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The effects of the steel's surface quality on the properties of anti-corrosion coatings

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Abstract: The requirements of painted vehicle construction in terms of corrosion resistance apply not only to cars but also to heavy duty lorries, trucks and agricultural machinery. Phosphating is the most commonly used method for the pre-treatment before painting of ferrous metals in the vehicle manufacturing industry. The task of the phosphate layer between the metal surface and the paint is to protect the metal from corrosion under the paint film and promotes the adhesion of the paint film to the metal substrates. In this study the zinc phosphate conversion layer was deposited onto the steel surfaces from a bi-cationic (nickel-free) phosphating bath by dipping using identical technological parameters. The developed crystal structure and morphology was examined in terms of surface roughness and blasting quality of the metal. The surface quality of the metal was tested by digital light microscopy (LM), and the structure of phosphate coating was investigated by scanning electron microscopy (SEM).

1. Introduction

Surface preparation of steel parts is one of the main factors influencing the effectivity and longevity of anticorrosion coatings. Improperly prepared surfaces prevent the formation of an even conversion layer, meaning insufficient paint layer adhesion, leading to corrosion under the protective layer and causing continuous peeling-off of the coating [1,3,4,5].

In addition to cleaning the surfaces also must be modified prior to applying the anti-corrosion lavers. A zinc phosphate laver is added onto metal surfaces, to ensure good adhesion of the additional layers to the raw metal surface and protects the base metal from water, carbon dioxide, sulfur oxides, ozone, aggressive ions and other harmful substances getting through the damaged paint coatings [1,4,5]. The performance of zinc phosphate layer on steel depends on the fraction of the total covered surface area. This coverage fraction is effected by process parameters and chemical composition of phosphating bath and surface morphology of the deposit [6].

Besides chemical surface cleaning, the blasting is used for cleaning, surface preparation, and surface treatment as well. This process reduces the susceptibility to corrosion, seal porous surfaces. A blasted surface can be a very clean surface providing excellent mechanical adhesion. Media selection plays an important role in effective blasting. Shoot blasting can be widely used to remove rust, oxides, oils and mill scales, even the welding beads, welding silicate layer from the surface and welding seams of steel parts, structures and even complex assemblies. Its main scope is to provide surfaces free of

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adhesion preventing materials. Also, increased surface roughness provides good adhesion for the first layer of the coating for the interfacial reactions. [2,4,5].

Quality of the phosphate layer is influenced by the material quality [2], surface roughness, method of surface preparation and parameters of the phosphating process (concentration of ingredients, temperature, time, etc.) [1,4,5], structural defects and presence of contaminants in the crystallizing method [7]. The purpose of this work is to investigates the properties of the zinc phosphate conversion layer on blasted steel surfaces with different surface roughness after blasting under the same technological parameters.

2. Materials and Methods

2.1 Metal substrates preparation

As a substrate for zinc-phosphate coatings deposition both sides of a S420MC steel sheet (70 mm \times 150 mm \times 10 mm) and for comparison a cold rolled steel Q-Panel (102 \times 152 \times 0,81 mm) were used.

Chemical composition of **Q-Panel** by SAE Material Designation 1008/1010 is as follows: max. 0.5 % manganese, max. 0.15 % carbon, max. 0.030 % phosphorus, max. 0.035 % sulfur.

Chemical composition of **S420MC** steel panel by EN 10149-2 (High-strength steels for coldforming, thermomechanically-rolled, normalized): max. 1.6 % manganese, max. 0.12 % carbon, max. 0.50 % silicon, max. 0.025 % phosphorus, max. 0.015 % sulfur. This steel is used for cold-formed components, easy to cut and bend, suitable for welding, and can be easily machined. Due to the favorable mechanical properties this is a commonly used sheet material in different sheet thicknesses in BPW axle and chassis manufacturing. Table 1 lists the chemical composition of samples.

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Table I. Chemical composition of samples												
		wt %										
Steel		Fe	С	Si	Mn	Р	S	Cr	Mo	Ni	Al	
S420MC	1.	98.8	0.0750	0.0118	0.960	< 0.004	0.0048	0.0287	< 0.004	0.0068	0.0405	
	2.	98.8	0.0764	0.0152	0.969	< 0.004	0.0052	0.0289	< 0.004	0.0100	0.0413	
	3.	98.8	0.0759	0.0083	0.977	< 0.004	0.0054	0.0288	< 0.004	0.0053	0.0393	
	mean	98.8	0.0758	0.0118	0.969	< 0.004	0.0051	0.0288	< 0.004	0.0074	0.0404	
Q-Panel	1.	99.2	0.0734	0.0146	0.355	0.0067	0.0095	0.0837	0.0076	0.0245	0.0394	
	2.	99.2	0.0756	0.0125	0.359	0.0058	0.0102	0.0830	0.0081	0.0246	0.0397	
	3.	99.2	0.0769	0.0129	0.361	0.0069	0.0098	0.0843	0.0081	0.0236	0.0394	
	mean	99.2	0.0753	0.0133	0.359	0.0065	0.0098	0.0836	0.0080	0.0242	0.0395	

To analyze the chemical compositions was use Metal analyzer PMI-MASTER Pro2 spark excited optical emission spectrometer (OES) from Oxford Instruments.

Different surface structure was visible on micrographs of the Q-panel and S420MC panel.



Surface roughness of S420MC steel panel before blasting Rz: 6.04 µm



The Q-Panel did not receive mechanical surface pretreatment (generally accepted industry specimen plate for corrosion testing). The surface roughness Rz: 4.50 µm



Figure 1. Surface measurements of steel surfaces: a) Micrograph of S420MC steel panel, b) Surface roughness of S420MC steel panel before blasting, c) Micrograph of Q-Panel, d) Surface roughness of Q-Panel

Prior to deposition of zinc-phosphate coatings, the S420MC test panel was blasted with steel shots in an automated equipment. One side of the panel was properly blasted ("good side"), while the other wasn't ("not good side"). The two different sides under the same conditions received the surface pretreatment.

2.2 Pretreatment and zinc phosphating process

The tests were done in day-to-day production conditions on a working production line of the company and within the limits of process capability. Free acid and total acid were determined by titrating of 10 ml bath sample against 0.1 N NaOH and total alkalinity was determined against 0.1 N H₂SO₄ using indicators. The classical volumetric titration methods were performed with Schilling burettes, in Erlenmeyer flasks.

A SenTix® pH electrode with IDS (Intelligent Digital Sensors) was utilized to measure and adjust the pH values of solutions. This electrode was normally calibrated every day by using buffer solutions of pH values 4.11, 7.0 and 10.0. The conductivity of solutions was measure with TetraCon® Conductivity cell. This electrode was normally calibrated every week by using 1.413 μ S/cm (25°C; 0,01 mol/l; KCl) calibration solution.

After shot blasting (Q-Panel without shot blasting) the test panels were pre-degreased at 60 °C temperature for 5 min. in 20 g/l of Gardoclean S5165 and 2 g/l Gardobond Additiv H7375 alkaline degreasing dip bath (pH = 12.7; total alkalinity = 21.5 points). Degreasing was done at 60 °C temperature for 5 min. in 40 g/l of Gardoclean S5165 and 3 g/l Gardobond Additiv H7375 alkaline degreasing dip bath (pH = 11.7; total alkalinity = 23.8 points) and dip rinsed with tap water in three successive cascade flushing baths. Treatment time was 1minute in each bath by stirring the rinsing water, at ambient temperature. The conductivity of the rinsing baths during the progress of the technological process were: 1871 μ S/cm and 875 μ S/cm and 717 μ S/cm.

Zinc-phosphate coatings were formed chemically after dip activation with 2 g/l Gardolene V6599 bath (pH = 9,17), by immersion in phosphating bath (pH = 2,84; free acidity = 2,0 points; total acidity = 23.4 points; accelerator = 5.5 points) for 4 min, at same temperatures of the nickel-free double cation Zn/Mn phosphating bath (58 °C). It should be noted here that nickel has long been known to significantly improve paint adhesion and corrosion protection. However, nickel compounds are noxious and closely regulated in the effluent stream. Nickel-free processes, therefore, are desirable to satisfy health and environmental demands. NaNO₂ – acting as an accelerator – was added to the phosphating bath (5.5 points).

Finally, all plates were dip rinsed with tap water (pH > 4,5), three times in a successive cascade flushing bath. The conductivity of the rinsing baths during the progress of the technological process were < 300 μ S/cm and < 150 μ S/cm and < 50 μ S/cm) and finally they were also rinsed by dipping and by spraying in deionized water (conductivity < 20 μ S/cm). Treatment time was 1 minute in each bath by stirring the rinsing water, the spraying was done with fresh deionized water at ambient temperature. Total acidity/alkalinity and free acidity were determined with acid – base titration.

All solutions were prepared with chemicals of Chemetall Ltd, according to the technical data sheets, with deionized or tap water. The pretreatments are applied in a dipping process, all technological parameters were set to the specified mean value within the allowable tolerances.

Examination of appearance after the pretreatment process: parts of different tones visible on the surface on "not good" side (Figure 2 a). On other side the coating is consistent and whole-colored (Figure 2 b)





Figure 2. Surface measurements of S420MC steel surfaces after blasting and zinc phosphating: a) photograph of "not good" side, b) photograph of "good" side



Surface roughness on "not good" side: $Rz = 21.62 \mu m$; $Rz_{max} = 28.35 \mu m$



Surface roughness on "good" side: $Rz = 60.13 \mu m$; $Rz_{max} = 70.15 \mu m$



Figure 3. Surface measurements of steel surfaces after blasting and zinc phosphating: a) 2D micrograph of S420MC steel panel on "not good" side, b) 3D micrograph of S420MC steel panel on "not good" side, c) Surface roughness of S420MC steel panel on "not good" side, d) 2D micrograph of S420MC steel panel on "good" side, e) 3D micrograph of S420MC steel panel on "good" side, f) Surface roughness of S420MC steel panel on "good" side,

There is a separating boundary section between properly blasted and not properly blasted surface. Scanning electron micrographs show irregular crystal growth at the border (see Figure 4).

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Figure 4. a), b), Digital light micrograph and 4.c) SEM micrograph of irregular crystal growth at the border line

2.3 Surface and surface coverage measurements

The weight per unit area in g/m^2 of the phosphate layers coatings was determined by chemical dissolution of the layers in a solution of 4 % TEA + 12 % Na₂EDTA x 2H₂O + 9 % NaOH + 75 % water at 70 °C degree. The phosphate conversion coatings weight of the Q-Panel was 2.65 g/m², which corresponds to the regulatory mean value of line.

Surface roughness (Rz and Rz_max) according to DIN EN ISO 4287 was measured by a MAHR/MarTalk Drive Unit GD 25 / tactile: MFW-250:1 .

2D and 3D structure of surfaces was visualized by a KEYENCE digital light microscope Model WHX J20T. Morphology, crystal shape and size, as well as orientation was measured by a ThermoFisher/FEI Apreo S scanning electron microscope (see Figure 5).

Results

A: Properly blasted base material B: Incompletely blasted base material C: Q-Panel surface



Figure 5. SEM micrographs showing the effect of shoot blasting on crystal structure and coverage A: Properly blasted base material B: Incompletely blasted base material C: Q-Panel surface

Structure of the metal surface, the micro- and macrostructure is just as important as the material composition. As the surface roughness increases, so does the calculated surface area per coating weight, and better coverage is achieved on steel surfaces due to reactions taking place on the boundary layer, corrosion resistance in case of damaged top coating is improved. Increased surface roughness correlates with finer structure of the coating, as smooth surfaces have weaker reaction to phosphating. If a surface contains lots of indentations and microcracks, then the acid corrosion effect is amplified during phosphating, leading to stronger layer adhesion but also changing the layer's microstructure.

3. Conclusions

The crystalline size and crystal type were found to be surface roughness after the blasting dependent. Surfaces properly prepared with shoot blasting have a regular and evenly covered microstructure (Figure 5A). Improper or incomplete shoot blasting causes irregular grain growth in the corrosion protection layer as shown in Fig. 5B and decrease the fraction of the total covered surface area by the deposit. On the sample plates representing the "ideal" surface to be phosphate layer, the structure of the zinc phosphate does not show the same structure as the phosphate layer structure used in the vehicle manufacturing steels exhibiting different surface roughness and quality. Irregular crystal growth for reason of improper shot blasting, on work pieces resulting from defective mechanical surface preparation causes subsequent corrosion problems because the base metal surface is not completely covered by the zinc phosphate crystals.

A completely different zinc phosphate crystal structure was deposited onto the surface of Q-Panel (Figure 5C). When evaluating SEM micrographs of zinc-phosphate conversion coatings on steel

surfaces in surface pre-treatments plants, it should be taken into account, that the SEM image of the zinc phosphate conversion layer formed on industrial sample plates (e.g. Q-Panel) should not be used for qualifying technology parameters.

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