

# Second **International symposium on** Microlayer Corrosion Protection Systems

A report by Dörken MKS-Systeme GmbH & Co. KG



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Dörken MKS-Systeme GmbH & Co. KG held its second international symposium on microlayer corrosion protection systems (MKS) at the Westfalenhallen Congress Centre in Dortmund on 27th and 28th October 2005. The 250 symposium attendees, from more than ten different countries, were presented with an extensive programme of talks and presentations. The core of the symposium, however, was dedicated to the differentiated requirement profile I and the broad application spectrum of chromium (VI)-free zinc lamella systems.



Car manufacturers across the world use microlayer corrosion protection systems on fasteners, springs and other functional parts. However, the use of these systems is not limited to this sector, but extends to all areas where corrosion and corrosion protection are of central importance [1]. Dörken MKS-Systeme GmbH & Co. KG is a manufacturer of microlayer corrosion protection systems. Being an independent subsidiary of Ewald Dörken AG, the company specialised in the development and manufacture of chromium (VI)-free corrosion protection solutions right from its beginning and has been dedicating its workforce of 80 employees to this purpose for many years.

Its DELTA-MKS® 100 series consists of functional coatings without cathodic protection, e.g. for phosphated steel bases, zinc diecastings and stainless steel. It is designed for applications where gliding properties, temperature resistance and optical properties take precedence over corrosion protection. The DELTA-MKS® 2000 series has been specifically developed to provide optimum corrosion protection for objects subject to high levels of chemical and thermal stress and is a functional duplex sealing system for electro-plated bases. The DELTA-MKS® 3000 series zinc lamella systems provide high-performance corrosion protection that is also suitable for use on high-strength steels, as it excludes hydrogen-induced stress corrosion cracking during the coating process.

In 2000, Dörken MKS-Systeme GmbH & Co. KG introduced a range of new inorganic corrosion protection systems. One of these, DELTA-PROTEKT® KL 100, is a silver-coloured zinc lamella basecoat that is suited for use on (high-strength) steels and cast steel. Due to the sacrificial protection provided by the zinc contained in this basecoat, a dry layer of only 5 to 15 µm will provide cathodic protection for a broad range of parts, e.g. such as bolts larger than M6.



Karl E. Dörken (left) and Hans W. Belz

The efficiency of this system is increased by the use of both zinc and aluminium flakes that overlap and hence create an effective barrier. However, the chemical and thermal resistance of this system is still further increased when used in combination with the DELTA-PROTEKT® VH 30x-series topcoats, which are water-dilutable and silicate-based resealers that are transparent when used in layers of 1 to 3 µm [1, 7].

The symposium was opened by Dipl.-Ing. Klaus Kayser following a welcome speech by Karl E. Dörken (member of the board of Ewald Dörken AG) and a review of more than 25 years of MKS's provided by Dipl.-Ing. Hans W. Belz (management board of Dörken



*MKS-Systeme GmbH & Co. KG*). *Dipl.-Ing. Klaus Kayser* started his opening speech with an overview of the production and chemical properties of zinc and zinc compounds. The corrosion protection provided by galvanized surfaces is primarily due to the formation of passivating zinc oxide, zinc carbonate and zinc hydroxide during galvanizing. Zinc lamella layers were first used at the beginning of the 1970's. Chrome can occur in a range of oxidation stages in chemical compounds, although it primarily occurs as chromium (VI) and chromium (III). The high toxicity of chromium (VI) compounds is primarily due to its high solubility and its ability to penetrate human cells.



### **The use of cadmium in the aircraft industry**

*Alain Viola*, manager of the materials and application technology department at *Messier Bugatti*, Molsheim/ France, reported on the newly founded *Harmony Advanced Surface Technologies* syndicate based in the Alsatian town of Duppigheim. This industrial consortium consists of seven companies and views itself as a comprehensive platform for the research and development of metal surface treatments. It endeavours to become a driving force for innovations directed at implementing legal requirements relating to environmental protection. Its areas of interest in this respect include [1-2]:

- Development of alternative methods to replace the use of chromium (VI) on aluminium and magnesium surfaces and in hard chrome plating and passivation;

- Development of a replacement for cadmium for use in connecting and structural elements;

- Avoidance of cyanide in silver, rhodium and palladium plating.

The development of a replacement for the use of cadmium in the aircraft industry is subject to a highly complex and sensitive list of requirements, which includes consideration of the following factors: Corrosion, hydrogen embrittlement, paint adhesion, electrical conductivity, thermal properties, layer homogeneity, substrate adhesion, compatibility with particular coatings and platings, aging behaviour and repair options. Potential alternatives to cadmium listed by *Viola* included zinc/iron, zinc/nickel, aluminium, aluminium/magnesium, zinc lamella/aluminium. Typical areas of application include exposed structural components and assemblies such as aircraft landing gear components, e.g. connecting and clamping bolts on rims [2].

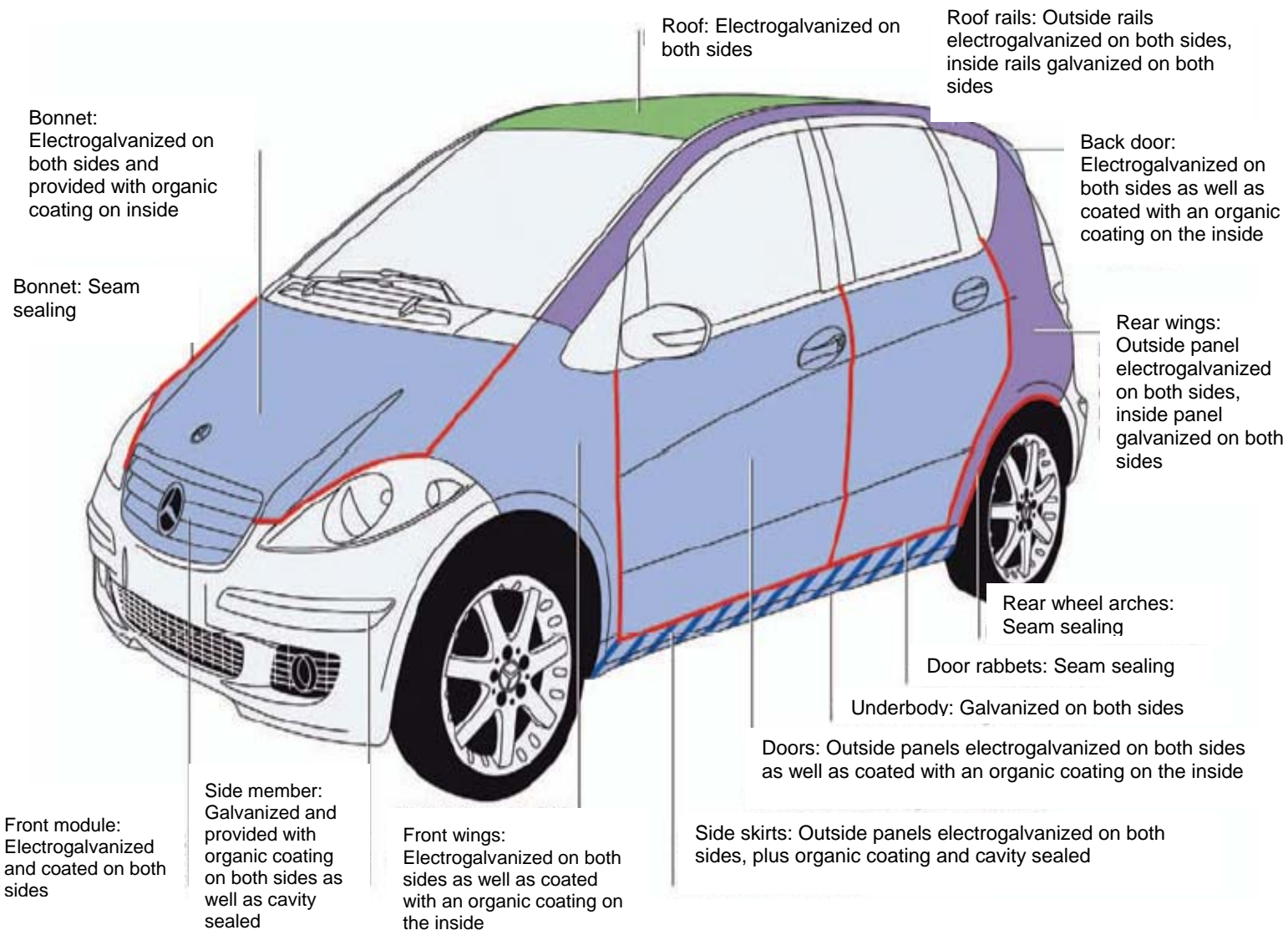


### **Chromium (VI)-free fasteners**

*Dr. Stefan Beyer*, head of R&D at *ABC Umformtechnik GmbH & Co. KG*, Gevelsberg, dedicated his presentation to the elimination of chromium (VI)-containing coatings for mechanical fasteners. This is a highly topical issue as the EC directive on electronic waste prohibits the use of chromium (VI) as of 1st July 2006 and the EC directive on End-of-Life vehicles prohibits its use in vehicle corrosion protection in vehicles with a total permissible weight of 3.5 tons as of 1st July 2007. There is furthermore a great likelihood that other industries will join in the ban on chromium (VI).

German car manufacturers are already committed to using chromium (VI)-free systems for all new vehicle components. However, the conversion of existing large-scale series-production runs is planned for the beginning of 2006, and the completion of that conversion process is scheduled for the middle of 2006.

The *Surface Protection System* working group of the Association of German Manufacturers of Fasteners (*DSV*) is currently developing



**The Mercedes Benz A-class – corrosion protected by galvanising, cavity preservation and seam sealing**

measures for increasing the safety and reliability as well as to speed up the introduction of the new chromium (VI)-free systems and provides regular, up-to-date information regarding the current state of the conversion process. Its work is characterised by its close cooperation with coating service providers and the *Mechanical Fasteners* working group of the German Association of the Automotive Industry (VDA) [3].

The aim of all work related to the substitution of current chromium (VI)-containing systems is to develop and provide equivalent corrosion protection that simultaneously fulfils other important functional properties. Chromium (VI)-free passivations – possibly used in combination with additional sealants to increase white rust resistance and/or to optimise red rust resistance – are highly suited for use as an alternative to galvanically induced, self-healing chromating systems. So-called reactive sealing methods also provide a certain self-healing effect, which enables the impact of damage to white rust resistance to be reduced. However, the sealant may have to be applied in thicker layers to achieve a level of corrosion protection equivalent to that provided by chromium (VI)-containing coatings. Another alternative

to zinc plating is the use of high-quality systems, such as zinc alloy plating. Water-based zinc lamella systems such as *Dacromet®* will also have to be substituted with suitable alternatives. However, any solvent-based zinc lamella systems currently used that are already chromium (VI)-free do not have to be substituted [3]. When analysing corrosion protection characteristics, the stresses components are characteristically exposed to when being handled and during transport must also be taken into consideration. These stresses are component-specific, i.e. they depend on the respective fastener dimensions and weight. These are issues that are also being addressed by the DSV, which is currently drafting a corresponding directive on transportation processes and the prevention or reduction of negative effects on corrosion protection. When it comes to testing, one of the most important disadvantages of conventional corrosion testing are the long test times that are often required. Components produced by the automotive industry are often installed in vehicles long before significant corrosion testing is completed, and this is another area where the DSV is involved with conducting a trend-setting



research project, i.e. on the subject of short-term corrosion testing. This is an area of research that is particularly demanding because it requires that natural corrosion processes are accelerated during testing without changing any of the physical and chemical corrosion processes involved (also see *Protection of components and surfaces against wear and corrosion* in [8]).

Another challenge, equal in magnitude to that of producing efficient corrosion protection, is the need to ensure that coatings meet many of the other functional property requirements associated with coated components, such as abrasion and wear resistance, friction coefficients and sliding properties.

Thick protective coatings, for example, can influence the accuracy to gauge and are problematic in particular for small components. The application of additional sealants or coatings always presents the danger of localised, excessive build up of coating, which in turn can cause mechanical damage, e.g. on the threads of small fasteners or other points at which force is applied. Since the thickness of any coating and plating directly affects the tolerances of the relevant geometries, it may become necessary to change the tolerances of metric threads from, e.g. 6g/6H to 6e/6G [3].

### ***Transport, handling and assembly cause mechanical wear***

Another important functional property is the abrasion behaviour of components, which is heavily influenced by the type of sealants and coatings used. The mechanical contact between parts created during transport and handling (pouring, automatic sorting, feeding) gives rise to wear, which in turn can affect the corrosion protection. Abrasive particles can, however, also seriously affect automated assembly systems and electronic components during operation. Abrasion resistance testing specifications

for alternative coatings are therefore urgently required and will be integrated into the forthcoming DSV directive [3].

Friction coefficients are another important functional property and have a significant impact on the tightening torque/clamp force characteristics and the breakaway torque ratio of screw fasteners. Tightening torques/clamp forces are tested in accordance with DIN EN ISO 16047, VDA 235-203 and DIN 256–27/–28.

Coatings and sealings are permitted to contain lubricants, thus removing the necessity of having to apply these separately. When integrating lubricants into a sealing, the extremely reproducible friction characteristics of the integrated lubricants can be used to reduce the spread of the friction coefficients. However, all of the parameters previously used for screwing in fasteners will have to be carefully monitored and adapted where required when replacing the current coating procedures used in series production. There is a possibility that the friction coefficients will increase when screwing in fasteners, which may give rise to stick/slip effects. When exposed to temperatures of up to 150 °C, organic constituents of or lubricants such as PTFE in passivations, sealings and coatings can reduce the loosening torque of fasteners – an effect that is particularly significant in dynamic transverse loaded fasteners [3-6]. Lubricants also affect other functional properties and, irrespective of whether integrated into sealings or applied separately, they also affect the ability of applying paint to and the electrical conductivity of components, which in turn impacts on their weldability [3].

The various effects associated with the legally required elimination of coatings containing chromium (VI) requires a comprehensive review of the entire process-chain involved in coating production. A review such as this would have to include coating material manufacturers,

coating service providers and manufacturers of fasteners, as well as a detailed assessment of the potential effects of different surfaces on transportation and assembly processes.

A review of these issues may focus on careful transportation and a reduction of potential drop heights in parts handling, as well as potential process modifications, such as the performance of more extensive analytics and online monitoring during the coating process where required. Many of these issues can be clarified in advance by conducting corresponding tests; others are only open to meaningful analysis once tested in continuous series production. This applies in particular to long-term and other variables influenced by large volumes, such as the consistent quality and stability, with regard to impurities and carry-overs, of the chemicals used [3].

The increase in costs associated with the conversion to chromium (VI)-free systems is a result of the additional expenses required for process and plant technologies and the adaptation of existing logistics systems and handling operations. In addition to the one-off investment costs, it is the additional costs for chemicals that account for cost increases of up to 100 percent. However, there is also potential for savings by, for example, using integrated lubricant systems, which removes the need for any additional process stages [3].

The symposium also included a number of presentations that provided information on additional areas of application and requirement profiles for zinc lamella coatings.

*Dipl.-Ing. Rolf Becker* (plant manager at *Knipping Verbindungstechnik GmbH*, Kierspe) reported on the requirement profiles of chromium (VI)-free surface protection systems for fasteners that require special handling, transport and assembly processes.

*Dipl.-Wirt.-Ing. Henning Brandenburger* (head of the Technical Bureau of *EJOT GmbH & Co. KG*, Bad Laasphe) and *Dr. Uwe Hasselmann* (head of QM/R&D/logistics, *August Friedberg GmbH*, Gelsenkirchen) gave a joint presentation on *DELTA-MKS®*-coated fasteners with extreme dimensions.

This included an examination of the particularities associated with direct screw coupling, coating requirements, typical areas of application and the limitations presented by extremely short fasteners that are no more than a few millimetres long, during the first part of their talk.



R. Becker (left) and H. Brandenburger



These extremely small fasteners are frequently used in the consumer-electronics sector, e.g. in mobile phones and electronic vehicle components.

The second part of the talk was dedicated to fasteners for wind energy plants ranging from M30 to M64 – a vast step up from the extremely small fasteners discussed previously. Fasteners used on wind energy plants are subject to complex stress profiles that are characterised by high static loads, stochastically distributed dynamic loads and extreme temperature changes.

The high level of corrosive stress offshore plants are exposed to is another vital factor to be taken into account. Wind energy plants are furthermore assembled at the site of installation and assembly is often associated with tight deadlines. Every connection must be able to be fastened manually, despite the large size of the components involved. Stiff threaded connections are therefore out of the question, and these fasteners are therefore also associated with strict restrictions regarding permissible drop heights, friction pairing, thread tolerances and layer thickness variations.

*Dr. Heinz Herzog* (H&S International Consulting & Service GmbH & Co. KG) gave a lecture on the European VOC directive and environmental protection. *Josef Schoppig* and *Frank Turck* reported on the work performed by the working committee of Qualicor MKS and presented findings from salt spray tests performed on black surfaces.

*Sharon Caruso* (General Motors) talked about strengthening the collaboration for the achievement of excellence in vehicle construction across the world. A contribution by *Massimiliano Testa* (A. Agrati S.p.A.) also focussed on the automotive industry and dealt with the production of fasteners for the automotive sector and the performance of surface coatings. *Fred Schultz*, on the other hand, provided an insight into the US market with a presentation about the various areas of application of zinc lamella systems in the USA.



*Reinhold Messner*, the extreme sportsman and former EU parliamentarian, had been invited by *Dörken MKS-Systeme GmbH & Co. KG* as a guest speaker and special surprise. *Messner* has successfully combined his career as one of the greatest mountaineers of all time, known for his perilous Himalayan and Arctic expeditions, with a keen insight into risk management and management motivation in industrial concerns.

It is our mental strength that enables us to survive, our enthusiasm and the will to survive, that motivate us to continue pursuing our dreams, so *Messner*. -C. B.

Nakhosteen-

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