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Investigation on the Applicability of Polyaniline in Primer Systems for Metal Protective Coatings in Corrosion Conditions

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The paper presents some results of comparative investigation on the efficiency of polyaniline (PAni) finely dispersed in polyvinyl butyral as primers in different anticorrosive painting systems. The PAni nanofibres were used for the protective coating purpose. The PAni have various dopants such as inorganic acids (HCl in ES-M samples, H_3PO_4 in ES-P samples) and organic acid (p toluene sulphonic acid in ES-T samples). The nanostructures of the PAni samples were proved by FE-SEM results. We have investigated comparatively 3 paint systems having the cover coat of polyurethane with different primers: L1 (with ES-M as active component); L2 (with ES-P) and L3 (with ES-T) using salt spray test and electrochemical impedance measurements. Results of salt spray test showed that all the systems having PAni as primers resist over 1440 h (60 cycles). Results of EIS showed that samples using L3 primers gave the highest protective efficiency (with $|Z|_{0,1Hz} = 10^8 \Omega.cm^2$ and its open circuit potential value reached –34.8 mV/SCE after 63 days immersed in 3% NaCl medium). All the research results demonstrated clearly that PAni nanofibres could be a very good component for primer coating systems.

Key words: Polyaniline; nanofibre; primer layer; protective coating systems; FE-SEM result; salt spray test; EIS measurements; protective performances

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After the first suggestion of Mc Diarmid, some papers dealing with the metal protection by intrinsically conducting polymer (ICP) were published during 1985–1990. In the last decade, a lot of work was performed with polyaniline (PAni), then expanded to other ICPs [1–3]. The use of PAni in traditional film-forming materials for anticorrosion protective paint is a new and promising direction of research. In this situation, PAni can play the role of an active, anticorrosive pigment, taking the place of other toxic, hazardous pigments containing heavy metals. In some papers, the PAni contents tested vary in a broad range (from 3 wt% to 50 wt%) leading to good and stable protection performances. The corrosion protection of mild steel by a novel epoxy resin (EP) - based coating system containing PAni as an anticorrosive agent was studied. The corrosion behaviour of mild steel coated with anf EP/PAni-EB (emeraldine base), EP/PAni-ES (emeraldine salt), EP/SPAN (PAni sulphonated), EP/PAni-fibres was investigated in 3.5% NaCl solution. The electrochemical impedance spectroscopy measurements were utilized. Results showed that, the coating containing SPAN was found to have the best performance in the in the protection of the metal among all the other samples containing PAni. The coating formed from paint EP/SPAN showed a resistance of $9.0.10^7 \Omega.cm^2$ [4]. Using PAni dispersed in polyvinylbutyral (PVB), polyurethane, epoxies, alkyd resins as film-forming materials, recently there were proposed some pigment systems applicable for marine coatings and other industrial works [5–7]. It is well known that PVB is a good primer, favouring the adherence of various cover coats, making an inhibiting effect by its active pigments [9, 10]. Our already published papers dealt with conditions of synthesis, modification and properties of different PAni derivatives [11, 12].

Different one-dimensional nanostructured polyanilines were synthesized in sulphuric acid solutions by conventional, interfacial polymerization and directmixed, respectively. The products were applied to the clean mild steel surface and characterized the anticorrosion performance of products on mild steel were studied using electrochemical measurement in 3.5% NaCl aqueous solution. Compared with uncoated mild steel, the E_{corr} of PAni coated mild steel is more positive than the potential at the bare olectrode about 27 mV to 58 mV, the I_{corr} reduced 21.43 to 68.08% [13]. Due to its very low solubility in almost all solvents and passivizing activity, PAni is considered a very good anticorrosive pigment for protective paints. The paint systems having PAni as an active pigments is very useful in the corrosive medium containing chloride ions [14, 15]. The mechanism of corrosion protection of steel by polyaniline coating has been studied by Kinlen *et al*. [16–18]. They have reported that doped polyanline coatings passivate the pin hole defects in the coatings. Further, it has been reported that steel coated with polyaniline has gained 100 mV–200 mV in corrosion potential in 3% NaCl due to decrease in iron dissolution reaction by passive film formation and shift the passive rigion [17, 19, 20]. In this work, we present results on assessments of dispersion efficiency of different PAni derivatives by various techniques and their applicability as pigment in primer layer for protective coatings.

EXPERIMENTAL PART

Materials

Resine. Desmophen A450 (Bayer, OH content of 1.01 ± 0.2 %, viscosity of 4000 mPas); Harderner N3300 (Bayer, NCO contents of 21.8 ± 0.5% viscosity of 300 mPas); Resine FA 703 (Bayer, OH content 1 ± 0.2%); PVB (Germany, butyral content of 75%–88%, OH content of 22%), H_3PO_4 (p.a. China); PAni doped by toluene sulphonic acid (ES-T); PAni doped by H_3PO_4 (ES-P); PAni doped by HCl (prepared by seeding method), denominated as (ES-M).

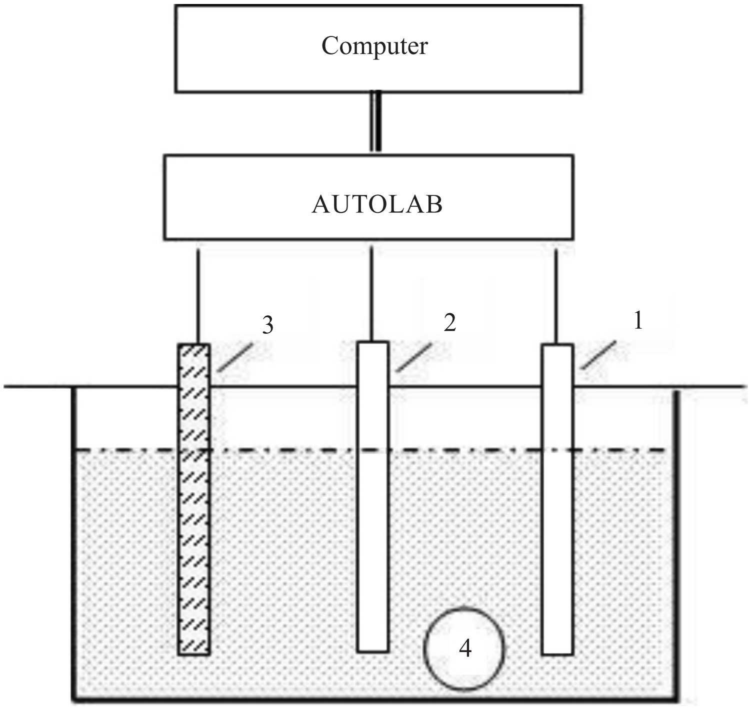


Figure 1. Experimental cell set-up:1–SCE reference electrode; 2–Graphite counter electrode; 3–Test electrolyte (Painted steel panel); 4–Electrolyte solution (3% NaCl solution).

Analysis and Measurements for Characterization

- Morphology analysis by FE-SEM method (Hitachi S-4800 for FE-SEM analysis of nano scale PAni) and SEM (Jeol-6600) for other surface morphologies).
- Salt - spray test: After *ASTM B-117-95*, the rust degree determined after *ASTM-D-1654-05*, using S-100 Weitechnik (Germany) apparatus.
- EIS measurement we used for assessment of protective capacity of the paint coating via impedances and open circuit potential (OCP) data (Autolab PGStat30, Ecochemie, Holland).

All electrochemical experiment were perfomer in a single compartment cell with a three-electrode configuration: the test electrolyte consisted of a steel plate with a dry film of the paint, with an exposed surface of 60 cm^2, the reference electrode was a the counter electrode was graphite plate, with an exposed surface of 60 cm^2 and saturated calomel electrode (SCE). Impedance data were measured periodically as the open circuit potential in 3% NaCl solution, and a frequency range of 10^5 to 10^{-2} Hz using amplitude of sinusoidal perturbation at ± 5 mV AC

Procedure

Preparation of PAni. PAni was synthesized by chemical oxidative polymerization, using ammonium persulphate (APS) as reagent in presence of different dopants (TSA, H_3PO_4 and HCl). After a carefully washing process with water (to pH=7), samples were treated with ethanol and ethyl acetate, extracting all the oligomers, low molecular fractions and water traces.

The dry solid content of the final paste products in ethyl acetate is 40 wt%. Some samples of polymer also were dried at moderate temperature to constant weight for structural analysis and comparative paint preparations.

Dispersion of PAni in PVB. The dispersion of PAni in the PVB medium was performed by three procedures:

(a) Traditional dispersion by hand milling of dried PAni;

(b) Conventional dispersion by ball milling then improved by a short ultrasonic treatment;

(c) Direct dispersion of PAni (already dispersed in a paste form) followed by mechanical stirring for 60 min then improved by short ultrasonic treatment (3 min–5 min).

The PAni contents of all three derivatives were 5wt% in PVB.

PVB primer. Part A: Dissolve 7.2 g PVB in 71.8 g butanol-isopropanol mixture. Then, PAni sample is dispersed in this solution for 5 wt% content. The dispersion was made by mechanical stirrer for 60 min. Part B: Concentrated H_3PO_4 in isopropanol (18 g) and water 64.5 g for making a 18.2 wt% solution. The ratio of mixing Part A and Part B is 4/1 v/v. Denomination for 3 primers was: L1 (with ES-M), L2 (with ES - P) and L3 (with ES - T).

The PU cover coat. Mix Desmophen® A450 and FA703 (80/15 wt/wt) in toluene/ butyl acetate (3/7 vol./vol.) for a solution of 40% dry content. The paint was cured by Demodur® N3300 (The ratio of resine/ hardener = 80/20 wt/wt).

The PU cover coat might be with or without pigments.

- GF0: Transparent coat, without pigment (varnish).
- GF5: With 5 wt% ES-T and 20 wt% TiO_2.
- DF5: With 5 wt% ES-T, 20 wt% TiO_2 and 20 wt% Fe_2O_3.

All these paints before spraying must be thinned by solvent to a suitable viscosity (18–25 second measured by Ford cup 4). Paint samples were prepared on the cold roll steel plates. The primer thickness is 8 µm-–10 µm and the cover coat is 50 µm–60 µm.

RESULTS AND DISCUSSION

Morphological Analysis

The morphological structures of PAni samples were investigated by FE-SEM technique (S-4800 Hitachi).

The ES-P samples, prepared with ultrasonic assistance in H_3PO_4 medium, were in the fibre form (of 50 nm–60 nm diameter and 500 nm–1000 nm length); see Figure 2b. The ES-T samples, prepared in presence of TSA (an organic acid, milder reaction conditions) was also in fibre form (of 50 nm–60 nm and 500 nm length); see Figure 2a. The ES-M samples, prepared with "seeding" conditions existed initially as fibres, then aggregated to soft bundles yet separated in fibres at their ends (see Figure 2c). Generally, all PAni samples obtained with different dopants showed clearly a fibre form in nano scales.

Morphology of PAni in PVB Systems

The PAni/PVB systems were investigated by SEM technique. The results obtained are presented in Figure 3. It could be observe that the hand-milling technique led to bad dispersions, the particles were dispersed only on micrometer scale. Some regions showed a clear tendency to aggregate to larger domains of 50 µm–100 µm (Figure 3g). Samples prepared with ultrasonic assistance were more uniform and the dispersion was fine (Figures 3b, 3e and 3h). Samples prepared by direct dispersion of PAni paste (stirred, then assisted by ultrasonic technique (3 min–5 min.) showed the best dispersion state of under 1µm scale, (see 3000×magnification images in Figures 3c, 3f and 3k).

Seen by naked eyes, the material surfaces were very smooth. The ES-T showed the best dispersion due to an organic nature of the dopant in this material. The ES-P showed a lesser successful case, making an uneven surface, even with phase separation. The results of the morphological investigations showed that the last way of dispersion gave the best distribution of the PAni nanofibres. This method was the chosen one for preparing all the primers.

The SEM investigation showed that ES-T proved itself as the best pigment in this case. Among the three pigments, this was the best compatible one with PVB solution.

Investigation on the Protective Capacity of the Paint Systems

The direct dispersion of the PAni paste in PVB (assisted by ultrasonic technique) was chosen for primers preparation. In this series of experiments, the double-layer paint system of primer coat and PU varnished over it [separately: L1 (ES-M); L2 (ES-P); L3 (ES-T)].

The test paint was compared to other coating systems painted directly in the bare steel surface,

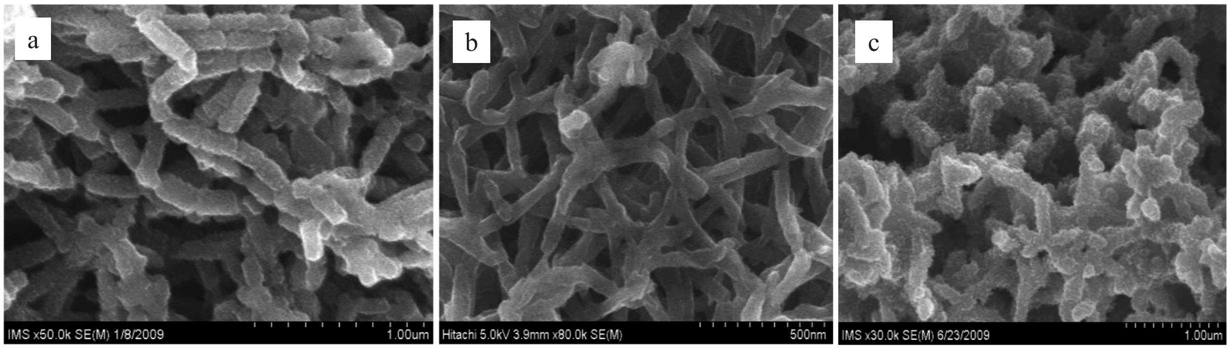


Figure 2. SEM images of PAni samples prepared in different conditions: (a) ES-T, with mechanical stirrer; (b) ES-P, prepared with ultrasonic assistance; (c) ES-M, prepared with nano PAni seeding powders.

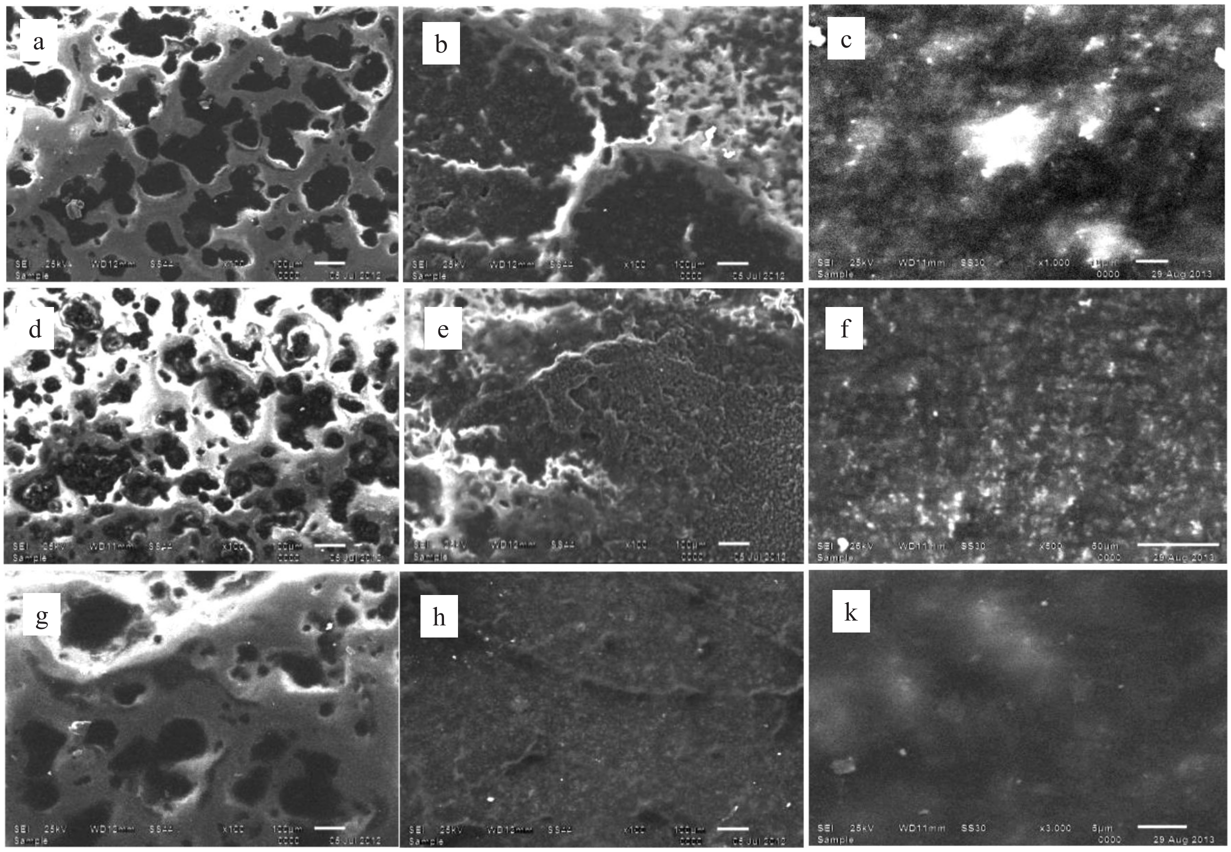


Figure 3. SEM images of PAni/PVB systems prepared by different techniques viz. ES-P/PVB: (a) Dispersed by hand-milling, using dry PAni powder; (b) Dispersed by ball-milling, then assisted by ultrasound, using dry PAni powder; (c) Direct dispersion from paste by mechanical stirrer then assisted by ultrasound. ES-M/PVB: (d) Dispersed by hand-milling, using dry PAni powder; (e) Disperded by ball-milling, then assisted by ultrasound, using dry PAni powder; (f) Direct dispersion from paste by mechanical stirrer then assisted by ultrasound. ES-T/PVB: g/dispersed by hand-milling, using dry PAni powder; (h) Disperded by ball–milling, then assisted by ultrasound, using dry PAni powder; (k) Direct dispersion from paste by mechanical stirrer then assisted by ultrasound.

namely (GF5 pigmented with 5 wt% ES-T and 2 0 wt% TiO_2); (DF5 pigmented with 5 wt% ES-T, 20 wt% TiO_2 and 20 wt% Fe_2O_3).

Salt-spray test. The results of salt spray test were presented in Table 1 showing a very clear difference between samples with and without primer coats. The same situation existed between samples with and without PAni in their pigment compositions.

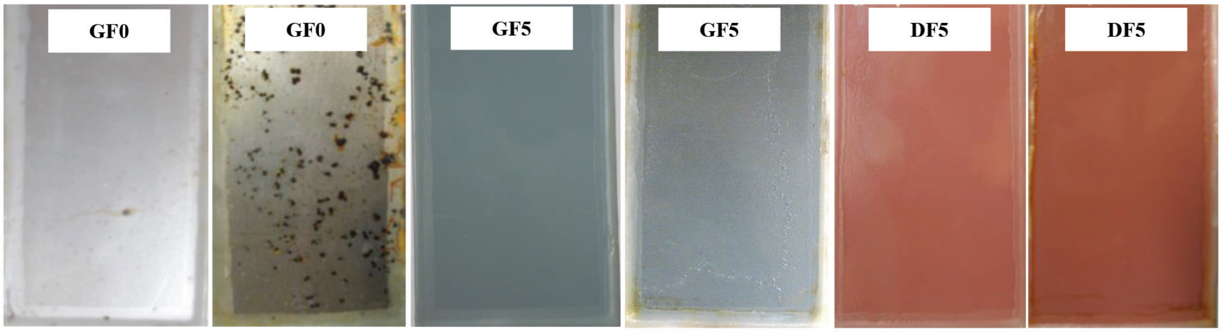
The PU varnish (GF0) painted directly on the steel surface with 60 μm thickness resisted 30 cycles then appeared with blistering points and rust (see Table 1, column 2). Paint samples having PAni (GF5, DF5) painted without primer coat on steel showed better performances. The GF5 paint showed sign of blistering but no rust after 30 cycles (see Table 1, column 6). The DF5 paint film was very good even without primer coat.

The results proved the positive role of PAni in protective polyurethane paints. The painted films during the salt-spray test were presented in Figure 4. All the paint systems on the PAni/PVB primer showed smooth, resistant coats after 1440 h of salt-spray test (60 cycles of 24 h). These results demonstrated that with only 6 μm–10 μm

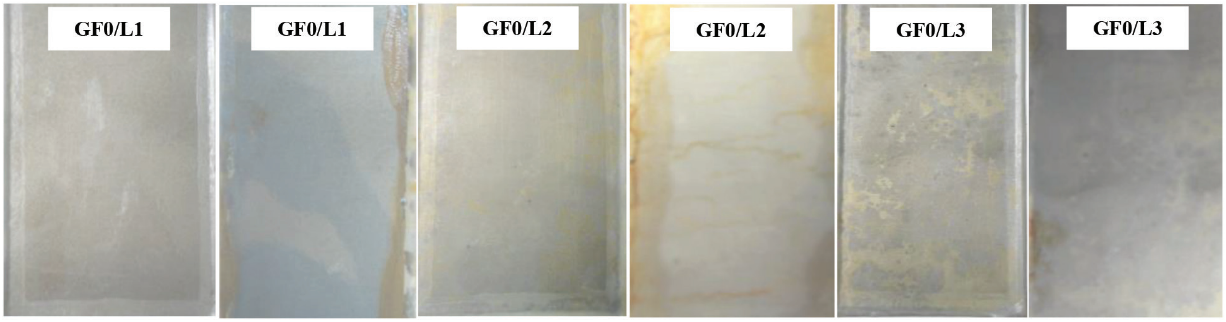
Table 1. The result of salt-spray test of the coating systems.

Number of cycle tested	GF0	GF0/ L1	GF0/L2	GF0/ L3	GF5	DF5
0	S	S	S	S	S	S
5	S	S	S	S	S	S
10	S	S	S	S	S	S
15	S	S	S	S	S	S
20	S	S	S	S	S	S
30	B(1)+R(0.3)	S	S	S	B(1)	S
40	B(1)+R(0.3)	S	S	S	B(1)	S
50	B(1)+R(3)	S	S	S	B(1)	S
60	B(1)+R(5)	S	S	S	B(1÷3)	S

Note: S—smooth, intact coat; B(d)—blistering (with its blister diameter, in mm); R(r)—rusted and % of rusted surface.



Original After 30 cycles Original After 60 cycles Original After 60 cycles



Original After 60 cycles Original After 60 cycles Original After 60 cycles

Figure 4. Paint samples before and after salt-spray test.

of film thickness, the PAni/PVB primer significantly improved the protective quality of paint systems. Even with clear PU varnish, the primer coat increased the resistance from 720 h to 1440 h (comparison in Table 1 between columns 2 and 3, 4, 5). For 100 μm thickness, PAni/alkyd coating (PAni loading 0.5%–2.5%) can withstand 900 h of salt spray test, is only 600 h for pure alkyd coating [2]. The presence of PAni derivatives in paint systems improved their salt-spray resistance sharply, confirming observations of other authors [2, 3, 6–8].

The situation was more interesting in the case of the GF5 paint film (with blistering without rust formation). That was possible because the steel substrate probably might have passivised.

Results of electrochemical impedance spectroscopy (EIS) investigations. At the same time, we made investigations with EIS method. The results for measurement of open circuit potential (OCP) and impedance of paint systems were showed in Table 2 and Figure 5. By comparison of the impedance and OCP data for GF0 (polyurethane varnish) on different primers; it was obtained and the following were the order of primers efficiency: L3 > L1 > L2 (see Figure 5).

The paint systems with L3 showed higher impedance $|Z|_{0.1\ \mathrm{Hz}} > 10^8\ \Omega.\mathrm{cm}^2$ (fair to good coatings: $|Z|_{f\rightarrow 0}$ values of 10^6 to greater than 10^9 $\Omega.\mathrm{cm}^2$ that maintained << 2 weeks in immersion [21]) and value of OCP = –34.8 mV/SCE. The samples have long lasting durability under salt-spray test (of more than 1440 hours of exposure), in good conformity to the electrochemical measurement results. The values of the OCP were initially positive (insulator) then decreased gradually during the first 15–20 days due to the process of diffusion. After this process, the OCP increased to the higher positive values which showed that after the diffusion process, metal surface was passivated. These results were in conformity with morphological investigation for PAni/PVB samples, leading to observations that a better dispersion in primer gave a higher performance for metal protection [2, 4, 21, 23].

Samples with lower impedance and OCPs (such as GF5, GF5/L1) suggested an eventual corrosion danger. In reality, these samples immersed in electrolyte solution for 63 days during EIS test showed no sign of rust, reconfirming the positive results of salt-spray test (resisting 60 cycles). All these paints have PAni in their compositions, as compared to GF0 (no PAni, no pigment) already showed rust after 30 cycles and its rust area extended step by step in course of the testing time. This result proved clearly the positive role of PAni derivatives for metal protection,

Table 2. Electro chemical data and situation of paint systems.

Sample	Primer	Impedance $\|Z\|_{0.1\ \mathrm{Hz}}$	OCP after 63 days (mV/SCE)	Situation
GF0	–	$10^6\ \Omega.\mathrm{cm}^2$	–582 to –796	● Electrolyte rapidly diffused through film, OCP decreased rapidly ● Rust appeared in many positions
GF0/L1	ES-M/PVB	$10^6\ \Omega.\mathrm{cm}^2$	~ –500	● Impedance decreased slower, OCP low ● No rust after immersion
GF0/L2	ES-P/PVB	10^5–$10^6\ \Omega.\mathrm{cm}^2$	~ –500 to –700	● OCP decreased rapidly ● Low impedance values during test period ● No rust appeared
GF0/L3	ES-T/PVB	10^7–$10^{10}\ \Omega.\mathrm{cm}^2$	~ –34.8	● High impedance, OCP increased stepwise to higher value ● Paint systems was stable and showed good protective performances ● No rust
GF5	–	10^5–$10^6\ \Omega.\mathrm{cm}^2$	–500 to –750	● Low impedance values ● No rust
DF5	–	10^7–$10^9\ \Omega.\mathrm{cm}^2$	–135	● High impedance, ● No rust

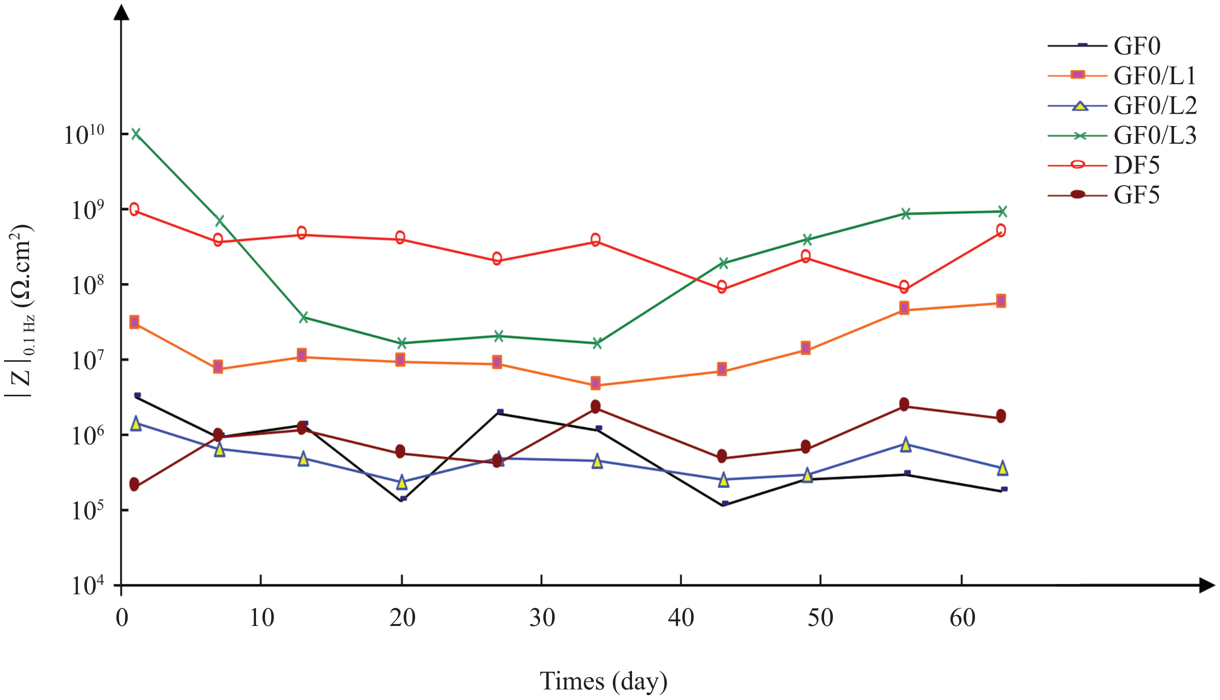


Figure 5. Variation of the impedance values for the PU coatings on the immersion times.

might be via mechanism of cathode protection or providing ions for inhibiting corrosion process by cutting electron transport from the metal substrate to oxidative medium [5, 6].

The DF5 film could be painted directly on the steel surface. Its impedance was high ($|Z|_{0.1\ Hz} >$ 10^8 Ω.cm²) and was stable during the whole time of sample immersion. Here, the presence of 20 wt% Fe_2O_3 beside 20 wt% TiO_2 in the pigment system contributed to the compactness of the paint film, which increased the inhibiting capacity of the paint system. The GF0/L3 showed a higher OCP value and much better protective capacity. The two layer coating systems, of PU on the L3 primer led to a markedly improved protective effect.

CONCLUSIONS

PAni with organic dopant (ES-T) prepared in the nanofibre was formed and very well dispersed in PVB. This pigment was the best compatible with PVB as compared to ES-M and ES-P. Dispersion directly from the PAni paste was also the best way for preparing primers with PVB. The ES-T gave the most finely and uniform dispersed systems. All the paint systems on the primer coat containing PAni resisted over 1440 h of salt-spray test. The primer had good compatibility with PU cover coat. The best primer composition was L3. Our experiment with other cover coats (epoxies and alkyd resines) also showed that the PAni primer could work well, leading to highly efficient protective paints.

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