehistory" (handling, transport, tipping, sorting operations, etc), because of the lack of a self-healing effect, than for fasteners using systems containing hexavalent chromium. The influence of such damage must be taken into consideration in the salt spray test in a suitable manner.
- The danger of damage to the surface finish is strongly dependant on the part. Large fasteners are more sensitive than smaller ones. Fasteners with more pointed threads with sharper thread angles (e.g. 30°) are more endangered than those with ISO-metric thread. For hexavalent-chromium-free coatings such part-dependant influences on corrosion resistance must be taken into consideration more than with coatings containing hexavalent chromium.
- For quality assurance and optimisation of new or altered coating processes, the salt spray test to DIN 50021-SS is of only limited value because of the long test periods required (e.g. 480 or 720h), Causes of possible process deviations or unsatisfactory corrosion protection results cannot be recognised in time to react at the right time and make improvements to or optimise the coating process. For this purpose it is necessary to develop a suitable quick test (if necessary taking into account a specified amount of deliberately applied surface damage): in particular for the discovery of weak points in coating, for example variants of the Kesternich-Test or dipping or spraying with acidic media are conceivable. The aim must be, especially during the changeover and introductory phase, to recognise and control unwanted changes in the process (e.g. reduction of chemical stability, lowering of the temperature of passivation baths as a result of dipping large parts with as low temperature, etc) as well as the influence of controlled process changes for optimising the process, within the shortest possible time (if possible within one day). The development of such test methods is a matter especially for the manufacturers of coating materials, but also for institutions and research facilities.

For the coating systems containing hexavalent chromium currently used in large-scale production, almost all the experience and results are available just for salt spray tests to DIN 50021-SS. Table 4 below shows the derived results for corrosion protection requirements which are currently seen as realistic by fastener manufacturers and coating companies.

Table 4: Suggested values for achievable corrosion protection for fasteners (barrel process) in a salt spray test to DIN 50021-SS

	System (film thickness 8-15µm) 1)	**min. resistance to zinc corrosion in h without/with sealer (topcoat)**	**min. resistance to base metal corrosion in h without/with sealer (topcoat)**
electro-plating systems	Zn, yellow passivated (reference system containing hexavalent chromium)	96 / 144	240 / 288
	Zn + "thick-film" passivation, transparent	48 / 120 2)	144 / 240 2)
	ZnFe + phosphate coating + pigmented sealer, black	- 3)/ 144 (S2 to DIN 34804)	- 3)/ 360
	ZnNi + "thick-film" passivation, transparent	120 / 240 2)	480 / 600 - 720 2)
	ZnNi + passivation, black	- 3)/ 120 (S2 to DIN 34804)	- 3)/ 600
zinc-flake systems	Dacromet 320/500 (reference system containing hexavalent chromium)	not relevant	720
	zinc-flake system, silver-coloured	not relevant	480 / 600 - 720 4)
	zinc-flake system, black	- not relevant / 120 (S2 to DIN 34804)	- not relevant / 600

1) The protection period against rusting depends on the film thickness. With higher or lower film thicknesses, higher or lower corrosion protection may occur. (ATTENTION: too great film thicknesses can affect tolerances)

2) Higher corrosion resistance is achieved when pigmented sealers are used.

3) Black finishes on electroplating are at present not to be recommended without sealers.

4) Higher corrosion resistance can be achieved with smaller sizes.

In order to understand this table, the following aspects should be considered:

- The estimates represent experience with fasteners which have been tested immediately after coating. Handling, transport, automated sorting processes and feeding equipment may be expected to lead to a reduction in resistance to both zinc and base-metal corrosion, which, depending on the state of the parts immediately after coating, may be as much as 30%.
- The estimated values can vary up and down depending on the part geometry and on the plant and process technology.
- The estimated values are based on metric screws in the size range M6 - M10. For larger screws with metric threads on account of their weight and for screws with sharp threads (e.g. fasteners for screwing into sheet metal, plastics or wood) the likelihood of surface damage is higher and thus a reduction in corrosion resistance is to be expected.

For metric threads the maximum possible coating thickness is reduced for small sizes. Here the application of sealers and topcoats in particular in a dip/spin process can lead to massive reductions in the gauge fit of threads and internal drive features. For a reliable high corrosion protection whilst simultaneously maintaining gauging, special equipment and coating technology, adapted to the requirements of small sizes, is necessary. This is especially the case for screws with a black finish.

3.4 Status of Introduction

In the following overview of the status of the introduction of hexavalent-chromium-free coatings for fasteners, firstly the most important practical experience from coating companies and fastener manufacturers is summarised. Thisis followed by some details of the status of the introduction, presented in tabular form.

Parallel coating with conventional coatings containing hexavalent chromium and the new hexavalent-chromium-free coating systems

From surveys and from discussions with coating companies and fastener manufacturers the following points of view have been emphasised:

- Especially with electroplating systems, but also with zinc-flake systems, the demand for conventional coatings containing hexavalent chromium is still very large. Only when other major industries follow the example of the automotive and electronic industries concerning the requirements of the EU for freedom from hexavalent chromium will the parallel usage of systems containing hexavalent chromium and hexavalent-chromium-free systems move in the direction of hexavalent-chromium-free systems.
- The legal deadlines of 1.1.2006 (EU Directive on Waste Electrical and Electronic Equipment) and 1.7.2007 (EU End-of-Life Vehicle Directive) mean a relatively long period until a large-scale changeover to the new systems is implemented.
- Parallel coating both using systems containing hexavalent chromium and hexavalent-chromium-free systems makes great demands on coating companies concerning the evaluation of future plant capacity (planning security) and the investments required for rebuilding existing equipment or installing new equipment. Today only coating companies with a very large coating capacity are in the position to be able to change individual lines over completely to hexavalent-chromium-free coating technology. Many electroplaters must rebuild their equipment in such a way that for a period of several years both systems can be used in parallel. As this affects both barrel and rack plating, the investment required is considerable.

  For water-based zinc-flake systems, parallel operation of the currently widely-used Dacromet 320© and Dacromet 500© systems and of the hexavalent-chromium-free Geomet© system (in conjunction with a topcoat, e.g. PLUS L©) in one line is not possible, because the chemicals involved in each case are completely incompatible with each other. Therefore either must such lines be completely changed over to the hexavalent-chromium-free system or new coating lines must be built. This has the effect that in the short term only those coating plants using the Dacromet© system which have several coating lines and sufficient capacity available will be in a position to change over to the Geomet© system in order to be able to operate a hexavalent-chromium-free system. The same is true here that the changeover to a hexavalent-chromium-free system involves both barrel- and rack-coating. Currently the Geomet© system is operated in large-scale production by two coating subcontractors.

  Solvent-based zinc-flake systems have already been available for some time in hexavalent-chromium-free form (e.g. the Delta Tone© system, also in combination with the topcoat Delta Seal GZ©). This system can therefore continue to be used. An alternative system in the form of a product improvement (Delta Protekt KL 100© + Delta Protekt VH 301 ©) can be used in the appropriate plant without needing equipment alterations. The basis system Delta Protekt KL 100© is in use with several coating subcontractors and one in-house facility. Newly- or further-developed solvent-based zinc-flake systems from other suppliers (for example the systems from Magni and Kunz) can also generally be operated in existing equipment.

Coating capacity, quantities and process stability

This aspect still represents one of the greatest uncertainties during the changeover period from coating systems containing hexavalent chromium to hexavalent-chromium-free systems. One of the basic prerequisites for the evaluation of process security and for the optimisation of a new system is the continuous operation of a plant with the new system with sufficient quantities of product under series conditions. This prerequisite only exists in very few cases at the moment.

At the moment the automotive manufacturers' standards or draft standards indeed contain instructions that only hexavalent-chromium-free coatings are to be used for new designs; uncertainties for designers concerning the suitability of the new coatings for special applications and requirements - and this is especially true for fasteners - have not entirely been removed. Thus drawings for new parts often still call for conventional surface finishes referring to the old standards or specifications.

Changeovers during running series production, which would immediately result in having large quantities for coating with the accompanying high plant capacity usage and the opportunity of continuous improvement of the processes have only occurred with fasteners in very few cases.

With respect to the present coating capacity for fasteners for hexavalent-chromium-free systems, the following can be said concerning quantities and process stability:

- ***Electroplating.*** For systems for zinc electroplating, at present mostly equipment is in use for providing a conventional hexavalent-chromium-free transparent or blue passivation (the so-called "thin-film" passivation) together with an additional sealer.

  At the moment only a small number of electroplating facilities have equipment in operation with which "thick-film" passivation can be applied to Zn and Zn alloy plating in series production whilst meeting the technical requirements. The aspect of the equipment technology, mostly remarkable for requiring the passivation baths to be made up new regularly, often leads to not inconsiderable fluctuations in the process and thence in quality. A few electroplating facilities - mainly larger plants which have in the past concentrated on exacting electrolytes (e.g. ZnNi or ZnFe) - have already installed online control and analysis, with which continuous and as a result more economical and technically and qualitatively better process operation is possible.

  As before many firms complain that not enough parts are available to allow processing with the new systems as a continuous operation.

  For screw of sizes < M5 a changeover to hexavalent-chromium-free black coatings is only possible to a limited extent. For electroplated surfaces in particular there is, with very few exceptions, a lack of a suitable chemical method for the creation of "black" hexavalent-chromium-free passivation in a secure process while at the same time maintaining good zinc corrosion resistance.

- ***Zinc-flake systems.*** For zinc-flake systems there is substantial uncertainty surrounding the changeover from the water-based Dacromet© system containing hexavalent chromium to the equivalent water-based hexavalent-chromium-free Geomet© or other hexavalent-chromium-free system because of the lack of continuity in series production. The quantities available for coating with Geomet© at subcontractors can normally be processed in one or two days per week. The fact that the chemicals are not in continuous use and are not continuously dosed can have a negative influence on the life of baths and thus on the quality of the corrosion protection achieved. This latter can only be tested on the finished products after the subsequent coating cycle and therefore possibly too late. Process security and quality could be decisively improved if sufficient quantities were available to enable continuous production to take place.

  With the solvent-based systems there are no problems if the equivalent hexavalent-chromium-free system and the related equipment has already been in use. Special attention is required when fasteners are changed from the Dacromet© system which contains hexavalent chromium to a solvent-based hexavalent-chromium-free system, because this normally involves a change of plant and equipment and possibly of operating technology.

If smaller diameter screws (<M6) are to receive zinc-flake coatings, at present only the operating technology for solvent-based systems can offer the necessary process security for large-scale production. The number of such plants is however still very limited. Equipment for coating screws in this size range with the Geomet© system with the corresponding topcoat (e.g. PLUS L©) is only at the trial stage and is not yet available for series production.

Overview of the status of the change to hexavalent-chromium-free coatings

In an up-to-date overview of the status of the changeover of fasteners from coatings containing hexavalent chromium to hexavalent-chromium-free coatings, the range of parts and especially the sizes play a major role.

The metric fasteners used by the automotive industry for car manufacture in the size range M6 to M16 use to a very large extent (a conservative estimate is 70%) zinc-flake coatings. Here the water-based Dacromet© system accounts for by far the largest proportion of the volume. In the truck sector, where diameters up to M24 are in use, this system finds even more widespread use. Therefore the greatest effort in changing over to hexavalent-chromium-free coating systems is required for the size range M6 - M24. This changeover is only in the starting phase and is taking place successively with the introduction of new parts. For smaller-diameter fasteners (< M6) with metric and other threads the situation is different. Here mainly electroplated or solvent-based zinc-flake surface finishes are in use. For electroplated finishes the changeover to hexavalent-chromium-free passivation, mostly in combination with sealers, is more advanced. The solvent-based zinc-flake systems used for smaller diameters are already mostly free of hexavalent chromium. In this case no changeover is required. Nevertheless currently product improvements and new solvent-based hexavalent-chromium-free systems are already in use. All in all more plant capacity with technology suited for these parts must be created for small screws and nuts.

Table 5: Status of changeover / introduction for hexavalent-chromium-free coating systems for fasteners.

	System	Status of changeover / introduction
electro-plating systems	Zn, yellow chromate passivated (reference system containing hexavalent chromium) + other passivation	approx. 50% of all Zn coatings still yellow, olive or black chromate
	Zn + "thin-film" passivation + transparent sealer	several process lines in series operation (barrel and rack) currently the most employed Zn system
	Zn + "thick-film" passivation (+ transparent sealer)	several process lines in operation since 1998 (barrel and rack)
	ZnFe, phosphate-coated + pigmented sealer black	in use for several years in one plant (barrel) only low capacity
	ZnNi + "thick-film" passivation (+ transparent sealer)	several lines in series operation since 2002
	ZnNi + black passivation (+ transparent sealer)	a few lines in series operation since 2002
zinc-flake systems	Dacromet© 320 / 500 (reference systems)	currently by far the most widely used zinc-flake system for the range M6 - M24
	zinc-flake systems silver-coloured	Delta Tone© + Delta Seal© system in very widespread use for series production
		Delta Protekt KL 100© in series operation with several coating subcontractors and one in-house operation, Delta Protekt VH 301© undergoing trials / being introduced
		Geomet© + topcoat (e.g. PLUS L©) in series operation at two coating subcontractors
		Further systems from various manufacturers at the development / trials stage
	zinc-flake systems black	Delta Tone© / Delta Protekt KL 100© + Delta Seal GZ sw© systems in series production
		further systems with black topcoats from various manufacturers at the development / trials stage, in some cases already in series use.

3.5 Costs

When examining costs within the scope of a changeover from coatings containing hexavalent chromium to hexavalent-chromium-free coating systems a differentiation must be made between

- costs of coating
- part costs
- other costs

In detail the following aspects play a role in a cost comparison:

- A cost comparison must relate to like requirements (e.g. corrosion resistance). From the presentation on the previous pages it will be clear that to reach requirements comparable to those of systems containing hexavalent chromium, considerably more effort and expense (chemicals, handling, process and plant technology, etc.) is required for hexavalent-chromium-free systems.

  Some automotive companies have increased their requirements in comparison with the former coatings simultaneously with the changeover of their standards to hexavalent-chromium-free systems.

- Often the current operation of equipment (e.g. discontinuous operation of individual items of equipment) for hexavalent-chromium-free coatings does not yet represent future planned operation. This present method of working is much more expensive than that envisaged for the future.
- The investments necessary to meet the technical requirements (see also the in-depth presentation in section 3.2) will affect costs, especially during the initial stages of the changeover to the new systems.
- When suitable lubricant systems are integrated into sealers or topcoats for the new hexavalent-chromium-free electroplating or zinc-flake systems, and if in the fulfilment of coefficient of friction requirements no other interference with other functional characteristics of the fastener is to occur, the currently usual additional operation of lubricant application with coloration can be omitted.
- During the changeover phase of new coating systems to large-scale production, all involved must expect a greatly above-average increase in testing as compared with the present to ensure process capability as well as corrosion resistance and other important requirements for fasteners (see section 3.1.2). For this, investment must be made in new corrosion testing equipment and in new processes for testing specific requirements. It would be a good idea here to form families of parts with similar requirements (e.g. parts subject to raised temperatures, dynamically loaded fasteners, fasteners for sheet-metal or plastics (application torque and torque to stripping), etc) and thus reduce testing effort.
- In some cases not inconsiderable cost optimisation is conceivable, if certain compromises can be made. This can be elucidated in the following example:

  A 3 mm screw is currently supplied in the condition "electroplated Zn, black chromate passivation". It has to be converted to a hexavalent-chromium-free variant. A black hexavalent-chromium-free passivation system does not exist. The variant ZnFe, phosphate-coated + black-pigmented sealer does not come into question because of the thick film involved and the resulting problems of thread gauging. The following alternatives can be considered:

  - Conversion to ZnNi black;
    Price increase: approx. + 200%
  - Conversion of the fastener material to stainless steel with black surface coloration (no zinc corrosion, no rusting);
    Price increase: approx. + 400%
  - Abandonment of the black finish and conversion to Zn + "thick-film" passivation:
    Price reduction : approx. - 20%

Table 6 below shows a comparison of costs of several hexavalent-chromium-free coatings with the coatings containing hexavalent chromium used hitherto. Here the following must be heeded:

- The relationships are rough values on the basis of M8 fasteners in the middle range of coating thickness 8-15µm.
- The factors are an indication of the increase in the plain coating costs, with which it must be reckoned with for the changeover from coating types containing hexavalent chromium to hexavalent-chromium-free variants.

Table 6: Cost comparison of coating systems containing hexavalent chromium and hexavalent-chromium-free coatings in the form of cost factors (rough guide)

	Conventional systems containing hexavalent chromium	**Conventional and new hexavalent-chromium-free systems**	**Cost factor**
electro-plating systems	Zn, yellow chromate passivation 1) 2)	Zn + "thin-film" passivation + transparent sealer	**1,2 - 1,4**
	Zn, yellow chromate passivation 1) 2)	Zn + "thick-film" passivation	**1,3 - 1,5**
	Zn, yellow chromate passivation 1) 2)	Zn + "thick-film" passivation + transparent sealer	**1,5 - 1,7**
	ZnFe, black chromate passivation 1) 2)	ZnFe, phosphate coated + black-pigmented sealer 2x	**1,9 - 2,1**
	ZnFe, black chromate passivation 1) 2)	ZnFe, black passivation + transparent sealer	**1,2 - 1,5**
	ZnNi, yellow chromate passivation 1) 2)	ZnNi + "thick-film" passivation + transparent sealer	**1,2 - 1,4**
	ZnNi, black chromate passivation 1) 2)	ZnNi + black passivation + transparent sealer	**1,2 - 1,3**
zinc-flake systems	Dacromet© 320 / 500 1) 3)	Geomet© + PLUS L©	**1,3 - 1,4**
		Delta Tone© + Delta Seal GZ©	**1,3 - 1,4**
		Delta Protekt KL 100© + Delta Protekt VH 301©	**1,3 - 1,4**

1) basis: screw M8
2) basis: coating thickness 8-15µm
3) 3x coating

The coating costs make up different percentages of the total costs of different fasteners. The percentage of the total costs can be of the order of 15- 30%, in extreme cases as much as 40%: This depends on whether it involves a simple standard screw or a complex fastening element and on whether these fasteners are combined with simple or expensive coating systems.

Additional costs for process measures to ensure sufficient corrosion protection at the end of the process chain (e.g. measures to minimise damage to the surface finish such as reducing fall heights) and for raised testing effort are difficult to estimate at present.

For these reasons it will normally not be possible to make cost adjustments on a global basis. This must be done for each individual fastener.

3.6 Summary

The current status of the changeover to hexavalent-chromium-free coatings can be summarised as follows:

- The members of the German Fastener Association and the coating companies with whom they are co-operating are vigorously pursuing the changeover to hexavalent-chromium-free coatings and have accepted the associated challenges.

- To achieve corrosion resistance comparable to conventional coatings containing hexavalent chromium, the process security of the new hexavalent-chromium-free systems must be worked on. Apart from aspects of process and application technology, process fluctuations can be mainly attributed to the fact that the new hexavalent-chromium-free coatings react in a much more sensitive fashion to variations in layer thickness of, and to surface damage to the new passivation types and/or their protective sealers or topcoats.

- The main task is the development of suitable technology for effectively reducing the danger of surface damage which requires measures in the whole process chain from the coating plant to assembly of the fasteners and which takes into account experience made so far. This is being worked on intensively.

- The application of new hexavalent-chromium-free coatings almost always involves extra expense in comparison with conventional coatings containing hexavalent chromium. Also the testing effort to measure the corrosion resistance and other important characteristics for fasteners is greatly increased.
- The greatest expense is the changeover of the size range = M6 from coatings containing hexavalent chromium to hexavalent-chromium-free coatings.
- For electroplated zinc and zinc alloy coatings the currently available combinations of conventional hexavalent-chromium-free transparent passivation and suitable sealers is a satisfactory alternative to chromate passivation.
- The quantities of fasteners requiring the new hexavalent-chromium-free coatings is, particularly in the size range = M6, not yet sufficient everywhere to allow optimisation of series production in the whole process chain.
- The uniform standardisation of requirements for the new systems within the automotive industry (VDA) and the electronics industry as well as harmonisation with the specific characteristics of hexavalent-chromium-free coatings must be completed speedily so that planning security can be achieved and the necessary investments made to ensure sufficient capacity at both the manufacturers of coating materials and the coating industry.
- The whole process for the changeover from coatings containing hexavalent chromium to new hexavalent-chromium-free coating systems carries not inconsiderable costs, including new chemicals, altered and more comprehensive process technology, additional measures for fulfilling special requirements and logistic measures (traceability, product liability, etc.).
- Cost increases also result from the required parallel coating with systems containing hexavalent chromium and with hexavalent-chromium-free coating systems. This results in increased demand on logistics, increase in number of parts and smaller production quantities.

4. Suggestions for Further Action

The members of the German Fastener Association, in partnership with their most important coating subcontractors, have made it their task to take on the currently existing problems with the changeover to hexavalent-chromium-free coatings for fasteners. By working out constructive suggestions, these problems should be successively removed, the systems should be made more secure and thus the changeover should be accelerated on a broad front. At the same time the potential and perspectives of new hexavalent-chromium-free coatings, which coatings containing hexavalent chromium cannot offer, should be presented. Some of these suggestions are elucidated below.

4.1 Assurance of Minimum Requirements for Corrosion Protection Electroplating

The basic platings Zn, ZnFe and ZnNi have not changed materially. The differences have their root in the new hexavalent-chromium-free passivation systems and sealers and their interaction with the basic plating. Process variation and damage to the passivation and sealing films affect in the first instance zinc corrosion resistance. This has been shown in all the tests which have so far been carried out. As this situation is not likely to change in the short or medium term, the following recommendation is made for electroplated finishes:

- As far as zinc corrosion resistance is concerned, compromises must be made in the short and medium term. At the same time an attempt must be made to achieve in every case the requirements for resistance to corrosion of the substrate metal. As the resistance to rusting is mainly proportional to the layer thickness of the basic layer, this relationship can be used to lay down minimum layer thicknesses for Zn-, ZnNi- and ZnFe-plating in such a way that, even in the worst case of a total failure of the passivation, sufficient reserves of rust resistance are maintained. In order to improve the current situation, as presented in Table 4, the following minimum thicknesses should be envisaged:

- Zn-plating: min. 15µm
- ZnFe plating: 8 - 15 µm (max 15µm desirable)
- ZnNi plating: 8 - 15 µm (max 15µm desirable)

For ZnNi and ZnFe the plating thickness should not be increased above 15µm, because otherwise the risk of peeling becomes too large. However for the time being - if no functional aspects speak against it - a sealer should be applied additionally to the passivation. In any case care should be taken - especially with smaller diameters - to make sure that tolerance to thread gauge is maintained (see Table 1). This can involve - if it has not already taken place - a change of thread tolerance from 6g to 6e. If for small screws the layer thickness which would be required to give sufficient corrosion protection cannot be used, a more expensive system must be used (e.g. ZnNi instead of Zn).

- The method of increasing the minimum layer thicknesses of the basic layers involves increased costs in the first instance, but offers the following advantages and possibilities:
  - hexavalent-chromium-free coatings can be implemented on a large scale immediately where resistance to rust is the chief requirement.
  - even for users who for functional reasons do not wish or are not able to use additional sealers a certain additional security is given.
  - in large-scale production the weak points in the application of hexavalent-chromium-free coatings and the problems of mechanical damage can be continually removed or at least minimised. Thus zinc corrosion resistance will be continually improved and variances reduced.
  - with increasing process security the basis layer thicknesses can be reduced. This improves the economics of the whole process and in the longer term cost adjustments can follow.

Zinc-flake coatings

The changeover of the zinc-flake Dacromet© coating system, which contains hexavalent chromium, to new alternative hexavalent-chromium-free systems is connected with several alterations. Whilst with the Dacromet© system a good stable corrosion resistance with self-healing effect can be achieved with relatively thin layers, mainly through the use of chromates, hexavalent-chromium-free systems are free of chromates. This requires different chemistry and the reduced corrosion protection, in particular the lacking self-healing effect, must normally be compensated for with a topcoat. As especially for water-based hexavalent-chromium-free systems the new chemistry as well as the application and process parameters still have to be optimised, there are at the moment still some uncertainties which show themselves in the form of fluctuations in corrosion resistance, especially that to rusting. Additionally, the topcoats used at present for stabilising the corrosion protection are, because of their hardness, sensitive to shock. Fluctuating film thicknesses or damage to the topcoat lead to further fluctuation in the life of the corrosion protection. Because of these continuing uncertainties the following procedure is suggested for fasteners with hexavalent-chromium-free coatings:

- In order to reach the required corrosion protection of 720h in a salt spray test to DIN 50021-SS, instead of the usual application for series production (2x coating with the basis-coating + one coating of topcoat), for the time being 3x coating with the basis coating + additionally one coating of topcoat should be envisaged. If necessary the layer weights must be adjusted again. Attention must be paid however to maintenance of thread tolerances - especially for small sizes.

  Note: for an attractive appearance of "black" zinc-flake coatings, the topcoat must be applied twice.

- The increasing of thickness from a 2x to a 3x coating with the basis coating leads, as with electroplated finishes, in the first instance to cost increases, but it does offer the following advantages:
  - Rust resistance is increased
  - The process fluctuations currently experienced, which appear to be larger in water-based systems than in solvent-based ones, can be to a large extent reduced.
  - Also process fluctuations resulting from damage to topcoats can be largely compensated.
  - New hexavalent-chromium-free zinc-flake coatings can be used in larger quantities. In series production the chemistry and the applications parameters can be optimised and the danger of damage can be reduced.
  - With increasing process security the layer thicknesses can be successively reduced and thus the whole process can be made more economical and cost-effective.
- Where it is not absolutely necessary for decorative purposes, the use of black coatings should be avoided for the present for all hexavalent-chromium-free coatings, because of their currently still unsatisfactory resistance to zinc corrosion.

4.2 Further Suggestions for rapid series implementation

In addition to the suggestions outlined in section 4.1, the following methods are suggested in connection with changing from coatings containing hexavalent-chromium-free to hexavalent-chromium-free coatings:

- Fasteners should be chosen from current production which are not important for safety and which could be changed from coatings containing hexavalent-chromium-free to hexavalent-chromium-free coatings without great problems. In this way the quantities of parts for coating urgently needed for the optimisation of the new systems could be greatly increased.
- If possible families of parts should be formed (e.g. from such areas as body-in-white, engine, suspension, etc.) where, because of their similar requirements, initial samples could be presented together.
- Regular training sessions and seminars should be held. The German Fasteners Association, together with coating companies and fastener manufacturers, offers to carry out such events either centrally or, if required, at automotive companies and their suppliers. In this way information about the status of changeover to hexavalent-chromium-free coatings can be exchanged on a wide front and discussions with all those involved from purchasing, technical and design departments can take place.

The German Fastener Association views this status report as a basis for an intensive dialogue with users from the automotive industry and their main suppliers. Questions, constructive ideas and contributions can be directed to the association's headquarters at any time.