Suitable Pre-Treatment of Hot-Dip Zinc to Increase the Adhesion of Organic Coatings

Jakub Svoboda, Jan Kudláček
Faculty of Mechanical Engineering, Czech Technical University in Prague. Technická 4, 166 07 Praha 6. Czech Republic.
E-mail: jakub.svoboda1@fs.cvut.cz

The article describes the possibilities of pre-treatment of hot-dip galvanized parts and their influence on the adhesion of organic coating. The main objective of this work was to compare the current possibilities of pre-treatment of hot-dip galvanized parts, this means phosphating, chromating and mechanical pre-treatment by light blasting and compare these technologies with today's alternative pre-treatment technologies based on chemical substances containing fluorozirconates. The basic function of these pre-treatments is to increase the adhesion of the organic coatings and to increase the lifetime of the entire corrosion protection. Another objective is to reduce the environmental impact of these pre-treatments, reduce energy for the technological process of pre-treatment and many other aspects. Last but no least to compare the different types of organic coating systems with using these pre-treatments on the hot-dip galvanized surface.

Keywords: Adhesion, Zr, Ti, Fluorozirconates, Conversion Layers

1 Introduction

Pre-treatment of hot-dip galvanized parts is very important for the subsequent application of organic coating, because the adhesion of organic coating is one of the main factors that show the lifetime of the entire corrosion protection. It is well known that if we do not perform a perfect pre-treatment of the zinc surface, delamination, cracking and other organic coating defects occur. Thus, the surface protection life is lost. It's problematic for duplex systems. Duplex system is one type of surface treatment of material, where the total protection is guaranteed protection by zinc coating and organic coating. These systems are frequent technology corrosion protection. With the highest life it is useful for protection of steel structures, especially in aggressive atmospheric conditions. Combination of the coating system and the zinc coating to prolong the lifetime of the system up to 50 years, but it depends on the aggressive corrosive environment, and many other factors [1]. The conversion layers are very fine grain layers that provide us the perfect base for the subsequent application of organic coating [2]. A lot of companies are currently solving the problem with pre-treatment of hot-dip galvanized parts for suitable base for organic coating. A big problem is the number of baths for pre-treatment, temperatures, times, automation of the process etc. Therefore, we are trying to ensure the right conditions for successful pre-treatment.

The main objectives of the scientific research was creating appropriate conditions for increasing the adhesion of organic coatings during creation of duplex systems. Another objective of the research was to compare the most frequent mechanical pre-treatment of the surface, ie light blasting with contemporary modern passivation of the surface. Last but no least was testing the impact of alternative methods on the adhesion of coating systems. Alternative methods are intended for applications, which are based on substances with fluorozirconates. The effort is to ensure the right conditions for successful pre-treatment.

2 Used pre-treatments of hot-dip galvanized material

2.1 Phosphating

It is the most chemical pre-treatment of steel in which are formed on the surface the tercial phosphates of zinc, calcium and manganese. Other capabilities of these layers are binding certain organic substances on their surface. These include petrolatum, impregnating oils, but especially paints. Phosphate coatings are also used to form the insulating properties at the surface of transformer sheets to reduce friction of the moving parts [3]. Using phosphates under organic coatings increases the corrosion resistance of the whole system. Phosphate layer prevents corrosion of paint systems and increases the adhesion to the metal surface. To increase adhesion is required fine grained layers (10-60 $mg.dm^{-2}$), see in Fig. 1, because thick layers of phosphate leads to the release of the individual crystals.

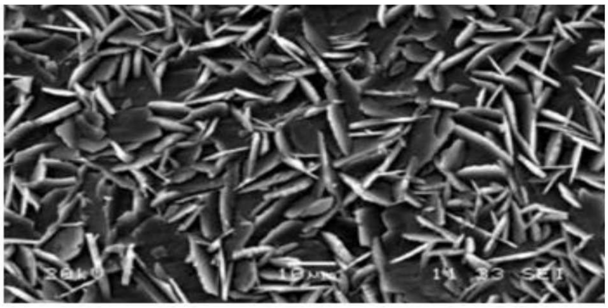


Fig. 1 *SEM image hopeit crystals of zinc phosphate [4]*

2.2 Chromating

It is a widely used method of passivation is used to improve the corrosion resistance and adhesion of organic coatings especially for non-ferrous metals, for example: zinc, aluminium and cadmium coatings. Electrolytic galvanizing and subsequent pre-treatment of the zinc surface with chromate conversion layers is now very widespread, but it is an effort to replace these conversion layers with new alternative chemical pre-treatments due the toxicity with using of hexavalent chromium passivation. Chromate coatings provide us improved corrosion resistance of zinc coatings mainly due passivation effect of chromium compounds present in the coating [3].

2.3 Alternative technologies for the ferrous phosphating and chromating

In the year 2000, the European Union Decree was adopted which restricts the use of hexavalent chromium to a minimum. In the case of the automotive industry, it's 5 grams per car. In this context, new methods are being developed as alternative technologies for phosphating and chromating based on substances contain fluorozirconates. These methods are environmentally friendly, energy saving etc. Traditional surface pre-treatment before application of organic paints are now turn into those more environmentally friendly. However, it was proved that some alternative conversion layers are not able to have a corrosion resistance, such as is the case of conversion layers based on Cr(III) [5], although certain sources describe an almost identical or even higher corrosion resistance of these alternative chemical surface pre-treatment of low carbon steel, particularly TiO_2 and ZrO_2 [6, 16].

Conversion layer based on Ti or Zr in recent years become a major alternative to the chemical pre-treatment based on chromium. Pre-treatment Ti / Zr have not been studied as extensively as chromium pre-treatment and their effects are less well known. For these applications, the most commonly used coatings based on zirconium and titanium secreted from solutions containing fluorozirconate (Bonderite NT 1 TecTalis) but also coatings hydrolysed organosilicate (Dynasilan Degussa ff.) [8]. In recent decades, proved another perspective technology that can well to replace phosphate. In particular, the use of zirconium oxide on the surface using the sol - gel method, or immersion in acid H_2ZrF_6. It was found that coatings ZrO_2, thicknesses of 18 to 30 nm provide a higher corrosion resistance compared to conventional phosphates [9-11]. These methods are also commonly used for chemical pre-treatment of hot-dip galvanized coating. Zircon absorbed in surface layers most often occurs as a zirconia (ZrO_2). It was found that zirconium oxide layers 50 nm or less, has comparable resistance to conventional chromate and phosphate. Today new TecTalis® surface pre-treatment, which is commercially available, is based on acid H_2ZrF_6 and fully replaces the phosphating process. This product can be applied by spraying or by immersion at room temperature does not require sealed with chromic acid and can be used on a variety of metal surfaces (steel, aluminium, zinc). The bath is based on dilute H_2ZrF_6 (Zr < 200 mg.l-1) with a small amount of Si and Cu for improved long-term performance bath. TecTalis reaction during layer formation: pH = 3.8 – 4.8, T = 10 – 50 °C, Time = 30 – 180 s. These are very fine grain layers that provide the perfect base for the subsequent application of organic coating. Using these products leads to shorter times, lower temperatures etc. [6, 7, 14, 15].

3 Experiment

In the experimental part were used paints ZINOREX (S2211) and AXAPUR (U2218) which were applied to the pre-treated surfaces of the zinc. Another objective of the experimental part was to verify the physical - mechanical properties of coating systems. For experimental section was created seven variants of the pre-treatment of hot-dip galvanized samples, six chemical and one mechanical surface pre-treatment:

1. SurTec 678, 2. Pragokor BP, 3. Nanotech cs-one, 4. Interlox 5705, 5. Activation with HNO_3, 6. Light blasting, 7. Degrease of hot-dipped galvanized samples

SurTec678 is trivalent passivation for zinc and alloys of zinc/nickel, is a highly concentrated product, containing Cr (III) and cobalt salts [13].

Pragokor BP is a composition that do not contain chromate ions, chromium or other environmentally harmful substances. Effect bath passivate surfaces microscopic pores or other inhomogeneities in the phosphate coating, so it is possible to increase the corrosion resistance [13].

The passivation effect of this product is higher than the range of compositions based on chromate ion. Furthermore, it can be used to passivate the active surfaces of non-phosphated steel, aluminum and magnesium alloys, zinc and tin coatings, zinc castings after degreasing or other activated surface [13].

Nanotech cs-one product is supplied from a Turkish company CHEMSOLL - chemical laboratories solution, it is an alternative method of phosphating iron and zinc. Eliminates the disadvantages of the use of phosphate baths and according to the manufacturer should provide effective adhesion and long life of the coating versus phosphate. On the surface material are formed transparent nano-ceramic surface [8].

Interlox 5705 contains a two-component bath free of chromium, which creates a conversion layer on aluminum, aluminum alloys, magnesium, zinc and steel. This is a composition which enhances the corrosion protection of parts of a cast and wrought aluminum alloys. It provides a basic layer on aluminum, zinc and steel before wet and powder coating and it's Qualicoat approved pre-treatment (A-65). This product is not recommended for steel passivation without subsequent painting [13].

Activation with HNO_3, the chemical pre-treatment of the surface of the zinc was the activation of the zinc coating with an alkaline degreasing and nitric acid (HNO3). With this chemical pre-treatment to achieve clarification of the surface, without the thin oxide layers [13].

Light blasting was used for comparison mechanical and chemical pre-treatments. Light blasting technology in the pre-treatment of zinc coatings still very popular and effective pre-treatment prior to application of organic coating systems. The main objective of this pre-treatment is to achieve a perfectly clean surface, free from corrosion products of zinc, and a rough surface for the subsequent application of other finishes. The experimental part was chosen abrasive resource (brown artificial corundum). Light blast zinc coating should ensure a minimum consumption of zinc layer, mostly in terms of removing the surface layer up to 10 microns. Samples were blasted by a pneumatic blasting equipment PTZ 100 I by S.A.F. setting the nozzle pressure of 0.5 MPa.

The degreased hot-dipped galvanized samples were used for comparison of the various pre-treatments of the hot-dip galvanization samples were prepared only alkali-degreased using a degreasing product Simple Green in a concentration of 1:30 [13].

3.1 Determination of the adhesion

To compare the pre-treatment of the hot-dip galvanized surface in terms of the adhesion of the organic coating, the following method was used:

- Determination of adhesion of organic coating by pull-off test according to DIN EN ISO 4624

The purpose of this test is to measure the mechanical adhesive strength of a coating. The sample will be subjected to increasing tensile stresses until the weakest path through the material fractures. The weakest path could be along the interface between two coatings, a cohesive fracture within one coating.

4 Comparison of various pre-treatments

For each pre-treatment three samples was created, then three measurements were performed on each samples. Tab. 1 shows the averages of measurements on individual samples. The measurements were made on two coating systems.

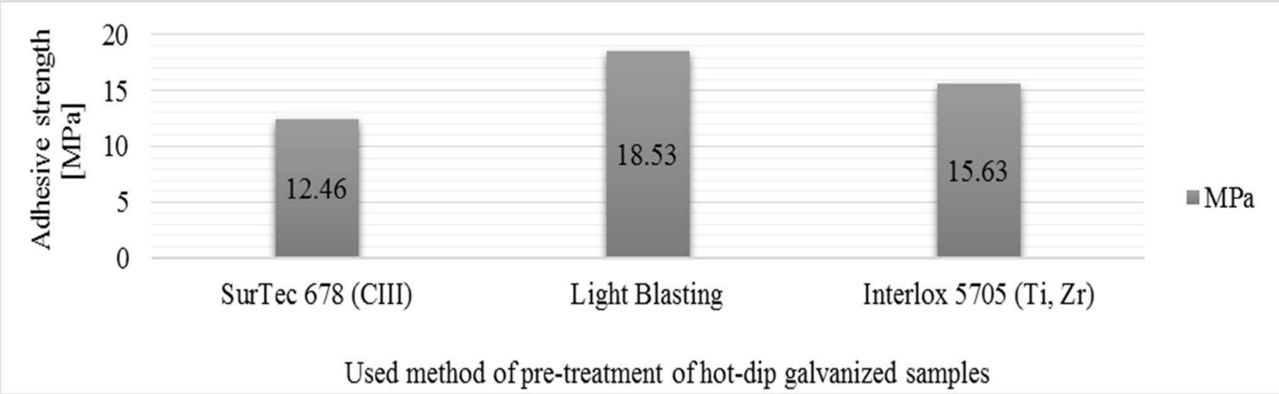
Tab. 1 *Summary of test results for individual adhesion of surface preparation the hot-galvanization zinc*

Pre-treatment + Coating system Zinorex(S2211)	**The average adhesive strength [MPa]**
Surtec 678	0.34
Pragokor BP	0.59
Nanotech cs-one	0.15
Interlox 5705	2.13
HNO_3	4.63
Light blasting	3.27
Degreased samples	2.69
Pre-treatment + Coating system AXAPUR(U2218)	**The average adhesive strength [MPa]**
Surtec 678	12.46
Pragokor BP	7.37
Nanotech cs-one	7.42
Interlox 5705	15.63
HNO3	18.13
Light blasting	18.53
Degreased samples	14.12

Tab. 1 shows the results that good adhesive strength reached with use a coating system AXAPUR (U2218), which was formed by the paint itself AXAPUR and hardener C 7002. These are polyurethane coatings which were applied with a ruler. In the case of an acrylate coating system ZINOREX (S2211) in many applications was achieved low values of adhesive strength and coating was non-quality. Reasons for the poor quality of the coating can be different, it could be an unsatisfactory application temperature or temperature curing paint shop also inadequate moisture for the application of paints or poor mixing of the individual components of the coating system. Finally, it could be a chemical reaction of the zinc surface pre-treatment with the ZINOREX (S2211).

5 Conclusion

As apparent from the Graph. 1 that some alternative method of passivating the surface of of hot-dip galvanized parts can compete with today trivalent passivation in the adhesion of paint systems. Particularly in comparison product SurTec 678, which is a trivalent transparent passivation to zinc and alloys of Zn/Ni achieved tension using coating system AXAPUR (U2218) values of adhesive strength on average 12.46 MPa, whereas the alternative methods Interlox 5705, which constitute a two-component spa containing chromium, which produces the conversion coating on aluminium, aluminium alloys, magnesium, zinc and steel, reached values adhesive strength of coating system AXAPUR (U2218) on average 15.63 MPa. When using other alternative methods of surface passivation of hot-dip galvanized components Pragokor BP, which is free chromate passivating agent based hexafluorozirconate ammonium and ammonium hydrogendifluoride, made a adhesive strength when using NS. AXAPUR (U2218) values. Adhesive strength on average 7.37 MPa. It should be noted that this is still an adhesive strength, which is corresponds with according of the internal regulations for the protection of hot-dip galvanized structures, more than 5 MPa. Another alternative method was investigated by Nanotech cs-one, which is a new generation of nano - ceramic coatings. In this application using the coating system AXAPUR (U2218) were achieved adhesive strength on average 7.42 MPa, the main advantage of this product is low temperature applications without necessarily degreasing.



***Graph. 1** Comparison of trivalent passivation SurTec 678, light blasting with brown corundum and alternative passivation (Ti, Zr)*

The best results in terms of adhesion of the chemical pre-treatment the zinc were reached with using degreasing and subsequent activation of the surface using HNO3 with coating system AXAPUR (U2218), but unfortunately, it's toxic substance and the Europen Unien bans these technologies for use in surface finishing. The adhesive strength average on 18.13 MPa. This chemical pre-treatment is from an economic point of view very interesting, but the problem is the high toxicity and the dangers of handling this acid, there is a problem with many European regulations. Under regulation European directive no.1272/2008 the substance is classified as dangerous. When activating the surface using HNO_3 is achieved comparable adhesive strength, as when using a mechanical pre-treatment light blasting, adhesive strength in average 18.53 MPa was achieved. It should be noted that duplex systems in this work have been tested only on verifying the adhesion of individual methods of pre-treatment with the zinc surface.

The results of the experimental part are obvious that some alternative chemical pre-treatment of the surface of the zinc are comparable with today trivalent passivations and many of them can compete even the most commonly used mechani-cal pre-treatment of the surface of the zinc, it's a light blasting. From the results is evident that for the pre-treatment methods used to compare the adhesive strengths above 5 MPa were achieved.

Acknowledgement

The research was financed by TE02000011 – Research center of surface treatment – WP5 – Power Engineering – Result TE02000011V016.

References

[1] STRYŽ, P. (2012). *Časopis povrcháři:Duplexní povlaky ocelových konstrukcí.* Praha, 2012, 2012(1), 7-10. ISSN 1802-9833. Available from: http://www.povrchari.cz/kestazeni/2012povrchari.pdf

[2] BAJAT, J.B.,MIŠKOVIĆ-STANKOVIĆ, V.B.,POPIĆ, J.P., DRAŽIĆ, D.M. (2008). *Adhesion characteristics and corrosion stability of epoxy coatings electrodeposited on phosphated hot-dip galvanized steel, Progress in Organic Coatings*, Volume 63, Issue 2, September 2008, Pages 201-208, ISSN 0300-9440, http://dx.doi.org/10.1016/j.porgcoat.2008.06.002.

[3] KREIBICH, V. (1996). *Teorie a technologie povrchových úprav*. Vyd. 1. Praha: České vysoké učení technické, 1996. ISBN 800101472X.

[4] POKORNÝ P., V. MEJTA a P. SZELAG. (2012). Povrchová úprava: *Příspěvek k teoretickým základům tvorby fosfátového povlaku* [online]. Hradec Králové: IMPEA, s. r. o., 2011, VII, [cit. 2012-05-01]. ISSN 1801-707X. Dostupné z: http://www.povrchovauprava.cz/uploads/assets/casopisy/pu-2011-03.pdf

[5] SAARIMAA, V., KAUPPINEN, E., MARKKULA, A., JUHANOJA, J., Bengt-Johan SKRIFVARS, STEEN, P. (2012). Microscale distribution of Ti-based conversion layer on hot-dip galvanized steel, *Surface and Coatings Technology*, Volume 206, Issues 19–20, 25 May 2012, Pages 4173-4179, ISSN 0257-8972,

[6] SAIKAT ADHIKARI, K.A. UNOCIC, Y. ZHAI, G.S. FRANKEL, JOHN ZIMMERMAN, W. FRISTAD (2011). Hexafluorozirconic acid based surface pre-treatments: Characterization and performance assessment, *Electrochimica Acta*, Volume 56, Issue 4, 15 January 2011, Pages 1912-1924,ISSN 0013-4686

[7] SZELAG, P. (2016). Pragochema, spol. s.r.o. – interní pdf dokument pro výuku. *Železnaté fosfátování.* [cit. 2016-04-29].

[8] Chemsoll.com – internetový zdroj. *Nanotech CS-ONE.* [online]. [cit. 2016-06-07]. Available from: http://www.chemsoll.com/kategori/nanotech-cs-one

[9] W.J. VAN OOIJ, A. SABATA (1989). Chemical stability of phosphate conversion coatings on cold-rolled and electrogalvanized steels, *Surface and Coatings Technology*, Volumes 39–40, Part 2, 15 December 1989, Pages 667-674, ISSN 0257-

8972, http://dx.doi.org/10.1016/S0257-8972(89)80028-3.

[10] XU, L., ZHANG, E., & YANG, K. (2009). Phosphating treatment and corrosion properties of mg-mn-zn alloy for biomedical application. *Journal of Materials Science: Materials in Medicine, 20*(4), 859-67. doi:http://dx.doi.org/10.1007/s10856-008-3648-2

[11] JIANHUA ZHOU, XIN CHEN, HAO DUAN, JIANZHONG MA (2015). Synthesis and characterization of organic fluorine and nano-SiO2 modified polyacrylate emulsifier-free latex, *Progress in Organic Coatings*, Volume 89, December 2015, Pages 192-198, ISSN 0300-9440, http://dx.doi.org/10.1016/j.porgcoat.2015.09.016. (http://www.sciencedirect.com/science/article/pii/S0300944015301338)

[12] Twgg.wordpress.com – Internet source. *Pull-off test.* [online]. [cit.2017-09-15]. Available from: https://twgg.wordpress.com/category/adhesion-cohesion/pull-off-tests

[13] SVOBODA, J. (2017). Comparison of chemical and mechanical pre-treatments and their influence on the adhesion of organic coatings. *International Conference on Innovative Technologies, IN-TECH 2017*, Ljubljana – Slovenia: In:: Faculty of Engineering, University of Rijeka, 2017, s. 251-254. ISSN 0184-9069.

[14] SVOBODOVA, J. (2014). SEM and EDS Analysis Used in Evaluation of Chemical Pre-treatment Based on Nanotechnology. *Manufacturing Technology*, Journal for Science, Research and Production, Vol. 14, No. 3, ISSN 1213-2489.

[15] SVOBODOVA, J., KRAUS, P., CAIS, J., LATTNER, R. (2016). Research of Chemical Pre-treatment Created by Sol-gel Process on the Polished Surface of Aluminium Substrate. *Manufacturing Technology*, Journal for Science, Research and Production, Vol. 16, No. 1, ISSN 1213-2489.

[16] SVOBODOVA, J., KRAUS, P., LATTNER, R., MRISOVA, A. (2016). Testing of the New Chemical Pre-treatments Types Applied on the Steel Substrate. *Manufacturing Technology*, Journal for Science, Research and Production, Vol. 16, No. 5, ISSN 1213-2489.

DOI: 10.21062/ujep/66.2018/a/1213-2489/MT/18/1/135