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ANALYSIS OF THE POLYANILINE WITH NANOPARTICLES OF ZINC IN THE AUTOMOTIVE INDUSTRY

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Abstract. *The protection against corrosion in the automotive industry is a high impact problem on the economic view. Besides of an antirust characteristics, the coatings used in the automotive industries needs do have a good appearance and technical resistance. The multilayer coatings are normally compound per e-coat, primer, base and clear coat, where the primer can also be used as an e-coat substitute in rework processes. In the other side, the conductive polymers has been widely discussed as a coating material and the polyaniline-zinc composite had presented good results as an efficient material concerning the corrosion protection. Considering the automotive industry necessities and the polyaniline-zinc results, this study had apply the polyaniline-zinc composite in a multilayer coating used in the automotive industry, substituting the commercial primer in a common rework process. In addition, the results were compared with the commercial primer used currently. Then, the painted sets were evaluated regarding the visual aspects, corrosion and technical resistance and the results presented the polyaniline-zinc performance when applied together with other technologies as base and clear coats.*

Keywords: *Polyaniline-Zinc Composite, Primer, Corrosion, Automotive*

1. INTRODUCTION

The search for methods that avoid the corrosion aspects on the materials has been guiding innumerable academic studies and investments per industries side. For the automotive industries, the customer requirements has been increased along the years, besides of it the concurrence between the competitors results in, between other things, increase of the guarantee time of the automotive components and against corrosion (Nam, *et al.*, 2015; Lebozec *et al.*, 2008).

The galvanized steel usage summed to coatings as electrophoretic paint, primer and topcoat build the common process used on the industries (Streiberg and Dössel, 2008).

Besides of that, the conductive polymers also has been focused in the academic studies and due the good results it compound a promisor class of coating material. The mainly advantage to use the conductive polymers against the metallic corrosion is the tolerance for the structural defects, in other words, discontinuity on the polymeric coating. In addition, this coating favors the passivation of the metal areas exposure for the environmental (Trived, 1997; Roth and Grauper, 1993).

In general, the conductive polymer Polyaniline – PANI is presented as an alternative material for the conventional coatings. The PANI act as a physical barrier, promoting the partial or complete isolation of the substrate with the environmental. Furthermore, the efficiency of this polymer is increased with the incorporating of micro and nanoparticles of Zinc. Not only the particles that are in contact with the substrate act as sacrifice anode but also all of the particles that interact electrically with the PANI, improving the corrosion resistance of the coating in case of damages of the layer (Wessling, 1996; Fahlman, *et al*, 1997).

The Polyaniline-Zinc composite (PANI-Zn) is a promisor coating against corrosion and had been presented in academic studies as Cruz (2015), Rajasekharan (2013) and Xavier (2013). It is a good alternative for new developments and applications.

The consolidation of the constant search for high efficiency coatings by the automotive industries and the good results and capacity presented by the PANI-Zn composite generate the objective of this study that is to apply the PANI-Zn as an intermediate coating between the galvanized steel and the topcoat in the rework process used in automotive industries.

Then, it will be evaluate the resistance and efficiency of the PANI-Zn composite used together with automotive industry coatings regarding the visual aspects, corrosion and technical resistance. In addition, the results will be compared with conventional primers already used in the industry for the rework processes.

2. EXPERIMENTAL

The experimental procedures are going to be divided in three steps: sample characterization, corrosion resistance and technical resistance. The first step comprise the substrate evaluation and the visual aspects using nondestructive tests. The second step are going to use the cycle test for corrosion and in the third step, it will be evaluate the technical resistance as adherence, flexibility and blistering, very important in cases of crash , for example. All the tests and determinations were done in triplicate.

2.1 Material

To support the objective of this study, the substrate and material used in the tests are the same currently used in the industry where the sample were prepared and where part of the tests were done. Only the PANI-Zn was synthetized and applied at the UTFPR lab.

The substrate were hot dip galvanized GI 50/50 (HDG) panels, with dimensions of 100 x 200 x 1 mm (WxHxD), with zinc thickness between 6.5 and 7.5 µm. The antirust coatings used were PANI-Zn, adherence promoter Bonderite NC100 by Henkel, Flash Primer by PPG and Glasurit Primer by BASF. The topcoat coatings were Basecoat and Clearcoat by PPG. The paint color used was a solid white, to minimize the metallic effects on the visual analysis.

2.2 Sample Preparatingn

The PANI-Zn was synthetized at the UTFPR according Cruz (2015), who follow the Mattoso (1996) procedure. In a sequence, after the vacuum dehydrating, the powder material was dissolved in n-methylpyrrolidone (NMP) with nanoparticles of zinc, constituting the coating used. The Zinc particles were characterized with transmission electronic microscopy at UFSCAR, and it showed god distribution of the particles inside of the composite and average size from 10nm (CRUZ, 2015).

The samples were prepared in three sets, using different antirust coating in each one: PANI- Zinc, FLASH primer and GLASURIT Primer. Figure 1 represents each set composition, where all the sets where previous cleaning with Isopropanol and have the same substrate, base and clearcoat composition.

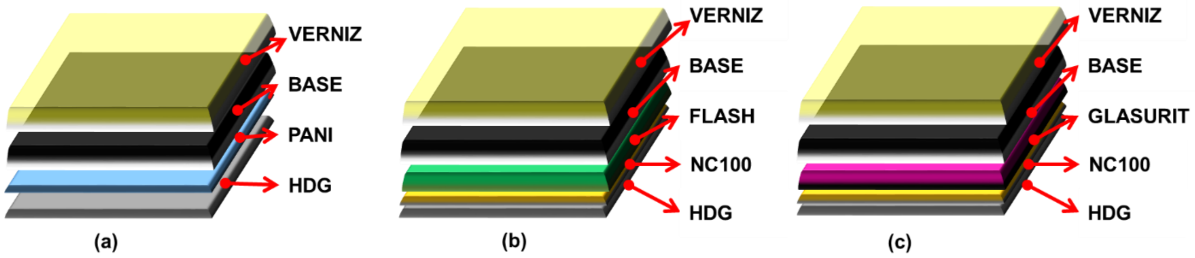

Figure 1. Painted Sets Representation (a) PANI, (b) FLASH and (c) GLASURIT

In the first set, the PANI-Zn was applied by immersion and cured at oven of the UTFPR lab. Considering the incompatibility between the materials the adherence promoter, it was not used. The second and third sets received the adherence promoter and in a sequence, the respective primers were painted manually using gravitational paint gun. The FLASH primer were cured at ambient temperature and the GLASURIT primer were cured according datasheet using infrared equipment. After the PANI and primers applications, all the sets were manually painted with base and clear coat and the cured according datasheet with infrared equipment.

The time between the paint preparation of the samples and the start of the tests were one week, to guarantee that all the coatings were completely cured.

2.3 Sample Characterization

In the HDG substrate were done Scanning Electron Microscope – SEM and Energy Dispersive Spectroscopy – EDS, to evaluate the morphology, composition and uniformity of the zinc surface. The equipment used was SUPRA 55VP by FEG-ZEIS® and the detector was EDX Flash 6/60 –QUANTAX 200/ Bruker from SENAI.

The paint sets were verified the total per layer thickness, color, gloss and appearance – orange peel. For thickness was used Fischer and Pelt equipment and for color, gloss and appearance was used equipment of BYK Gardner Brand.

2.4 Accelerated Corrosion test

The accelerated corrosion was done in a cyclic test methodology. The equipment used is a model SC 100 of WEISS brand and together with the methodology, follows the standard DIN EN ISO 11997-1. The painted samples were prepared for the test, doing a transversal cut where it was possible to see the substrate, with thickness higher then 0,3mm.

According Fig.2, each cycle corresponds of one week and in this test it was evaluated ten cycles, following the industry standard. The evaluation was done considering the corrosion rating, the general changes on the surfaces, as corrosion migration since the transversal cut done. To evaluate the rating is necessary to remove with a spatula the coating without adherence of the sample and then, the corrosion dimension is measured along the cut.

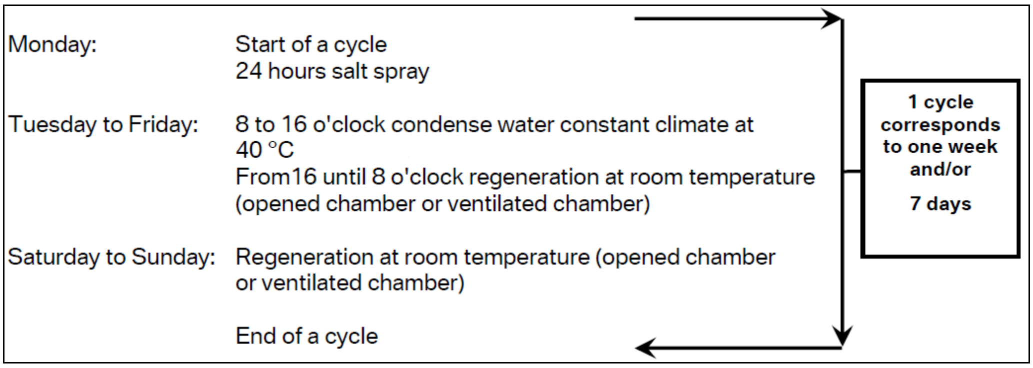

Figure 2. Cyclic Corrosion – Cycle Diagram

2.5 Technical Resistance

For evaluate the technical resistance, it was done the tests: condensation water constant atmosphere, stone chip, single impact, steam jet, cross hatch and flexibility.

The condensation water constant atmosphere equipment and methodology follows the standard DIN EN ISO 6270-2 and 4628-2. The equipment used is a K 300 model of the Liebisch brand. The test was done in ten days with 100% of humidity and 40°C. After this period, the samples are cleaning and evaluate regarding color, blistering and in a sequence the cross hatch test is performed.

The stone chip test is done to evaluate the adherence between each layer of the set painted and the paint with the substrate. It follows the standard DIN 20567, which define metal pellets GH-K 4-5mm and adhesive tape according DIN 2409. The test used pressure of 2 bars and the sample was shot twice with 500 g of metal pellets. After shooting the pellets on the sample, loose paint particles are removed with the adhesive tape. The evaluation and rating of the stone chip is performed according to the pictures in DIN EN ISO 20567.

The single impact test serves to identify the separating layer on multi-layered coatings. For this test, the samples are cooled down to –30°C in a freezer to achieve the low temperature condition. Immediately after removal from the freezer, the sample is put on the instrument with the side to be tested facing down and the impact test is performed. Loosely adhering paint particles are removed after the impact using the adhesive tape. The equipment and methodology follows the DIN 55996-2 definitions.

The steam jet test is done to determine the paint resistance and adherence when is used water jet, simulating the car washing machines. This method is defined of the standards DIN 16925 and 2409. The samples are prepared with five longitudinal cuts and one orthogonal until the substrate. The cuts had at least 200 mm of length and 10 mm of distance between each cut.

To evaluate the adherence of single and multi-layered coatings on different substrates as well as the different layers to each other is evaluated the cross hatching test. It is a simple test, which is done two transversal cuts with tools with angle of 90° approximately. Then, the loosely adhering paint particles are removed after the impact using the adhesive tape. The definition of the equipment, procedure and table for evaluation are described in the standard DIN 2409.

In the flexibility test, the samples are fixed in a conical mandrel and are bend over the equipment. The distance between the failure occurred due the bending until the minor border of the mandrel is measured. Then, it is measured the elongation of the coating until the failure. The standard that defines the equipment and method is ASTM D 522.

3. RESULTS AND DISCUSSION

The results are going to be presented in the same sequence used to describe the experimental chapter: sample characterization, accelerated corrosion test and technical resistance tests.

3.1 Sample Characterization

In the substrate panels, the SEM analysis demonstrated a typical galvanized surface, according Cavalcante (2010), demonstrated in the Fig.3.

Figure 2. SEM picture: HDG Surface of the Sample Panel

The table 1 presents the results of EDS. The chemical composition is similar to the results presented by Cavalcante (2010) for HDG GI. Then, SEM and EDS analysis presented good results regarding the substrate.

Table 1. EDS – Weight % - HDG Sample Panel

Spectrum	Average	Reference Value (1)
Zn	98,1	98,8
Al	1,0	0,7
Fe	0,5	0,5

(1) CAVALCANTE (2010)

For the painted sets, the total paint thickness were measure for all the plates. The other tests and determinations follow the triplicate rule. The Table 2 shows thickness measurements results, for total film build and per layer.

Table 2. Average of Paint Thickness – Total and per Layer

Thickness (µm)	Total Fischer	Primer µPelt	Base µPelt	Clearcoat µPelt	Total µPelt
PANI	43,33	6,74	17,03	22,17	45,94
FLASH	47,00	16,99	15,28	20,35	52,62
GLASURIT	49,00	19,60	16,21	20,13	55,94
STDEV	2,9	6,8	0,9	1,1	5,1

The PANI set presented the lower thickness, when compared with the commercial primer, due the lower solids content in the composition, and the standard deviation of this layer was 6,8. For the base and clear coat it was verified more uniformity of the results and the standard deviation was 0,87 and 1,1 respectively.

The color and gloss determination, Table 3, had presented low variation between the primer painted sets. But the PANI set presented the color deviation (ΔD) around 40% and the gloss 4% lower than the primers. Considering that lower ΔD values represents better samples and that the gloss was near of the primers, and also that gloss can be improved with polishing, then the PANI set had the best results concerning color and gloss.

The appearance – orange peel are also presented in the Table 3, and it represents the visual evaluation with a inspection at one meter of the piece and at 3 meters of the piece. The results are in percentage, where the zero is a piece without any rework. The PANI and the FLASH primer had the same results, with 17% of deviation when compared with the zero. But, the GLASURIT primer had worst results when evaluated at one meter from the piece. Then, the PANI and FLASH primer had the better results for appearance.

Table 3. Average of Color, Gloss and Appearance Results

	Total Thick. Fischer (µm)	Color (∆D)	Gloss (GU)	Appearance N1	Appearance N1
PANI	40	0,71	86,37	8%	17%
FLASH	41	1,23	89,87	8%	17%
GLASURIT	48	1,24	88,00	17%	18%

3.2 Accelerated Corrosion test

After the tests, the plates were cleaning with fresh water and where evaluated concerning the general corrosion. In a sequence, the paint material that had lost the adherence were removed with a spatula (not sharp) and the peeling were measured. Any painted set had general corrosion and the rating results are presented at the Table 4.

Table 4. Average of Cyclic Corrosion Results

	Total Thick. Fischer (µm)	Cyclic Corrosion Average (mm)(1)	Minimum (mm)	Maximum (mm)
PANI	53	41,3	22,5	62,5
FLASH	62	43,5	27,5	67,5
GLASURIT	55	29,4	12,5	57,5

(1) Objective: ≤ 40 mm

Considering that the requirements used for the industry where this study was done for this test is zero for general corrosion and lower than 40 millimeters for corrosion migration – starting in the cut done at the beginning of the test, then, only the GLASURIT primer is consider approved. The PANI set had better results than the FLASH primer, lower peelings and consistent regarding the migration.

3.3 Technical Resistance

The third step of technical resistance comprises the testes described above: condensation water constant atmosphere, stone chip, single impact, steam jet, cross hatch and flexibility.

The condensation water constant atmosphere test was done at 40°C and 100% of humidity for 10 days. Then the painted sets were cleaned and dried and the visual aspects were evaluated: color and gloss losses and blistering. In a sequence, the cross hatch test was performed. In the Table 5 the results are presented. The PANI set had the worst results with 50% of the sample with blistering and rating 5 in the adherence test. The FLASH primer had intermediate result, with 26% of blistering and rating 3 in the adherence test. Moreover, the GLASURIT primer was the better one with only 3% of blistering and rating 1 for adherence test. Even though the GLASURIT primer had the best performance, but any painted set was approved, considering that, the industry requirements are minor or equal 1 for adherence rating and don´t allow any blistering in the surface.

Table 5. Average of Condensation Water Constant Atmosphere Results

	Total Thick. Fischer (µm)	Blistering (1)	Cross Hatch (2)
PANI	45	50%	5
FLASH	50	26%	3
GLASURIT	54	3%	1

(1) Objective: 0%
(2) Objective: ≤ 1

The stone chip, cross hatch, single impact and flexibility tests was performed and all the sets were approved, according Table 6. In the cross hatch, the PANI set had the result worse than the primers, but it is approved according the industry requirement. The only test that present different results was the steam jet, which uses water to attack and remove the coatings. In this test the painted set PANI had the worst result, followed by the FLASH primer. Only the GLASURIT primer had a good result and was approved according the industry requirement.

Considering the Condensation Water Constant Atmosphere and the Steam Jet tests, it is possible to notice that the PANI and the FLASH sets are less resistant in humid environmental. In the other side, the GLASURIT primer kept the performance in all the tests.

Table 6. Average of Stone Chip, Single Impact, Steam Jet, Cross Hatch and Flexibility Results

	Total Thick. Fischer (µm)	Stone Chip (1)	Cross Hatch (2)	Steam Jet (3)	Single Impact (4)	Flexibility (5)
PANI	34	2	1	4	0	0
FLASH	39	2	0	3	0	0
GLASURIT	45	2	0	0	0	0

(1) Objective: ≤ 2,5
(2) Objective: ≤ 1
(3) Objective: ≤ 1 mm
(4) Objective: 0
(5) Objective: 0

4. CONCLUSION

The painted set PANI had around 10µm of thickness lower than the other sets. However, it presented similar results for the visual aspects, when compared with the current material used in the industries. This set had presented also intermediated results in the corrosion tests and similar results in the dry adherence tests, compared with the commercial primers painted sets. Nevertheless, the results of the tests that involves humidity were worse for the PANI sets, revealing fragility of the painted set PANI.

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