University of Pannonia
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THE EFFECT OF MICROSTRUCTURE AND COMPOSITION ON THE PROPERTIES OF CORROSION PROTECTION COATINGS ON IRON AND STEEL SURFACES

Ph.D. THESIS

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Introduction and Aim of Research

Nowadays, in the field of vehicle production, anti-corrosion coating of metal surfaces is not only important for automotive vehicles (cars), but also for trucks and agricultural vehicles. In recent years, the surface pretreatment technology of agricultural machines and components before painting has already caught up with the quality standarts expected in car manufacturing. My research was based on samples made under industrial conditions on the surface treatments- and paintings lines of BPW-Hungária Kft. factory in Szombathely, specifically focusing on the production of agricultural and road vehicle production.

My dissertation work focuses on phosphate conversion coatings, with special emphasis on zinc phosphate coatings on iron and steel surfaces, supplemented by new knowledge gained from research, such as the zinc phosphating of aluminium alloys together with ductile iron castings and steel alloys.

Phosphating is the most widely used metal pretreatment process for the surface treatment of iron and other metals. Due to its economy, process speed and excellent corrosion resistance, wear resistance, adhesion and lubrication properties, it plays a significant role in the surface pretreatment of metal surfaces in car and vehicle production. The designers of the vehicle manufacturers assemble the complex workpieces from various metals according to the future requirements, which undergo different processing phases (welding, machining, sheet metal working, forging, etc.) and mechanical surface pretreatments. The engineers must be develop a process during the surface pretreatment before painting, in which the coating systems created with “multimetal” processes satisfy the corrosion resistance and quality expectations set by the customers in such a way that these processes do not influence or deteriorate the physical-mechanical properties determined during the design of the vehicle structure. Based on my practical experience, I have assumed that within the specified operating limits of the controlled phosphating technological process, the properties of the conversion coating on metal surfaces with different compositions and surface properties will be different, thus will also vary the corrosion resistance properties of the final multi-layer coating.

Based on the test results obtained during my research, I present that the morphological and compositional properties of the conversion coatings created on various metals in zinc phosphate baths with a low zinc content differ from the properties that can be predicted based on literature data in the case that these metals are installed next to each other in the same vehicle industry superstructure .

Experimental

In order to ensure uniform coating quality, I also examined the crystalline conversion coating created in the zinc phosphating process and the metal substrates. For the experiments, I chose metal substrates that are often used in vehicle manufacturing and we created the samples used for the research with the machines, tools and operations used in daily production (laser cutting, sawing, machine and manual sandblasting or shotblasting), thus simulating the mechanical effects on the metal and contaminations on the surface in the production processes. The metals involved in the tests: S420MC steel (raw, sandblasted, shotblasted surface), SAE 1008/1010 (AISI 1008/1010) CRS steel, EN-GJS-450-10 (5.3107) nodular graphite cast iron, EN-AW-6082 forged aluminum alloy, AA 6014 aluminum sheet.

The tests of sample plates prepared during the phosphating process include chemical analytical analysis, destructive and non-destructive material tests, material composition measurements with an optical emission spectrometer (OES), digital light microscope (LM) tests, and scanning electron microscope (SEM) and the attached energy dispersive X-ray analyser (EDX) tests carried out. The crystal structures, surface defect sites, the structure and composition of the defect sites identified by imaging methods provide essential information for setting up the phosphating processes.

In addition to the influence of the surface structure of the base metals, I also investigated the effect of the technological process parameters on the crystal structure and composition formed on the surface, especially the influence of the accelerators of the phosphate baths on the corrosion protection of the final multi-layer coating. I have established that the electrophoretic applied paints protect from corrosion effects the crystalline zinc phosphate layers formed on metal surfaces with different structures, covering the surface to varying degrees and with different morphologies, regardless of the crystal size of the layers, the composition of the coating, or the porosity of the coating.

My research focused on testing methods that are in common use at most vehicle manufacturers or easily available through a future investment or in an external laboratory. The samples prepared for the tests were made on industrial production lines during normal daily production, so that most of the disturbances that occur in the technology under industrial conditions could be simulated.

New scientific results: thesis statements of the doctoral dissertation

1. I have demonstrated by a series of measurements that S420MC steel, EN-GJS-450-10 ductile cast iron, EN-AW-6082 (AlSi1MgMn) forged aluminium castings and AA6014 (AlMg0.6Si0.6V) aluminium alloy materials are in the same tricationic bath with low zinc content (Zn^{2+}=1.3 g/L; Mn^{2+}=0.9 g/L; $Ni2^{+}$=0.9 g/L), during zinc phosphating process, both 0.5 g/L nitroguanidine and 2.4 gas points of nitrite accelerator can create a crystalline zinc phosphate conversion coating with a suitable crystal structure and composition on each metal substrate within 180 seconds of exposure time, if the fluoride content of the 53°C bath is 140-150 ppm. It has been demonstrated by SEM images that the variation of the accelerator dosage amount, affects the structure and coverage of the conversion layer that forms on the surface, therefore the dosage amounts must be adjusted according to the surface area ratio of the together zinc phosphated metal products.

2. In my studies, I have demonstrated by XRD X-ray diffraction analysis that the coating formed on the surface of CRS/SAE 1008/1010 steel in the phosphating reaction by using both nitrite-containing and nitroguanidine accelerator contains in addition to the main crystalline phosphophyllite phase a small amount of hopeite phase, the presence of 0,9 g/L of manganese ion in the bath or the dosage amount of the accelerator, or presence of fluoride in the bath, does not affect or change the composition of the coating when co-treated with aluminium alloys. Based on the tests, it can be stated that nitroguanidine can completely replace nitrite-containing accelerators in the zinc phosphating treatment of steel, when it is necessary to replace nitrite-containing accelerators arises for environmental or occupational health reasons.

3. Based on the results of XRD elemental analysis measurements, I have found that during the mechanical surface preparation by sandblasting, the components and impurities of the blasting sands pressed into the surface layer cannot be completely removed by chemical pretreatment, and therefore the impurities remaining on the surface can be also detected in the conversion layer formed on the sandblasted surface. I have demonstrated by SEM images that the structure and composition of

the crystalline zinc phosphate layer formed on the sandblasted surface, will be different from the zinc phosphate layer formed on the shotblasted surface, due to the fact that a surface with different microgeometry is created with different scattering material, which will cause the formation of a zinc phosphate layer with different structures.

4. Based on several series of parallel experiments, I have demonstrated that on sandblasted and on shot blasted steel surfaces and the raw steel surfaces – compared to each other - form a zinc phosphate layer of different colour shades, which, when visually inspected, provides immediate information for engineering decisions to adjust the production processes. The zinc phosphate coating is dark grey on a raw steel surface, medium grey a on sandblasted steel surface, and light silver grey on a shot blasted steel surface, even when nitrite and nitroguanidine accelerators are used. This difference in colour shade is equally visible in both bicationic (containing Zn^{2+}, Mn^{2+}cations) and tricationic (containing Zn^{2+}, Mn^{2+}, Ni $^{2+}$cations) bath surface pretreatments, both in dip and spray processes and in baths containing 0,7 g/L or 1.07 g/l zinc content, applied by spraying.

5. I verified with EDX elemental analysis and XRD phase diffractograms that the case of AlMg0.6Si0.6V and AlSi1MgMn aluminium alloys, on line set up for surface pretreatment of steel, in a bath containing 140-150 ppm fluoride, both nitroguanidine and nitrite containing accelerators, hopeite is the main phase in the crystalline layer, with only an additional manganese-containing crystalline phase, but the bath 0,9 g/L manganese and 0,9 g/L nickel contents are incorporated into the crystal structure to a greater extent than in the case of steel. I have found that in the combined phosphate treatments – at this fluoride dosing amount - the surfaces of the different aluminium and steel alloys behave similarly to their separate phosphating and do not deteriorate the coating reactions of the other metal. By comparing the effects of the accelerators, I have shown that the use of the nitrite accelerator can achieve a higher coverage and better quality surface protective layer on the surface of aluminium alloys.

6. In the case of combined zinc phosphate coating of S420MC steel and EN-GJS-450-10 ductile cast iron in a dip process at a temperature of 53° C in a tricationic zinc phosphating bath (containing Zn^{2+}, Mn^{2+}, Ni $^{2+}$cations), a uniform phosphate layer

formed on the steel surface only with nitroguanidine accelerator dosage of 1,0 g/L, whereas a uniform zinc phosphate layer with good coverage of the base metal is formed on the spheroidal graphite casting, which is not affected by the variation of the accelerator dosage amount. In the case of nitrite accelerator, uniform phosphate layer does not form on the steel surface with an accelerator dosage of only 1,4 gas points, however irregular crystals appear in the coating on the ductile cast iron which does not affect by the dosage amount. Based on these results, I have determined that the nitrite accelerator is not a suitable accelerator for ductile cast iron, but the nitroguanidine accelerator produces uniform, fine crystalline layers on the surface of ductile cast iron even at dosage of 0,2 g/L – 0,5 g/L – 1,0 g/L. In the combined surface pretreatment of steel and cast iron, the nitroguanidine accelerator at dosing amount of 0,5 g/L can be used on both substrates.

7. Based on SEM images, I have verified that the increase in surface roughness on S420MC steel plate is related to the increase the fineness of crystal structure in coating. In case of surface roughness R_z<10 µm the crystal structure is uneven and containing irregular, large crystals, between R_z=10-30 µm surface roughness the coating crystal structure is not uniform, it contains peaks and valleys, although it covers the base metal, in case of surface roughness R_z=30-60 µm, it is already a regular based on the tests, fine crystalline zinc phosphate coating with a good coverage of the base metal surface can be achieved.