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Enhanced Corrosion Protection Performance by Novel Inhibitor-Loaded Hybrid Sol-Gel Coatings on Mild Steel in 3.5% NaCl Medium

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The sol-gel methodology has been applied successfully in the synthesis of a novel hybrid coating based on dimethoxymethyl-n-octadecylsilane precursor. The newly synthesized parent coating was functionalized further with two commercially-available corrosion-inhibitive pigments Moly-white® 101-ED and Hfucophos Zapp®, applied to mild steel panels, and immersed continuously in 3.5% NaCl electrolytic solution for 288 h. The corrosion protection performance of the prepared functional coatings was evaluated using electrochemical impedance spectroscopy (EIS) and DC polarization techniques. An enhancement in the barrier properties has been revealed from the electrochemical characterization data of the hybrid films, in comparison with untreated mild steel substrates following long-term immersion in 3.5% NaCl. The corrosion resistance properties of the newly developed coatings over mild steel substrates found to be largely dependent on the type of the loaded inhibitive pigment in which the Moly-white inhibitor has a positive impact on the corrosion protection performance of the parent coating, while an opposite behavior was observed upon mixing the base polymeric matrix with the commercially-available Zapp corrosion inhibitor.

Keywords: *Sol-gel, Coatings, Mild steel, Inhibitor, Impedance spectroscopy*

1. Introduction

The corrosion problem of metal surfaces and its total cost and environmental consequences have been considered a major concern for many industries, especially the gas/oil industry [1]. Mild steel is an essential component that has been used in large tonnages in the infrastructure of marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction, and metal-processing equipment. Due to the nature of limited alloying content of this substrate (usually less than 2% by weight total addition), it is ready to corrode heavily with very high corrosion rates in aggressive environments [2]. The application of coatings is among the best corrosion-mitigation methodologies used generally to protect the steel surfaces from various deterioration problems. Chromate and phosphate-based conversion coatings have been used extensively to protect steel surfaces against corrosion. However, the hexavalent chromium Cr (VI) ingredient is highly carcinogenic and it is on the way of being abandoned. Thus, there exists an urgent need for environmental friendly alternatives with high resistance and equivalent or enhanced corrosion protection [3].

One of the promising alternatives for the replacement of Cr (VI) processes has been attained via the development of hybrid inorganic-organic sol-gel polymeric coatings which, in comparison with pure inorganic coatings, present the advantage of elasticity and low densification temperatures that do not affect the microstructure and the mechanical properties of the steel substrate [4-6]. These multifunctional materials are mainly produced through the hydrolysis and condensation reactions of various organo-functionalized silane precursors [7,8]. The corrosion resistance of these coatings is considered to be attributed to their physical barrier properties, which prohibit the passage of the corrosive ions through the coating film to the metallic substrate [9]. Controlling the chemistry and processing parameters of the sol-gel coatings to be developed will allow the preparation of hybrid materials that lack the presence of micropores, cracks, and areas of low cross-link density [10]. To achieve this, the chemistry should involve a good selection of the organo alkoxysilane precursors which will help to induce the desired barrier and mechanical properties into the hybrid coatings prepared from these precursors. Another approach to limit the

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corrosion process is the incorporation of corrosion inhibitors into the sol-gel coatings. The parent sol-gel matrix acts as a reservoir for the embedded corrosion inhibitor that, in an aggressive medium, diffuses through the coating and become active for the corrosion process [11].

In this work, we have successfully synthesized a novel sol-gel hybrid coating using the silane precursors, tetraorthosilicate (TEOS), methyltrimethoxysilane (MTMS) and dimethoxymethyl-*n*-octadecylsilane (DMODS). The as-prepared coating was further mixed with two different commercially-available corrosion inhibitors "Moly-white® 101-ED and Hfucophos Zapp®". The effectiveness of the above coatings in protecting mild steel substrate against corrosion in 3.5% NaCl solution was evaluated using EIS, DC polarization, and scanning electron microscopy (SEM) techniques, in addition to the visual observation testing. The results revealed an improved corrosion protection performance for the inhibitor-loaded sol-gel coatings compared to the free sol-gel coating following a long term immersion in the saline medium.

2. Experimental

The chemicals TEOS, MTMS, DMODS, and isopropyl alcohol (IPA) were purchased from Sigma-Aldrich Company (USA) and used as received.

The base sol-gel coating was prepared by mixing TEOS, MTMS, and DMODS using the volume ratio 10:8:5 mL for 2 h while mechanical stirring. The inorganic silicon-oxygen network of the parent hybrid polymer was obtained by adding 1.5 mL of 0.05 N HNO_3:IPA mixture (the ratio is 1:2 by volume). This coating was left under mechanical stirring for 24 h and named hereafter as "5C". It was further loaded individually with two corrosion inhibitors by suspending the appropriate amount of inhibitor (up to 5% w/v) into the coating solution. The two used corrosion inhibitors were "Moly-white® 101-ED" and "Hfucophos Zapp®" and the resulting coatings were denoted as 5M, and 5Z, respectively. The inhibitors used in our study were selected because of their excellent anticorrosive behavior that has been proved and reported previously in the literature [7,8]. All coatings were deposited (using the blue bar of K101 rod coating applicator) on S-35 mild steel Q-panels sheets (Q-Lab Company, USA) and the coated panels were allowed to dry for an hour under room temperature and open to air, followed by a curing process in an oven at 80 °C for 24 h.

The corrosion behavior of the coated samples was monitored using EIS and DC polarization techniques during immersion in 3.5% NaCl solution, open to the air, and at room temperature. Gamry paint test cell (PTC) was used to install the coated samples for electrochemical analyses. Electrochemical polarization testing of the coated samples was conducted using the GAMRY3000 corrosion measurement system. The potential of the electrode varied from - 0.25 V to 0.25 V. The electrochemical cell used for the electrochemical experiments consists of the prepared coated electrode as the working electrode, a graphite rod as a counter electrode, a saturated calomel

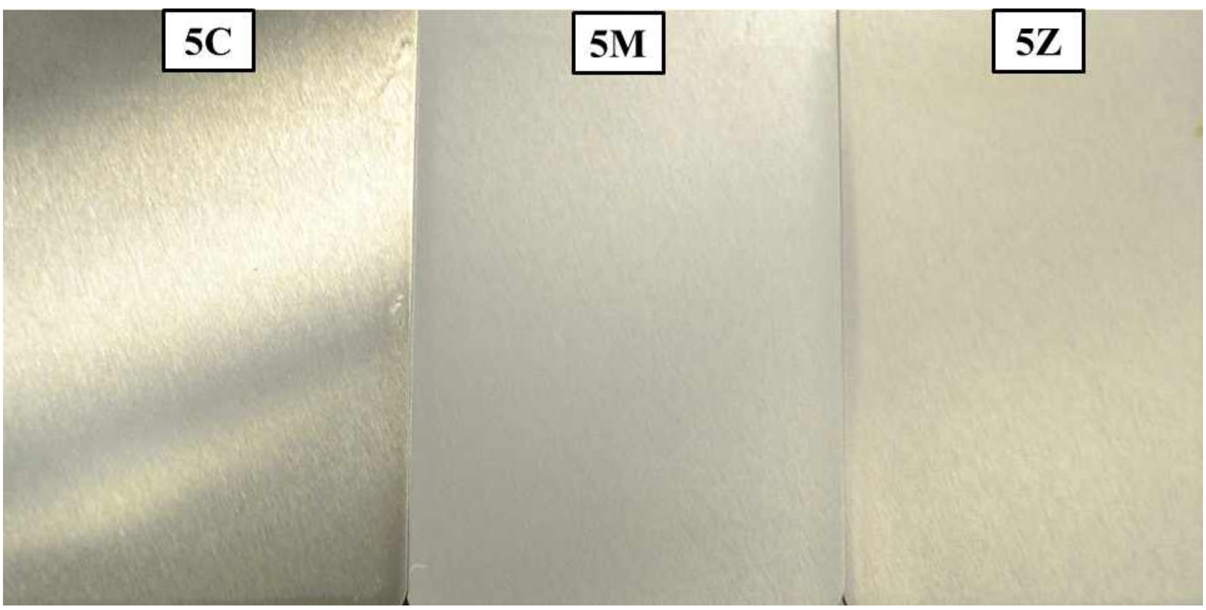

Fig. 1 The surface of all coating formulations on steel after curing.

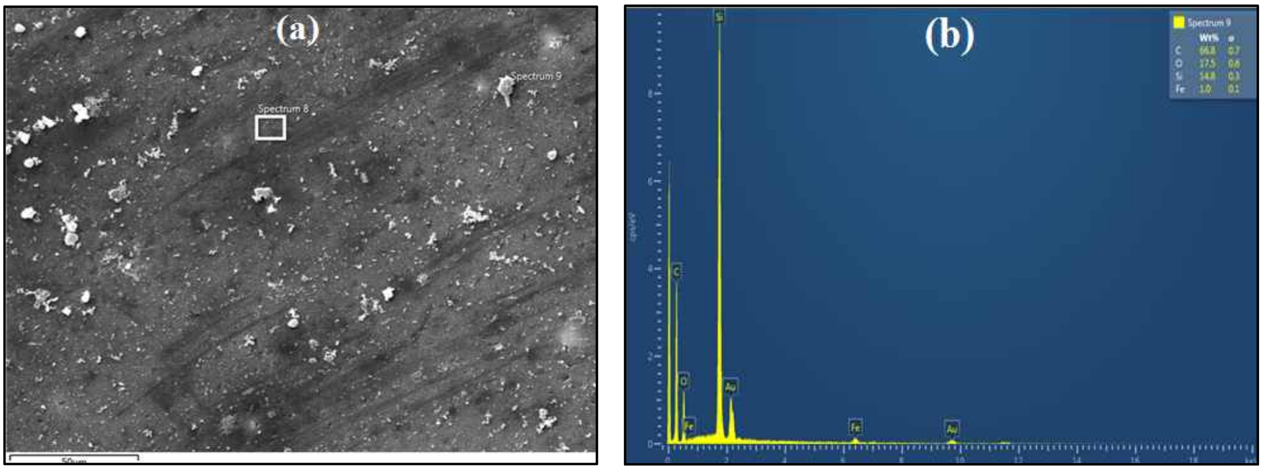

Fig. 2 (a) SEM micrograph of the top surface of sample 5C, and (b) EDS analysis on a single-point on the surface of this sample.

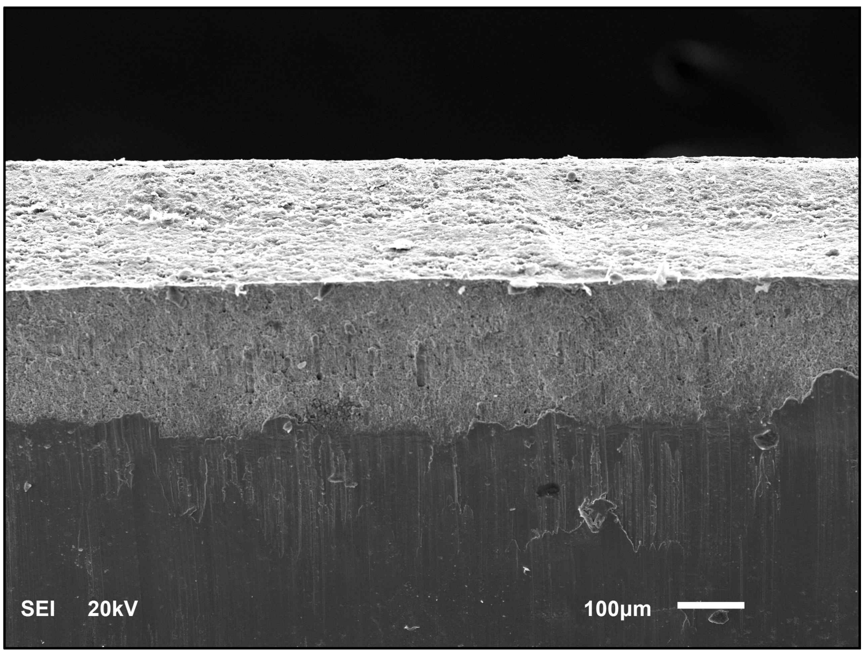

Fig. 3 SEM image of a cross-section of the 5C coating on steel surface.

electrode (SCE) as a reference electrode, and 3.5% sodium chloride as an electrolytic solution. Surface Masks (GAMRY) of an area of 10 cm^2 were used to mask the analyzed surface.

EIS data were collected using a GAMRY3000 potentiostat with a frequency ranged from 100 kHz – 10 mHz (0.01 - 100000 Hz). The Number of points taken was 10/decade with AC Voltage of 10 mV. The data obtained from the EIS measurements were plotted using an Excel spreadsheet.

The top-surface and cross-section SEM analysis of the surface of the coating formulations on mild steel substrate before and after exposure to the saline medium was achieved using an FEI Nova Nano SEM 230. The aqueous contact angle of the hybrid coatings was measured by Attension contact angle meter (Biolin Scientific, UK). The measurements were done using a pendant-drop method and an average of 3 readings is reported.

3. Results and Discussion

In this study, the silane precursor DMODS has been incorporated in the synthesis of the parent coating 5C in

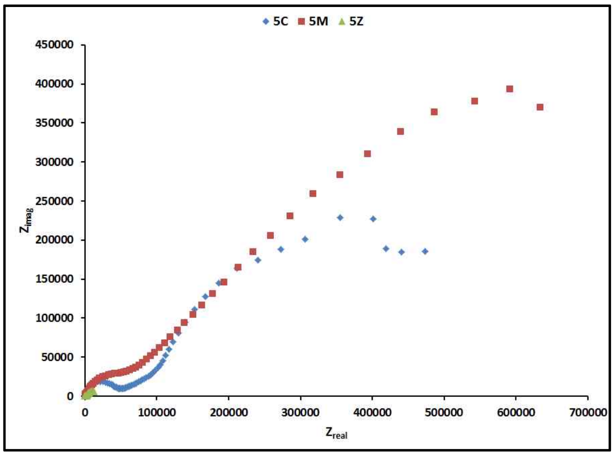

Fig. 4 Nyquist plots of 5C, 5M, and 5Z mild steel coated samples after 24-hour immersion in 3.5% NaCl solution.

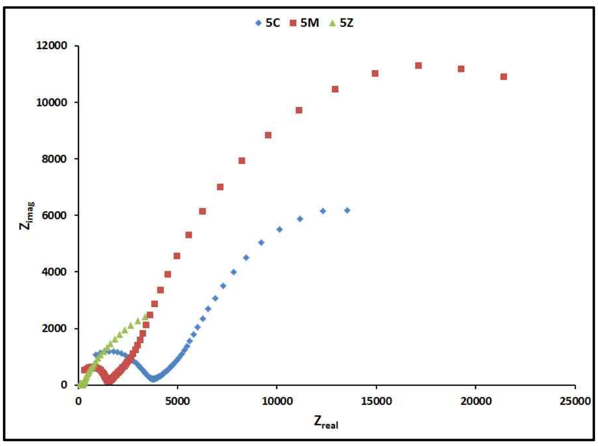

Fig. 5 Nyquist plots of 5C, 5M, and 5Z mild steel coated samples after 288-hour immersion in 3.5% NaCl solution.

order to utilize the outstanding hydrophobic nature of its long aliphatic chain (C18) structural moiety, which will induce more of the desired hydrophobic property to the final polymeric material. The number "5" used in coding the newly developed coatings in this study refers to the optimum volume of DMODS required to produce a stable sol-gel system. The ratio of silane precursors needs to be carefully optimized during the preparation of hybrid sol-gel polymeric materials as the balance between the relative content of organic and inorganic components is necessary to achieve excellent barrier properties without deteriorating the desirable mechanical performance of the coating [12]. During the optimization process, we found that an amount of DMODS higher than 5 mL will result in a fast gelification of the prepared hybrid polymer. The contact angle value obtained for the coating 5C is 102°, which proves the excellent hydrophobic nature of this coating.

After the application and curing of all the coating formulations on steel surfaces, the samples, with and without the inhibitors, appeared very similar and showed no visible signs of corrosion, delamination or cracks (Fig. 1). The SEM micrographs of the top-surface of sample 5C depicted in Fig. 2a showed a regular nonporous coated surface without cracks, while the EDS spectrum of a single point on the surface of this coating (Fig. 2b) indicates that its elemental composition is composed mainly of the elements Si, O, and C.

Fig. 3 shows a typical SEM photograph of a cross-section of the 5C sol-gel coating on mild steel. It can be observed that the coating is well bonded with no sign of any mechanical damage. The approximate thickness of this coated sample is around 100 ❍m.

The protective character of the newly prepared hybrid sol-gel coatings with and without doping an inhibitor was assessed using electrochemical measurements and in particular the EIS technique. This technique has the advantage of allowing scientists to monitor continuously the progress of corrosion, with instantaneous corrosion rate measurements, and it can provide also information on the reactions that take place at the coating/substrate interface [13,14]. The impedance response of the system consists of the outer coating layer, the activity at the substrate/coating interface, and the corrosion process that might take place. The impedances of the hybrid sol-gel coated matrices at open-circuit potential were measured over a period of up to 288 hours of continuous exposure to 3.5% NaCl solution.

Fig. 4 depicts the EIS Nyquist spectra of the hybrid sol-gel mild steel coated samples after 24 hours of exposure to the electrolytic solution. The spectra showed clearly the presence of two semi-circles for all coatings on steel. Wider semi-circles are normally associated with better barrier properties for the coated samples. It should be expected for a coating embedded with a corrosion inhibitor to display higher coating resistance values compared to a free control coating without an inhibitor. However, from the data plotted in Fig. 4, it is clear that the impedance for the coated sample 5M was excellent and in the range of 10^6 $\Omega.cm^2$ compared to the other two coated samples 5C and 5Z which their coating resistance values are in the range of 10^5 and 10^4 $\Omega.cm^2$, respectively. An impedance value of 10^6 and above indicates generally an integrated and cross-linked sol-gel coating that lacks the presence of pinholes and micro cracks in its structure. Compared to the control 5C sample, it was surprising for us to find that the addition of Zapp® inhibitor to the sol-gel system seems to have a considerable negative

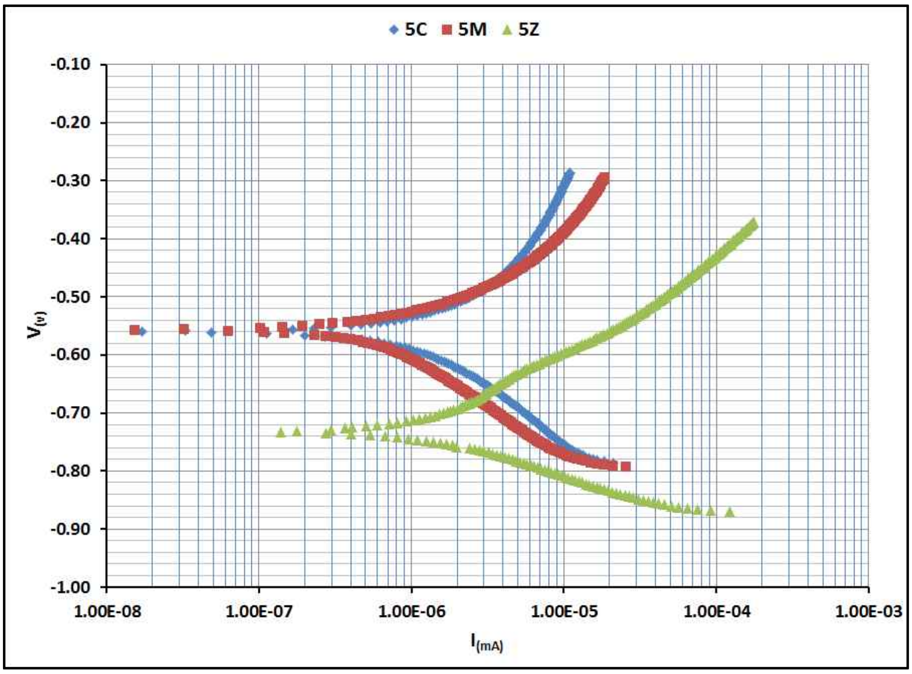

Fig. 6 DC polarization scans of the three developed hybrid organic – inorganic coating matrices on mild steel after 288-hours immersion in 3.5% NaCl solution.

effect on the barrier properties of the parent coating. Nyquist plots of the coated samples indicate the presence of a capacitive arc for sample 5M, which implies that the coating acts as an intact capacitor prohibiting permeation of corrosive species such as water, oxygen, and other corrosive ions towards the surface of the steel substrate.

The EIS Nyquist spectra of all coating matrices on mild steel after 288 h of continuous exposure to the saline medium indicated a minor decrease in the impedance value of sample 5M (Fig. 5). Again, an unsatisfactory corrosion resistance value was also obtained for the 5Z sample, which indicates that our synthesized hybrid sol-gel coating system is not a good matrix for the embedment of the Zapp inhibitor that seems to affect negativity the integrity and homogeneity of the sol-gel system.

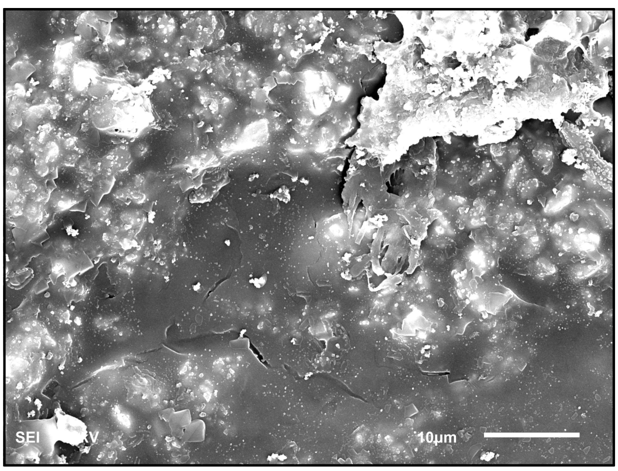

Fig. 7 SEM micrograph of the top surface of sample 5Z after 288-hours immersion in 3.5% NaCl solution.

The improvement in the corrosion protection properties of the coating mixed with Moly inhibitor has been also evidenced by the results obtained from conducting the polarization tests the coated samples after 288-hour immersion time in the chloride solution (see Fig. 6). Electrochemical polarization techniques have been reported vigorously in the literature as a fast tool to study the capability of the metallic substrates to resist harsh corrosive environments. The graphical presentation of the data generated from the electrochemical polarization method involves the plotting of potential versus the current density. Normally, higher corrosion of metal ion results in increased corrosion current density (i_{corr}) which is directly proportional to the corrosion rate. The results depicted in Fig. 6 show that the i_{corr} of sample 5M is much less than the other two samples, which confirms the excellent barrier properties of this inhibitor-doped coating. Moreover, the shifting of the corrosion potential (E_{corr}) of sample 5Z to a more positive value proved again the non-advantageous role of Zapp inhibitor on the

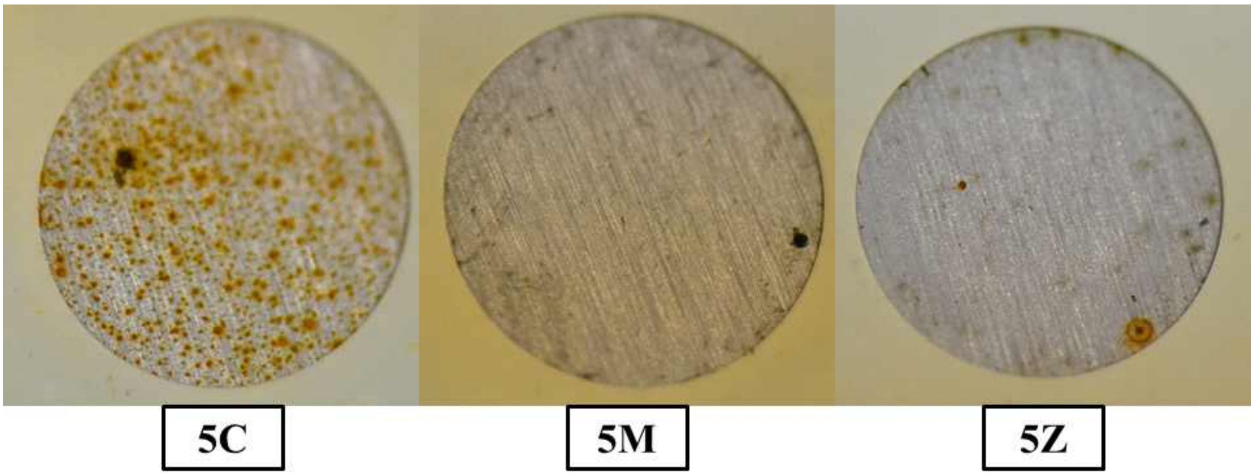

Fig. 8 Photo-digital images of sections of the coated panels shown in Fig. 1 after 288 hours of exposure to 3.5% NaCl.

corrosion performance of the parent hybrid polymer.

In order to investigate further the poor corrosion protection performance of sample 5Z after long immersion time in NaCl Solution, we have conducted the SEM analysis of the top surface of this sample (Fig. 7). The images showed clearly the presence of multiple cracks in the coating film and the attachment of chloride ions on the surface of coated samples, which facilitates the diffusion of these corrosive ions to the metal surface.

The photo-digital images of the surface of all coated samples after 288 hours of exposure to the saline medium is displayed in Fig. 8. The excellent corrosion protection performance of sample 5M compared to the performance of the two other samples is proved by the intact nature of the surface of this sample and the presence of minor corrosion phenomena on the surface of other samples.

4. Conclusion

A novel silica-based hybrid sol-gel coating was developed to protect mild steel substrate from corrosion. Two commercially-available corrosion inhibitors were introduced in the above coating system in order to maximize the active protection performance. The corrosion-resistance performance of the newly developed coatings was evaluated by electrochemical testing and visual observations. Results obtained showed that the parent hybrid coating has relatively promising barrier properties towards the passage of corrosive ions to the steel surface and ultimately protection was achieved. These barrier properties could be attributed to the hydrophobic character of the hybrid coating which resulted mainly from the long hydrophobic octadecyl chain of the DMODS silane precursor incorporated in the sol-gel structure. Moreover, an improvement in the coating performance in time was evident for coating doped with Moly® inhibitor comparing to the undoped coating. Zapp® inhibitor has a negative contribution to improving the corrosion protection efficiency of the newly developed parent hybrid coating.

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