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Mechanics of Organometallic Surface Adsorptivity Using EIS and Correlative Data Mining Method

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Abstract:*Sorption processes address issues of physical and chemical conditions that necessitate the attraction of one substance to another. Adsorption is one of such processes and requires the bonding of particles such as ions and molecules onto surface pores of target materials. The lack of understanding of the nature of this process has often resulted monumental financial losses in implementation of metal surface protection strategies. Confirmed studies in this regard, have indicated that the process of organometallic surface adsorptivitypotentials commences by the distribution of layers of primary chemical reaction thin films which settles on the pores of the surface of the adsorbent. While this exothermic process is in contrast to the endothermic principle of absorption; adsorption is a surface tension phenomenon that is crucial to the development of engineering materials for specialized industrial use. The study is therefore an attempt to advance thisspecialized knowledge of structural integrity of metal surface by considering the operational dynamics of pore distributions and the relative process equations that determine the system's thin film parameters; which makes it suitable for advanced metal surface protection technologies. Thus, implying that efficiency ratios of organic corrosion inhibitors are largely responsible for the structural integrity and general substrate conditions of the metal. Simulations were performed on the basis of acquired experimental data and their associated practical results which were used to correlate impedance determinations on the viability of the use of structural mechanics in the determination adsorption profiles of metals surfaces.*

Keyword: *organometallic surface, adsorption, structural integrity, structural kinetics, dissociation energy, pores*

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I. INTRODUCTION

Adhesivity is a process of attachment of the molecules or atoms of a fluidic substance to the surface of another material. Thus, adhesion is the proclivity of dissimilar parties clinging together within a confined or defined state, and it is the opposite of cohesion where similar or identical particles stick together. Consequently, adhesivity is a crucial component of the degree or extent of surface roughness of the adherend material. In view of this condition, an increase in total contact area also enhances the process of adhesion. This is due to interface correlation or intermolecular attraction between the substance and the surface of the material; thus increasing the specific contact area will also increase the available total surface tension and surface energy.

Further, in view of this study, it should be noted that cohesion is the inner strength of a material defined by the molecular forces in the entirety of the material structure. The determinant of this strength is not limited to conventional tensile and elongation tests, such as the ASTM [1], since such tests do not specifically address issues such as thickness of molecular and ionic level thin film, dimensional pore distribution, surface energy determination, etc. However, for considerations dealing with thin films as advanced in this paper, such measurements are conducted on the basis of atomic sizes, bond dissociation energy and layers of atoms, held together by their bond strengths and lengths. A crucial step in this determination deals with aggregate interactions of intermolecular forces.

Consequently, in the determination of adhesion forces, specific test method varies, depending on the parameters of choice and the extent of required information [2]. This study shall draw inferences from the view and findings of Lu *et al* [3], Huang *et al* [4] and Siongo*et al* [5]. The findings in these referenced studies show that organic coating technology can be advanced by proper understanding of the structural interlacing of thin film produced by the combination of acrylic resin and *hexamethylenediisocynate(HDI)Biuret* which characteristically yield the thin adsorbate film and the bulk protective coating with varying degrees of aqueous permeability depending on the ratio of combination [3].

It is therefore important to state that adhesivity of a metal surface is enhanced by the quality of its substrate condition such as, its roughness which provides the surface pore required to create sufficient static friction to maintain tensional forces for stability of the thin film. The paper thus views surface integrity of the metal as the basis for coating efficiency; implying that adhesivity which is a mechanical property of the coating material establishes the extent of pore efficiency. In the opinion of this paper, as supported by empirical assessments, the adhesion of the organic coating on the material of choice is on the basis of the nitrogen-hydrogen bond which forms the thin adhesive film and chemically attaches itself to the substrate of the metal by van der Waals and associated surface tension forces.

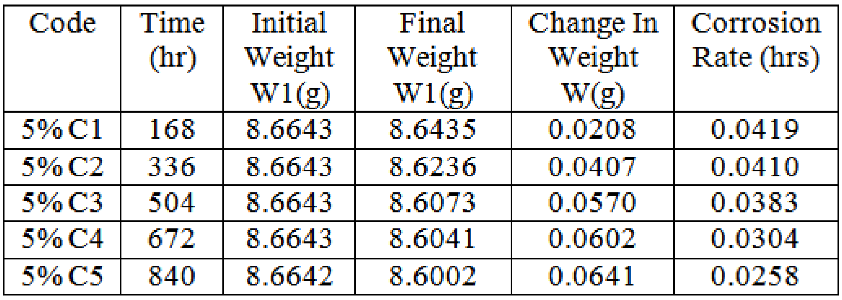
Additionally, the theory of adsorption relates adhesion to the resultant molecular contact between two materials and the surface forces that develop as a result of such contact [2]. The implication of this condition, is that adsorption is a bonding process between the reacting molecules of the organic coating and the metal substrate on the basis of nucleic attractive forces, which are viewed as secondary or van der Waals forces. Studies have postulated that these secondary forces require separation distances of about 5Å to allow direct contact between the two surfaces. This phenomenon was applied to this investigation to show that the thin film which is composed of N-H molecules fills this separation distance by the process of adsorption.

For this process to occur, there must be wetting, which implies a smooth flow of the thin film material across the individual pores of the substrate surface. Consequently, interfacial flaws are controlled by ensuring that surface energy is evenly distributed by homogenous pore condition of the metal substrate. Conversely, where poor wetting is occasioned, it means that absorption process was partially achieved, in not having intermolecular combinations at the coating and metal substrate interface. The two conditions portend varying surface quality effects on the integrity of the material.

II. STRUCTURAL KINETICS OF ADHESIVITY OF COATING AGENT

It should be stated that the effectiveness of any organic metal coating agent is its adhesivity factor [2]. In this study adhesivity refers to the resistance offered to an external force intending to disassociate the coating agent from the surface of its metal host. Although his definition may not possess the theoretical relevance of the subject, suffice to say that it is adequate for the purpose of this study. Hence, adhesivity from the viewpoint of this study deals with the structural mechanics of bonding elements that necessitate the stability and economic viability of the organic coating. This implies that the force of attraction between the thin film and the metal substrate should possess the capacity to chemo-structurally bind the bulk of the protective coating to the metal surface, with the thin film as an intermediary component. This view is further supported by the experimental findings in Siongo*et al* as depicted in the data of Tables 1-4 below being 5% wt. of the applicable organic inhibitor on cold and heat treated coupon specimens. These data sets are predicated on our investigation reported in the said study.

Table 1: parameters of cold worked coupon (5%)



Code	Time (hr)	Initial Weight W1(g)	Final Weight W1(g)	Change In Weight W(g)	Corrosion Rate (hrs)
5% C1	168	8.6643	8.6435	0.0208	0.0419
5% C2	336	8.6643	8.6236	0.0407	0.0410
5% C3	504	8.6643	8.6073	0.0570	0.0383
5% C4	672	8.6643	8.6041	0.0602	0.0304
5% C5	840	8.6642	8.6002	0.0641	0.0258

Source: Siongo*et al*

Table 2: correlation between weight loss and corrosion rate (cold work coupon, 5%)

Code	Time (hr)	Change In Weight W(g)	Corrosion Rate (hrs)
5% C1	168	0.0208	0.0419
5% C2	336	0.0407	0.0410
5% C3	504	0.0570	0.0383

5% C4	672	0.0602	0.0304
5% C5	840	0.0641	0.0258
5% C6	1008	0.0691	0.0232
5% C7	1176	0.0750	0.0216
5% C8	1344	0.0815	0.0205

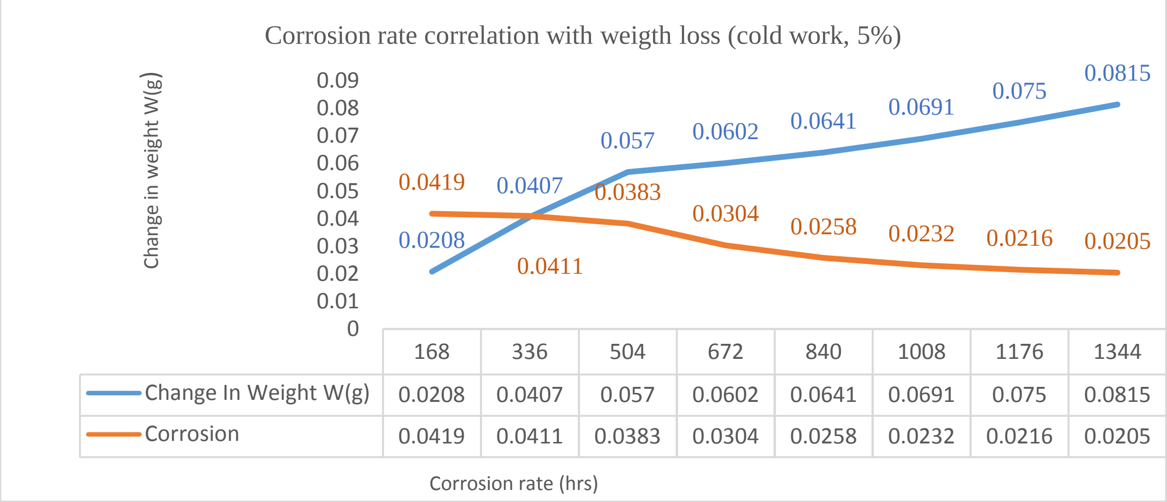


Fig 1: corrosion rate correlation with weight loss for cold work coupon at 5% concentration

As could be seen from Tables 1 & 2 and Fig 1, above, 8 specimens of cold worked coupons were exposed to 5% wt organic inhibitor, thus creating a sense of a brine environment. The corrosion rate was noticed to decline as time progressed (see progression of the red line in Fig. 1). The impact of this to the coupon was an increasing weight loss. However, this weight loss is significantly reduced when compared to coupon specimen without inhibitor, where weight loss was very high. In that study, when the 20% inhibitor was introduced, the weight loss significantly reduced to a technically viable minimum. The implication of this tendency is that the adhesivity of the coating agent on the substrate of the coupon reduced the corroding impact of the environment on the metal. Consequently, post immersion PMI test and micrographic exposures of the coupon would reveal details of structural changes due to the attachment of the organic inhibitor agents on the specimen by van der Waals and related forces. As has been observed in this study [6], adsorption of the thin film is intended to enhance the surface integrity of the metal.

In addition to the foregoing, heat treated coupons were also tested for their behavior when organic inhibitor is added to the corroding environment and Tables 3 and 4 resulted from the 5% wt of organic inhibitor exposure.

Table 3: parameters of heat treated coupons (5%)

Code	Time (hr)	Initial Weight W1(g)	Final Weight W1(g)	Change In Weight W(g)	Corrosion Rate (hrs)
5% H1	168	8.3342	8.3182	0.0180	0.0363
5% H2	336	8.3342	8.3037	0.0305	0.0308
5% H3	504	8.3342	8.2925	0.0417	0.0281
5% H4	672	8.3342	8.2842	0.0500	0.0253
5% H5	840	8.3342	8.2773	0.0569	0.0229
5% H6	1008	8.3342	8.2725	0.0617	0.0208
5% H7	1176	8.3342	8.2688	0.0654	0.0188
5% H8	1344	8.3342	8.2621	0.0721	0.0182

Source: Siongo et al

Table 4: correlation between weight loss and corrosion rate (heat treated coupon, 5%)

Code	Time (hr)	Change In Weight W(g)	Corrosion Rate (hrs)
5% H1	168	0.0180	0.0363
5% H2	336	0.0305	0.0308
5% H3	504	0.0417	0.0281
5% H4	672	0.0500	0.0253
5% H5	840	0.0569	0.0229

5% H6	1008	0.0617	0.0208
5% H7	1176	0.0654	0.0188
5% H8	1344	0.0721	0.0182

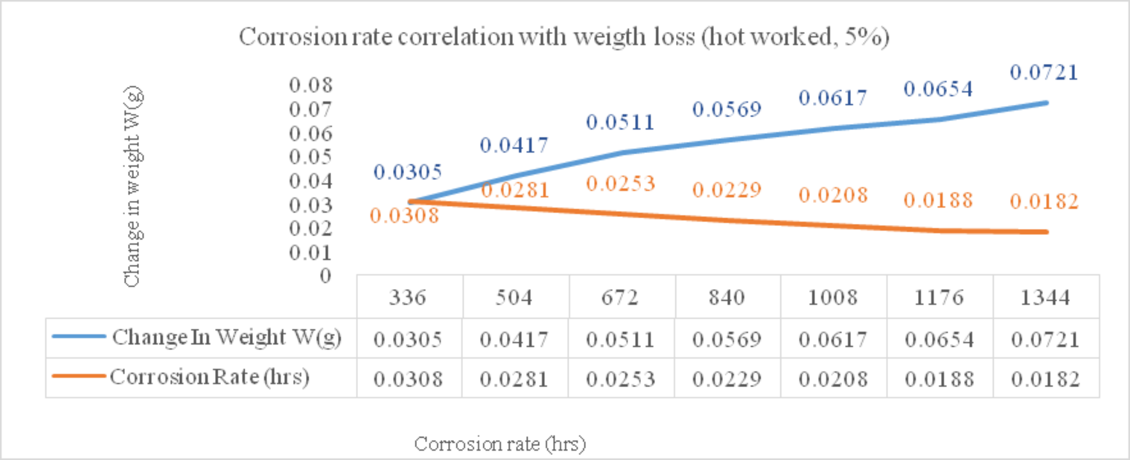


Fig 2: corrosion rate correlation with weight loss for hot worked coupon at 5%

It should be noted the Tables 3 &4 and Fig. 2 indicate the behavior of the heat treated coupon specimens. Thus, corrosion was impeded at a higher ratio on account of lower corrosion rate and less weight loss. The effect of this finding is that heat treatment of metals promotes their structural integrity and makes their substrate not easily permeable when exposed to corrosive environment. Further, a difference of 0.0094g occurred between Fig 1 and Fig 2 weight loss, respectively, where all parameters are the same. Hence, the rate at which heat treated materials corrode is significantly reduced on account of the structural realignments of their valence electrons and their entire external conditions of physical and chemical reactivity.

III. METHOD OF MEASUREMENT OF ADHESION FORCES

Structurally, we have observed in this paper that adsorption precedes adhesion in sorption processes. Adhesion therefore is a physical process that deals with the relative quality of binding forces. In order to determine these structural forces, required pull-off energy was experimentally measured for NCO/OH organic coatings using the following experimental set-up.

A hanging stand of height 609 mm was fabricated of 1.5 mm reinforced angle steel with a flat bed and side crossing support fixed on the base plat. 304 mm horizontal boom length was welded to the top frame of the stand and braced to the vertical frame to increase stability. The samples were firmly clipped to the force pre-loaded newton meter or spring balance which was anchored on the fixed U-lock at the front terminal of the 304mm boom. Five sample ratios of NCO/OH coating were peeled-off by pinch-pulling and reading of force impact and distance traveled by the newton meter needle was recorded for all samples and Table 5 below represent the readings obtained from the experiment.

Further, the findings on neem leaf as an efficient organic inhibitor [5] corroborates with the views of the experiment detailed above and concludes that the molecular adsorption profile of organic coatings on the surface of the metal substrate is enhanced by the adhesivity of organic corrosion inhibitors [3] as observed in the experiment. In addition to these views, it has been observed that the surface integrity of the metal in terms of defined pore distribution is crucial to the molecular-pore interfaces promoted by the chemo-structural adhesivity phenomenon [2]. As could be seen in Table 5 and accompanying Fig 3 below, the peel-off force for the NCO/OH organic coating increases as the concentration ratio increases, signifying that the adhesivity of the N-H thin film to the metal substrate is on the basis of highly interactive frictional forces inherent in the pore distribution of the respective surfaces in addition to the concentration of the active component of the chemical.

Table 5: NCO/OH ratio and surface adhesivity forces

NCO/OH ratio	Adhesivity (MPa)
0.6	10
0.8	14.2
1.0	18
1.2	18.7
1.4	19.5

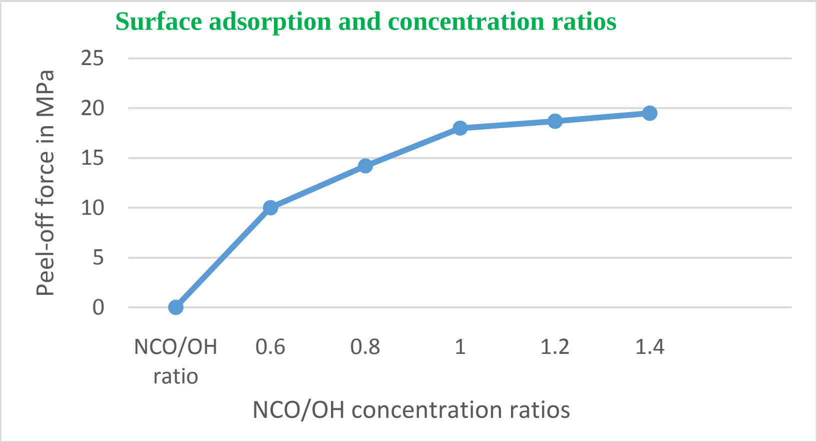


Fig 3: peel-off force / NCO-OH concentration ratios

In view of Table 3 above, it should be pointed that adhesivity as a surface oriented structural process converts chemo-structural reactions as in the case of the NCO/OH organic coating into physical forces with high energy relativities. This finding is predicated on the adhesion and chemical bonding measurements conducted by several studies where it was demonstrated that adhesive binding forces are responsible for the interface between metal surface and the organic coating agent as Table 5 above affirms. Consequent on Table 5 above, Fig 3 was generated to affirm the correlation between adhesivity on the surface of the metal and absorption isotherm. This implies that internal cohesion of the components molecules of the organic coating increased N-H thin film's efficiency within the permissible range of application parameters.

This view is further supported by the general equation for the statistically absorbed thin film thickness [t(nm)] as a function of the external impact of the bulk of the organic coating on the N-H film adsorption process [3], the film thickness is expressed as;

$$t(nm) = 0.354\left[\frac{5}{\ln\left(\frac{P_o}{P}\right)}\right]^{1/3} \qquad 1$$

where, 0.354 nm is the thickness of one nitrogen molecule, $P_o$is the vapour pressure, P is the working pressure. It should be noted that the Kelvin equation for capillary condensation in the filling of surface pores by the adhesive film, is the pressure at which the thin film condenses or evaporate and is equal to the vapour pressure of the organic coating, resulting the ratio $P/P_o = 1$. However, where vertical absorption and desorption are required in the filling of the pores, the ratio $P/P_o < 1$. Further, in view of Equation 1 above, a threshold pore radius (referred to as Kelvin radius r_K) which corresponds to the film thickness of pressure P for adsorption process and can be stated as;

$$r(P) = t + V_M\sigma/R_gTln\left(\frac{P_o}{P}\right) \qquad 2$$

where, t = thickness of the thin film, σ= thickness of one layer, V_M = coating molar volume, R_gT = molar thermal energy. Thus, the pore radius constitutes the surface structural conditions that must be present for high adhesion efficiency [2]. Technically, where the metal substrate is low in friction, then pore radius is small and in such a case, adhesivity would be low, thus resulting weak adsorption of the N-H thin film, the industrial and economic relevance of this finding is that increasing surface tension of a metal before coating, increases the longevity and durability of that coating and also elongates the time required for the first corrosion initiation.

In addition, as Fig 3 indicate above, the peel-off force increases with rising NCO/OH concentration ratios which relatively support the view that the structural conditions that favours higher adhesivity also enhances adsorption of the organic coating materials within the characteristic range of data available for mining, inference and analysis.

From Fig 3 above, it can be seen that adhesive strength of the organic coating agent increased with increment of NCO concentration in NCO/OH ratio. This imply that the physical peel-off forces were higher in practical terms than the force encountered during the test. This view is largely due to the structural kinematic support of the binding energies resulting from the reaction between the N-H film molecules and the substrate of the metal. The thin film is thus viewed as the base upon which the bulk of the organic coating rest and has the thickness of 0.354nm requiring almost 20 MPa of force to pull it out of the substrate at the 1.4 NCO/OH ratio. Hence, the thin film is the reaction product of valence combination of the lone electron of the hydrogen atom which bonds with a nitrogen atom in a sub-chain as shown. The Lewis structure of this bond can be seen in Fig 4 below.

Fig 4: Lewis structure of H-N bond in the reaction of acrylic resin and *hexamethylenediisocynate (HDI) Biuret*

In the view of this paper, the N-H bond represents the fluidized compound that permeates the mixture of the *acrylic resin and hexamethylenediisocynate* coating agent and finds its way to the substrate of the metal by reason of gravity, and deposits itself as a thin film. It would be noticed that the extra four lone pairs of electrons in the Lewis structure above binds the N-H pair to the surface of the metal with an average single bond energy of 390 kJ/mol. This paper is of the view that the bonds established by the four lone pairs of nitrogen electrons with the valence electrons of the metal accounts for the high energy requirement during the peeling-off of the organic coating agent from the metal surface and consequently, the structural bond length of the N-H molecule is 1.01 Å and since the structurally permitted distance between the substrate pore and the bulk of the organic material as has been noted above, is about 5Å, it implies that about 4 to 5 layers of N-H thin film can be interlaced in the pore, subsequent to the bulk of the organic coating resting on the outer layer of the thin film. In respect of the foregoing, the structural kinematics incidental to the high strength of this bond applies to the bond distance between the nuclei of the two atoms.

Further, since the Lewis structure is supported by the positive forces of attraction from the nuclei, it can be safely said that the extra four lone pairs of electrons on the nitrogen contributes structural kinetic forces to sustain the hydrogen ion and same time engage surface electrons of the metals. In addition, since the adhesivity strength increases with increasing ratio of NCO/OH, it implies that such increased concentration of NCO supplies more nitrogen to increase the number of lone nitrogen pairs to bond with the orbital electrons of the metallic lattice. In view of this condition, the crucial impact of increased concentration of NCO/OH ratio also causes a decrease in bond length, partly as a result of predominant nitrogen valence electrons and the external pressure impacted on the thin film from the rest of the mixture. Consequently, this investigation reveal that the structural kinetics of the reaction indicate that the result of this decreased bond length also causes an increase in the dissociation energy, thus increasing the adhesion strength of the organic coating agent.

IV. CORRELATION OF MATERIAL SURFACE MORPHOLOGY ANDPARAMETERS OF ELECTROCHEMICAL ELEMENTS

It should be noted that although the referenced study of Lu *et al* developed equivalent electrical circuits of their investigation, this paper shall only consider some of the simulated data from their EIS measurements that are relevant to this study as to generate the relationship between the measurement and the structural integrity of the materials upon removal of the corrosion inhibition agent. In this regard, the following table of measurement shall be dependent on the inter-relationship between the coating resistance *(R_c)*, charge transfer resistance *(R_{ct})*, and the Warburg impedance *(Z_w)*, which determines the resistance offered to the penetration of diffused ions from the electrolyte to the surface of the organic coating.

Table 6: impedance parameter measurements

NCO/OH	**R_c (ohms/cm^2**	**R_{ct} (ohms/cm^2)**	**Z_w (ohms/cm^2)**
0.8	2.93×10^5	1.67×10^4	2.6×10^{-6}
1.0	8.19×10^5	1.14×10^5	
1.2	8.13×10^5	1.79×10^9	
1.4	1.19×10^8	7.30×10^{10}	

Source: Lu *et al*

As could be seen from Table 6 above, the organic coating resistance increased with the increasing ratio of NCO/OH concentration. This phenomenon implies that materials with more concentration of the coating's active ingredient produced better coating resistance to the flow of electric current. The same phenomenon is occasioned by the simulated values for active charge transfer resistance (R_{ct}), where it is noticed that R_{ct} was significantly increased with higher NCO/OH ratios, thus implying that the coated barrier also acted as an electric charge inhibitor, by preventing any form of penetration beyond the point of contact [3], [7]; thus the result for NCO/OH ratio of 1.4 at $7.30x10^{10}$ indicates excellent charge transfer resistance of the coupon specimen. As shown in Table 6, the result for Warburg impedance is only indicative for NCO/OH ratio of 0.8 at $2.06x10^{-6}$, which implies that only the 0.8 ratio was affected by the Warburg impedance while the other higher ratio specimens were not affected. The relevance of this Warburg value is that, diffused ions in the electrolyte could not penetrate higher NCO/OH ratios beyond the 0.8 specimen. This finding also agree with the use of ceramic corrosion coating prepared on low carbon steel from aluminate electrolyte [8].

Consequently, this current and charge impeding property of the coating agent is better appreciated in comparison with the micrographs of the specimen after peeling-off of the coating upon the completion of 50 days' exposure in 3.5 wt % NaCl solution at 50^0C.The micrograph could be seen in seen in Fig 5 below.

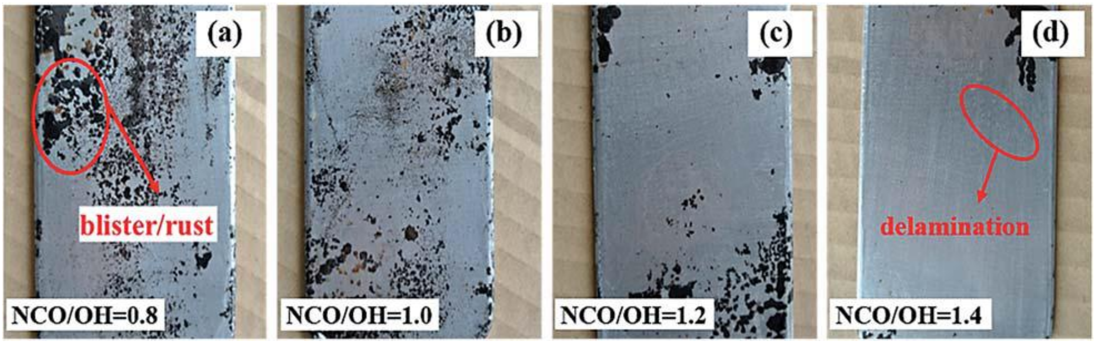


Fig 5: micrographs of ratios (a) 0.8, (b) 1.0, (c) 1.2, (d) 1.4 indicating various surface impacts on account of peeling-off of the top coating and thin film adsorbed into the pores of the metal substrate. Notice that ratio (a) has more blisters due to weak adhesivity of the thin film. This significantly account for the Warburg impedance value of $2.6x10^{-6}$ $ohms/cm^2$ Source: Lu *et al*.

The micrographs in Fig 5 indicate deep blisters and rust presence on ratio 0.8 specimen and same progressed through to ratios 1.0 and 1.2 at a reducing impact respectively. However, the trend is not noticeable with ratio 1.4 due to the current and charge impeding property of that ratio of chemical combination.

V. CONCLUSION

Practically, any material deployment for engineering services should significantly consider materials whose EIS measurements has higher impedance in terms of coating resistance, charge transfer and structural mechanics of the metal's substrate. All other parameters are dependent on these three as data mined synergy agreed with applicable experimental results discussed in this paper. The implication of this view is that materials for deployment must have satisfied their fatigue stress and strength, toughness, machinability and other parameters for the specific project. After these assessment and materials scoping, the materials engineer is allowed to test the materials by utilizing the EIS machines on the basis of the understanding of the mechanics of metal surface adsorptivity profiles. Additionally, knowledge of the impact of heat on metals before organically protecting them from corrosive tendencies is crucial to deployment of materials that are structurally reliable. These confirmatory tests are crucial to the success and durability of manufacturing projects, as they are necessary for predicting maintenance or replacement actions on the facility.

Further as could be seen, the use of impedance measurement devices for pre-deployment assessment of material properties and subsequent application of the knowledge of the mechanics of unit adsorption of the thin film barrier preceding the bulk of the organic coating is a quality assurance measure since it attempts to put the future of the material into perspective of the present. As discussed, the adhesivity of the organic coating material is a function of the chemo-structural reaction of its N-H inner lamination thin film with the substrate of the metal on the one hand and the bulk of the mixture on the other hand. This crucial finding of this study is anticipatory of the performance of the structural kinetics of the bond strength which is enhanced by the four lone electron pair reactivity possibilities of the nitrogen atom.

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