Monitoring of changes in the roughness of the metal surface after the application of the conversion layer

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Abstract: *The article is focused on the study of the integrity of the material that is used in the automotive industry in process of creating joints by combined technology. The article describes the study of the properties of chemically pretreated surfaces by phosphating technology. When creating new surfaces by phosphating, a new type of phosphate layer was used using modern conductive compounds of polyaniline salts. The pretreated surfaces were investigated in terms of structure, 2D and 3D microgeometry, contact angle in relation to the determination of surface wettability and surface energy. The experiment was realized in order to identify the connections between individual factors of the process and roughness characteristics.*
Keywords*: surface integrity, microgeometry, roughness, contact angle*

1. Introduction

In automotive industry, when constructing cars, they also emphasizes the use of increasingly progressive steel materials that have improved properties, in order to achieve better efficiency in the operation of cars. This fact contributes to the development and acceleration of adhesive bonding technologies, but this pace cannot be at the expense of the quality of the given joints. Therefore, constant precise testing of the joints and the quality of the surfaces that the joints create is necessary to ensure reliability at the required quality. The quality of the materials to be joined is increased by the conversion layers representing the chemical pretreatment of metal materials, which are created by the chemical reaction between the metal and the applied coating. In the final phase of a given chemical reaction, a surface layer is formed – conversion layer.

Phosphate layers are often used as conversion layers in the automotive industry. The primary advantages of phosphate layers include, for example: improved corrosion resistance, increased surface functionality and support for adhesion of organic coatings or adhesives. [1]

Usually, these phosphate layers are made of zinc or iron phosphate. Application of phosphates can be carried out by spraying or immersion. Phosphating technology is constantly evolving. The paper deals with the possibility of creating such phosphate layers by applying polyaniline salts and their influence on changes in surface properties.

2. Material and method and results

2.1 Used material

Uncoated deep-drawn steel DC04, thickness 0.8 mm (abbreviation designation DC). The chemical composition of the materials is in Table 1.

Table 1: *Chemical composition of used steel DC04*

Material	C	Mn	P	S
DC	0,04%	0,25%	0,009%	0,008%

The tested samples were pre-treated by a new approach to creating the conversion layer by chemical pre-treatment using modern conductive compounds of polyaniline salts – polyaniline phosphate and polyaniline citrate.

2.2 Used pre-treatment

a) Exclusion of polyaniline salt (PANI-H_3PO_4) by precipitation polymerization (conc. H_3PO_4 = 0.8 M) - Sample (DC_1)

Polyaniline is prepared by oxidation of aniline with ammonium peroxodisulphate in an acidic environment. The reaction takes place in air at room temperature. This is an exothermic reaction. In the practical version, 9 ml of aniline was dissolved in a beaker in 250 ml of distilled water acidified with phosphoric acid in an amount of 13.6 ml. In the second beaker, a solution of ammonium peroxidizate was prepared by dissolving 28.5 g of the substance in 750 ml of distilled water.

After complete dissolution, the prepared solutions were mixed and stirred with a glass stirrer for the entire time of polymerization due to increased diffusion of reaction substances. After mixing the solutions, panels were inserted into the beaker, on which the polyaniline salt was secreted.

The course of polymerization was accompanied by color changes. From the initially clear reaction mixture through blue to the final deep green color of polyaniline. [2, 3]

b) Exclusion of polyaniline salt (PANI-Citr) by precipitation polymerization (conc. citric acid = 1.6 M) Sample - (DC_ 4)

In this part, the pre-preparation of the phosphate was carried out as follows: in a beaker, 9 ml of aniline was dissolved in 250 ml of distilled water acidified with citric acid in the amount of 84 g.

In the second beaker, a solution of ammonium peroxidisate was prepared by dissolving 28.5 g of the substance in 750 ml of distilled water, and both were mixed throughout the polymerization.

2.3 2D surface roughness measurement method

The surface roughness of the evaluated samples was measured by the touch measurement method with a profilometer type Surftest SJ-201, Mitutoyo (Japan). The measurement was carried out in accordance with the ISO 21920-2 standard. For the purpose of the experiment, parameters were chosen that could accurately describe the differences in the roughness of the evaluated surfaces.

The following parameters were chosen:

Ra [μm] – mean arithmetic deviation of the surface

Rz [μm] – average value of the largest profile heights

RPc [-/cm] - number of profile elements per cm of length

RSm [μm] - average width of profile elements

2.4 Measured values of roughness parameters

According to the mentioned methodology, individual surface roughness parameters were evaluated, Table 2. The sample marked DC_0 presents the measured values of the unprepared surface.

Table 2: *Average values of measured roughness parameters*

Sample	Average values of measured roughness parameters			
	Ra [µm]	Rz [µm]	RPc [-/cm]	RSm [µm]
DC_0	1,08 ± 0,09	6,01 ± 0,59	56,07 ± 10,65	187,3 ± 30,27
DC _1	2,07 ± 0,56	14,44 ± 5,78	56,941 ± 12,58	172,5 ± 62,39
DC _4	2,60 ± 0,45	15,55 ± 2,12	32,95 ± 3,81	284,5 ± 39,73

On the basis of the achieved values, we can conclude that the application of phosphate layers resulted in an increase in the average values of the observed roughness parameters compared to the original surface. Sample DC_4, phosphate with polyaniline salt (PANI-Citr) by precipitation polymerization (conc. citric acid = 1.6 M) has the highest and the most appropriate values in all selected roughness parameters. [4,5] In the attached profilograms of individual surfaces of materials Fig. 1a – Fig. 1c we recorded a change in the surface roughness of tested materials and on the basis of this fact we can state that the chemical surface pretreatment has an effect on the individual roughness parameters of the monitored samples.

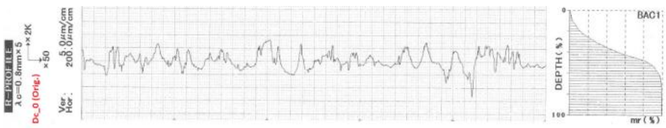

Fig. 1a *Profilogram + Firest-Abbot curve for the sample DC_0*

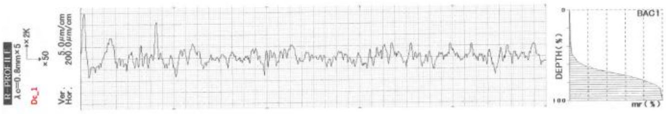

Fig. 1b *Profilogram + Firest-Abbot curve for the sample DC_1*

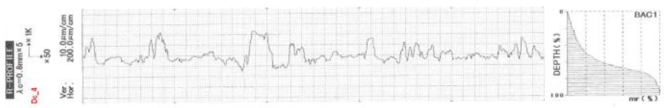

Fig. 1c *Profilogram + Firest-Abbot curve for the sample DC_4*

The geometric state of the surfaces has a decisive influence on its function. The requirements for the accuracy of the geometry of individual surfaces that are in contact with others are very high. Since it is assumed that the studied surfaces will interact with others, e.g. in the case of adhesive bonding, these were also subjected to a spatial evaluation of the surface in order to obtain a comprehensive image that tells about the character of surface. This measurement was carried out in a non-contact way using a ZEISS Smartproof 5 confocal microscope. 3D representation of the surfaces is in Fig.2a– Fig. 2c.

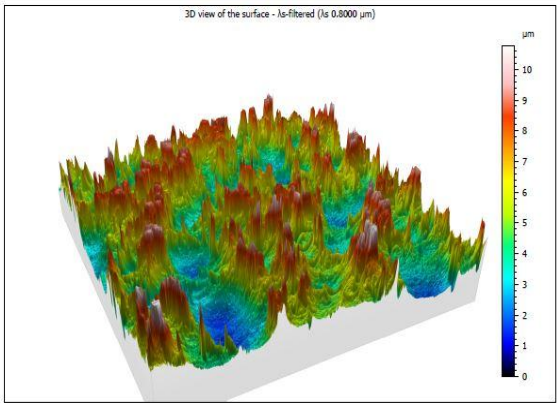

Fig. 2a *3D surface of the sample DC_0*

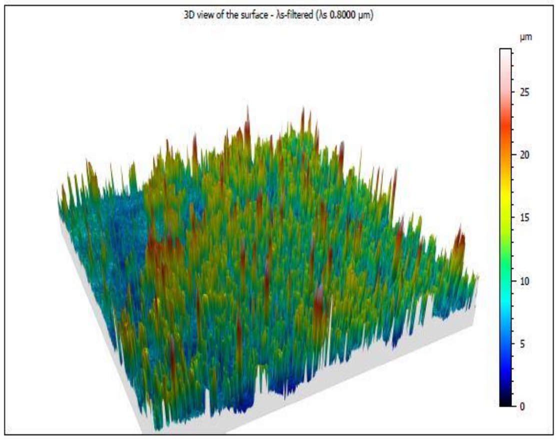

Fig. 2b *3D surface of the sample DC_1*

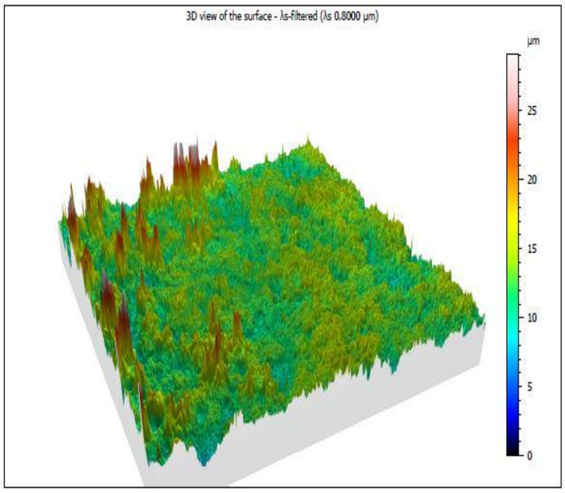

Fig. 2c *3D surface of the sample DC_4*

2.5 Measurement of the contact angle of the samples

The next step was to compare the contact angle. The contact angle of the surface of the materials was measured by a direct optical method. See System E Advex Instruments was used as the device. The method consists in placing a small drop of liquid on the measured surface, photographing it and determining the contact angle from the photograph, Fig. 3. Table 3 represents the values of the measured contact angles of the observed samples with an average value.

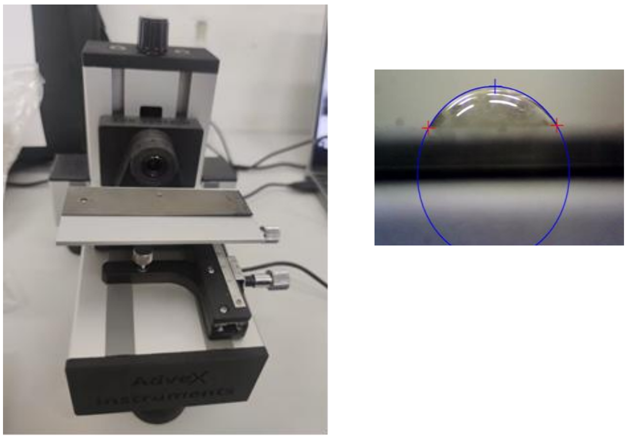

Fig. 3 *The principle of contact angle measurement*

Table 3: *Values of measured contact angle values*

Measurement number	**DC_0**	**DC_1**	**DC_4**
1.	70,2°	77,5°	75,1°
2.	68,5°	77,6°	81,3°
3.	65°	68,8°	79,2°
Average	**67,9°**	**74,6°**	**78,5°**

2.6 Morphology of films of polyaniline salts (PANI.H_3PO_4 and PANI – Citr)

The morphology of the samples with films of polyaniline salts was evaluated using the AFM method. The mean square thickness of the surface of the excluded film of polyaniline salts was measured. The root mean square thickness value provides information about the distribution of the polymer film on the material on which the film was deposited. [2]

The applied film of polyaniline salt PANI.H_3PO_4, which was formed in an environment of 0.8M phosphoric acid, reached a mean square thickness of the film surface up to 68 µm, while the film of polyaniline salt PANI – Citr, which was formed in an environment of 0.8M citric acid, reached mean square thickness of the film surface with a value of up to 0.82 µm.

Microscopic images of synthesized polyaniline salts are shown in Fig 4a and Fig. 4b.

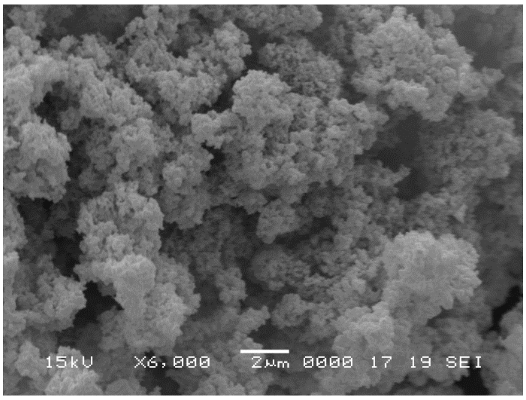

Fig. 4a *Microscopic image of synthesized polyaniline salts H_3PO_4*

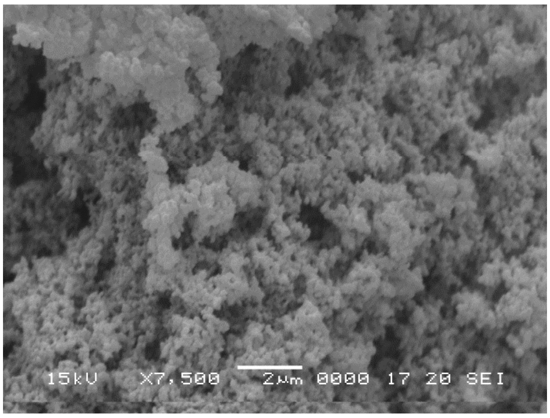

Fig. 4b *Microscopic image of synthesized polyaniline salts polyaniline citrate (PANI-Citr.)*

From the comparison of the morphology of the polyaniline salts, it is possible that there was an increase in thick layers of the applied coating film on the surface of the sample DC_04 (PANI-Citr). This means that, despite the relatively large contact angle, good anchoring of the glue is a prerequisite. Contact angle values can be improved in future research by correcting the parameters during the phosphating process.

3. Conclusions

Based on the presented results of experimental measurements, it is possible to state the following conclusions:

- when measuring and evaluating the 2D roughness parameters, it was demonstrated that the DC_4 sample has more favorable results for the further application of the adhesive coating or glue.
- the samples that were phosphated in polyaniline salts in this experiment showed satisfactory values of contact angles. It is necessary in future research to focus on the optimization of technological parameters during phosphating.

Experimental verification of the use of specific compounds of polyaniline salts in the phosphating process from the point of view of their applications for adhesive bonding is promising, but attention needs to be paid to further research from the point of view of obtaining the most optimal surface fragmentation.

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