ECO-FRIENDLY CORROSION PROTECTION BASED ON HYBRID NANO-MATERIALS

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Abstract:

Within a joint project scientists of Fraunhofer ISC, Fraunhofer IWU and IKS have worked together to develop an ecologically sustainable concept for a corrosion protection method based on hybrid nano-composites and have evaluated the process as an alternative to environmentally harmful chromating on top of galvanized steel panes. Different types of zinc-plated surfaces have been investigated. Selected hybrid polymer nano-composites have been applied on various zinc surfaces in a dip coating process and finally provided with a standard polyester powder coating.

The performance of these samples have then been compared with relevant, commercially available anti-corrosion systems in defined test procedures in order to assess the adhesion strength and the degree of corrosion of the laminated composites. In addition, the deformability behaviour in bending and deep-drawing processes has been examined.

Especially on electro-galvanized surfaces, samples with the newly developed hybrid nano-materials exhibited good adhesion and corrosion-protection characteristics after 360 h in the salt spray test (DIN EN ISO 9227-NSS). Test samples coated with these hybrid materials and covered with polyester powder could easily be bended and deep-drawn, no matter what type of galvanization had been applied. The nano-materials on the whole displayed a tolerant behaviour against the tested galvanizations and showed levels of performance comparable to commercial systems of yellow chromating and Cr(III)-based passivation.

Keywords:

“pre-treatment”, “eco-friendly”, “chromate-free”, “sol-gel”, “hybrid nano-composites”

Introduction

The processing of galvanized steel panes has covered a huge market for chromium-(VI) compounds. For some time now, however, hexavalent chromium compounds have been classified as toxic and carcinogenic and therefore have to be replaced by alternative materials. For example, under the EU directive on "end-of-life vehicles" [1], new vehicles are no longer allowed to contain any chromium-(VI) compounds since mid-2007. The EU directive "restriction of the use of certain hazardous substances in electrical and electronic equipment" [2] has claimed chromium-(VI) free devices as early as 2006.

During the last years, several chromium-(VI) free protective coatings have made their way into industry – but they still do not render the same degree of protection as chromium-(VI) plating, and cannot be used on all types of metal surfaces [3-5]. Not least for these reasons and despite the urgent need for action, no alternative method providing chromium-(VI) free corrosion protection has succeeded in gaining overall acceptance yet.

Given this situation, scientists of Fraunhofer ISC, Fraunhofer IWU and IKS have worked together within a joint research project to develop an ecologically sustainable concept for a corrosion protection method based on hybrid nano-composites and have evaluated the process as an alternative to environmentally harmful chromating as well as to commercial substitutes. Industry supported the project through a committee (named "pbA", i.e. an industrial advising committee) composed of representatives from 12 companies with activities in the fields of steel production and processing, surface engineering and nanotechnology.

Metal substrates investigated

In automobile manufacture, electro-galvanized steel sheet is mainly used for the outer skin, whereas hot-dip galvanized steel sheet is used for the vehicle interior. In building and appliance industries, mainly electro-galvanized materials are applied (see fig.1).

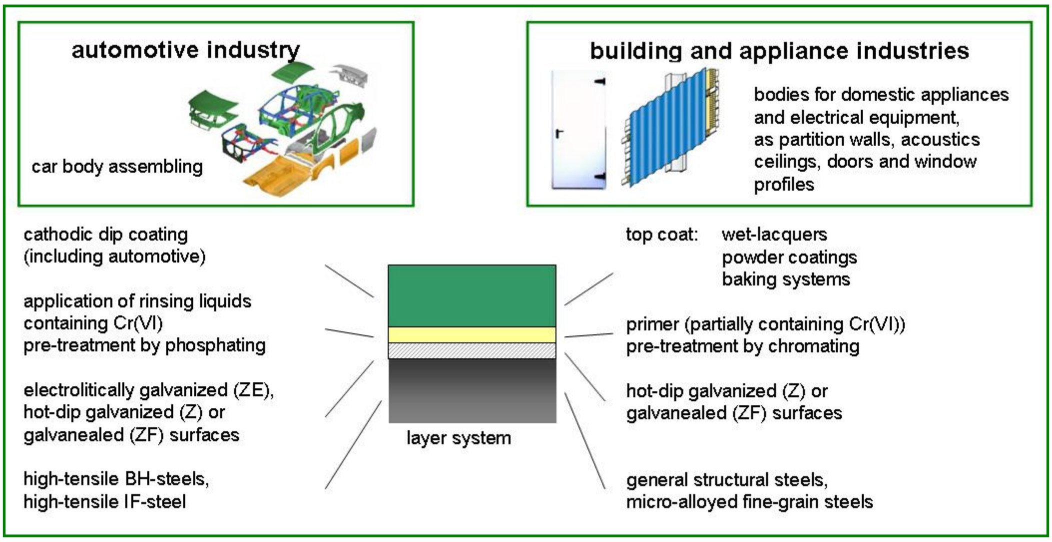


Figure 1: Surface-treated refined cold rolled strips in different applications

Hence, based on the relevant applications, the following five galvanized steels out of the product range of the pbA members have been chosen for the investigations: electro-galvanized coil material, acidic electro-galvanized sheet material, alkaline electro-galvanized sheet material, hot-dip galvanized coil material and hot-dip galvanized sheet material.

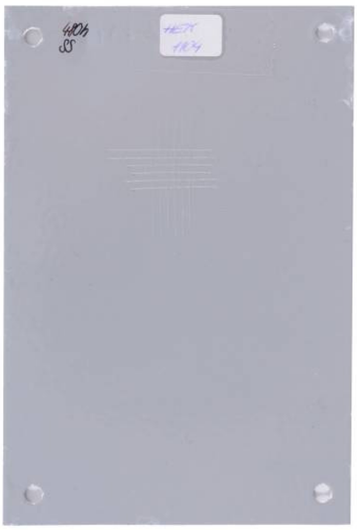
Composite layer systems with hybrid nano-materials

A variety of hybrid polymer based nano-composites with good adhesion on various metal surfaces [6-9] have been investigated as prospective substitutes for chromium-(VI). These hybrid sol-gel systems were applied to various zinc surfaces in a dip-coating process and then provided with a standard powder coating. The behavior of these samples was then examined in defined testing procedures, such as the cross cut test (ISO 2409), the boiling test (DIN 58196-2/C60), the condensated water test (DIN EN ISO 6270-2) and outdoor weathering (DIN EN ISO 2810; up to a maximum period of two years) to assess, in particular, the degree of corrosion and the adhesion strength of the laminated composites. In addition samples, some of which had been damaged deliberately by scratching, were subjected to the extreme conditions of the salt-spray test (DIN EN ISO 9227-NSS) in which they were exposed to an aggressive moist climate for a period of 480 hours.

The adhesion between the zinc layer, the hybrid nano-composite and the covering paint was good to excellent for all the investigated layer systems (cross cut value Gt 0), irrespective of the type of galvanization, even after exposure to wet climates like the boiling test or the condensated water test. No corrosion, either, has been found under these test conditions on any of the tested samples. In the end, the composite layer systems also resisted a two-years' outdoor weathering without damage.

Only after the particularly severe stress of the salt spray test, and only on test samples which had been additionally damaged by scratches, differences were found in the corrosion resistance of the coated samples. In this test, different levels of corrosion were observed, depending not only on the investigated hybrid nano-composites, but also on the type of galvanization. All the sol-gel systems with a high proportion of inorganic components proved especially corrosion-resistant under these conditions. In particular, two hybrid polymer sol-gel systems on the basis of silane-aluminum and silane-aluminum-zirconium, respectively, showed the best characteristics (fig. 2) and were therefore selected for further investigations.

a)



b)

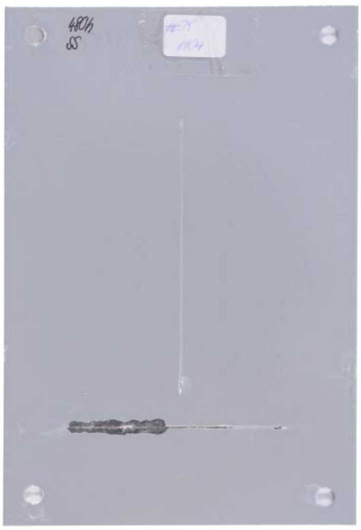


Fig. 2: Alkaline electro-galvanized sheet material; pretreated with hybrid nano-composites and covered with a commercial powder coating after 480 hrs in the salt-spray test; **a**) test sample has not been damaged prior to the salt-spray test; **b**) test sample has been damaged by scratches prior to the salt-spray test (after the salt-spray test, all the detached layer material has been removed with a scalpel)

Sheet samples coated with layer compounds consisting of these systems have been put at the disposal of IWU for bending tests, corresponding hybrid polymer sols have been supplied to IKS for coating tests.

<u>Hybrid nano-materials versus yellow chrome plating and commercial alternatives</u>

At the Institute for Corrosion Protection (IKS) in Dresden, the hybrid nano-composites have been compared with corrosion protection systems already available on the market. Coated samples have been produced together with the hybrid nano-composites and all the comparative materials previously selected by the pbA members. Besides the tests mentioned above, the coated samples were subjected to additional strains in the ΔT-test (according to AGK-work sheet B 1; these test conditions were especially designed for zinc-plated surfaces) and the adhesive strength was determined in the pull-off test for adhesion according to DIN EN ISO 4624.

Especially on the electro-galvanized surfaces, the hybrid polymer nano-composite systems displayed good bonding strengths in the layer compound. The samples which had been pretreated according to ISC procedures on the basis of hybrid nano-composites, and whose corrosion protection characteristics were determined after the stress in the ΔT- and the salt-spray test, displayed a performance comparable to the commercially available samples with a yellow chromating and a Cr(III)-based passivation (fig. 3). With respect to electro-galvanization, the nano-materials were tolerant towards the different surfaces. Only on top of hot-dip galvanized surfaces, the corrosion protection is still insufficient in combination with the hybrid material. Here, the powder coated samples to some extent displayed lateral delaminations after the ΔT-test and the salt spray test.

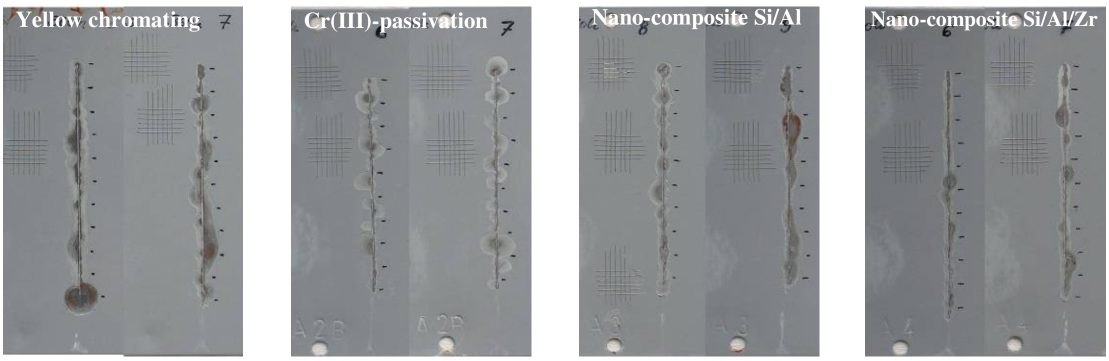
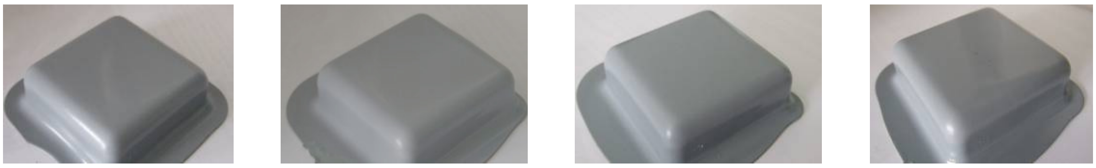


Fig. 3: Image sections of electro-galvanized strip material pretreated by different methods and covered with a commercial powder coating after 360 hrs in the salt-spray test (prior to the salt-spray test each sample had been scratched as deep as to the galvanization; after the test, all the detached coating material has been removed with a scalpel).

Powder-coated sample sheets produced at ISC and at IKS were investigated at IWU with respect to their deformability by exposing them to typical industrial applications like bending or deep drawing processes. Here, too, the hybrid nano-composite systems of the ISC have been contrasted to various products from the market. Within these tests, the nano-composites developed at the ISC displayed a deformability capacity comparable to standard market systems based on yellow chrome plating and Cr(III) passivation.

With respect to forming processes, the sol-gel systems were tolerant against all the investigated zinc layers - both electro- and hot-dip-galvanized (Fig. 4).



Yellow chromating **Cr(III)-passivation** **Nano-composite Si/Al** **Nano-composite Si/Al/Zr**

Fig. 4 : Deep drawing ability of the composite layer systems consisting of the electro-galvanized strip material with different pretreatments and a powder coating on top

Perspectives

By now, the hybrid polymer nano-composites can be produced in laboratory scale very easily. One challenge for future development will be the upscaling of the hybrid polymer coating materials with respect to production and storage. Furthermore, this novel route for substituting chromium-(VI) compounds has to be adapted to the process requirements of the customers. Although a universal applicability, like it is known from the yellow chromating, has not been verified yet, the protective effect of these coatings on electro-galvanized materials is comparable to that of the commercial yellow chrome plating which had been investigated in parallel. Laboratory experiments have revealed that the pretreatment with hybrid nano-composites was even easier to carry out than the yellow chromating process.

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References

[1] Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles; OJ L 269, 21.10.**2000**, p. 34–43; incl. Council Decisions 2002/525/EC; 2005/63/EC; 2005/437/EC; 2005/438/EC; 2005/673/EC.

[2] Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment; OJ L 37, 13.2.**2003**, p. 19–23; incl. Council Decisions 2005/618/EC; 2005/717/EC; 2005/747/EC; 2006/310/EC; 2006/690/EC; 2006/691/EC; 2006/692/EC.

[3] J. Pietschmann, JOT **47** (2007) 42.

[4] A. Hasse and H.-D. Hesse, JOT **44** (2004) 30.

[5] http://fao.dfo.info/ergebnisse/a_veranstaltung.htm (latest access 26.05.**2009**).

[6] J. Kron, K.-J. Deichmann and K. Rose, Proceedings, EUROCORR 2007, ed. DECHEMA e. V., Freiburg **2007**.

[7] J. Kron, K.-J. Deichmann, K. Rose, G. Schottner and K.-H. Haas, Proceedings, 1. Korrosionsschutz-Symposium „Korrosionsschutz durch Beschichtungen in Theorie und Praxis“, ed. Technische Akademie Wuppertal e. V., St. Goar **2005**.
[8] J. Kron, K. Rose, M.-L. Righi and K. Deichmann, mo 57 (2003) 23.
[9] J. Kron, Proceedings, Sol-Gel Workshop, ed. ccNanoChem GmbH, Saarbrücken **2008**.