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Predictive Evaluation of Corrosion Signatures in Materials Selection and Fabrication for Deployment in Marine Environments

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Abstract- Materials selection activities have been known to be a difficult phase of manufacturing service as the entire production process is dependent on the reliability and durability of the deployed materials. The inability to utilize tested materials selection methods has often resulted significant losses of very large proportions, especially if the poorly selected materials would not be able to withstand environmental corrosive tendencies inherent in marine environments. This study has considered the imperatives of corrosion initiators and how a knowledge of the fundamentals of the thin film substructure of organic coatings can be leveraged alongside electrochemical impedance spectroscopy testing to predict materials structural viability for marine services deployment. The result of the proportional application on the basis of concentration of the active NCO component of the organic corrosion inhibitor indicates a rise in various impedance computations as the concentration of NCO increases in ratio. The technical implication of this finding to the materials testing engineer is that the ratio of combination of constituent elements of the organic coating should be the basis of the testing and selection instead of the traditional determination of the depth of coating

Keywords—corrosion signatures, materials selection, absorption, impedance relativity, hybridization, oxidation processes, electrochemical series

I INTRODUCTION

Corrosion is nature's attempt to reverse human technological gain in natural raw materials development. It is a physiochemical process that has retrogressive effects on engineering materials longitivity. As a result, the cumulative attack of corrosion on fabricated structures is therefore due to the interaction between the materials and the environment to which it is exposed. This means the environment of exposure is a crucial issue in any discussion on corrosion [1]. Consequently, corrosion also implies the deterioration of a metal or its properties as a result of its physical and chemical interactions with its surrounding conditions of existence. In the view of this paper, these conditions include directional flow of energy and their thermodynamic relativities necessary for such material reversal to occur, tending towards natural conditions of existence.

This paper shall view corrosion prediction from the angle of energy flow consequences incidental to thermodynamic proclivities. Thus, the position would be better understood if we consider the fact that so much energy is required during metal extraction processes from their ores. For instance, hematite (Fe_2O_3) is an ore of iron and bauxite (H_2O_3, H_2O) is an ore of aluminum; while it can be said that other complex ores exist, suffice to state that there are metals that has dual natural originality in the sense that they can occur as pure metals and can also be extracted from their ores. An example is copper which exist in its pure form and also as copper glance (Cu_2S) or pyrite ($CuFe_2$,). This investigation found that copper explored in its pure form is free from corrosion imprints, this imply that copper extracted from the ores and copper extracted in its pure form have different responses to the flow of energy, and as such display different potentials to corrosion signatures. Accordingly, a better understanding of the energy relativity involved in corrosion signatures and dynamics can be understood under the following reactions.

$Fe \rightarrow Fe^{++} + 2e^-$ (removal of electrons- oxidation process, anodic reaction).

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
(presence of oxygen –reduction and evolution of hydrogen ions of water, a cathodic reaction).

$2H_2O+2e^- \rightarrow H_2+OH^-$ (aqueous environment- reduction and evolution of hydrogen ions of waters, a cathodic reaction).

From the equations above, it can be safely stated that oxidation reaction is anodic in nature resulting loss in metal, while the reduction reaction is cathodic. This implies that energy flow from the anode to the cathode is by means of charge transfer which travels through electrons. The positively changed electrons excites the surface elections of the cathode which in turn relinquish their positions leaving electron holes to be filled by oxygen from atmospheric air or dissolved in water. The consequences of this redox action is surface corrosion of the metal. Further, the reactions are electrochemical in nature and are necessary ingredients for corrosion signatures and imprints. Consequent on the foregoing, it must be pointed that oxidation losses at the anode of the electrochemical cell, must be compensated by the exchange or electronic consumption of emitted electrons at the cathode. This create a sense of neutrality and an impetus for progression in the material degradation.

The foregoing process can be truncated if there are large negative charges between the metal and the electrolyte for which there are no positive charges to engage the cell in a sense of neutrality. This condition brings to a halt the corrosion process. Thus, where the metal which is the cathode fails to produce the positive charges to support the constant production of electron holes, corrosion is prevented. The implication therefore is that corrosion inhibitors shield the metals from donating excited positive electrons in exchange for the negative electrons from the anode.

In view of the foregoing, this investigation centers on the methods of predicting the presence of corrosion cells or signatures before the active selection of materials for fabrication and deployment in marine environments. In order to achieve this, the investigation will show how energy difference between a defined anode and the metal of choice can be used to detect the presence of corrosion signatures or imprints. Hence, the energy difference causes a potential difference in electrical energy flow, which results the streaming of electrons from the surface with higher potential to the surface with lower potential. This principle shall be applied in this study to predict materials that are suitable for fabrication and deployment in marine environments, on the basis of their propensity towards corrosion, and the expected conditions that can make the corrosion attack become noticeable.

II FACTORS RESPONSIBLE FOR CORROSION SIGNATURES

There are pre-disposing factors that increase the chances that engineering materials may be prone to corrosion at an earlier date. These factors are incidental to the behavior of the material given the various conditions of its existence. The factors include:

A. Structural conditions of the material

i) material position in the electrochemical series:

It should be pointed that different metal/ metal ion combinations have different electrode potentials values and can be arranged in order of increasing or decreasing values of their standard reduction potentials. This imply that the extent of corrosion depends upon the position of the metal in the electrochemical series, consequently, the greater the oxidation potential, the greater is the rate of corrosion. In view of this potential strength computation, where two metals are in electrical contact but buffered by an electrolyte, the metal higher up in the electrochemical series becomes anodic and suffers corrosion effects. Consequent on this phenomena, the rate and severity of corrosion depend upon the difference in their positions in the electrochemical series. Thus, as could be seen in the electrochemical series and their respective reduction reactions of Table 1 below, the greater the difference, the faster is the corrosion of anodic metal [2]. Conclusively, the structural nature of a metal affects its corrosion rate.

ii) Proportional areas of the anode and cathode position:

Experimental results have shown that the rate of corrosion increases when the area of the cathode is proportionally larger. Consequently, when the cathodic impact area is larger, the demand for electrons will be more and this would result higher rate of dissolution of metals at anodic regions [3].

Table1: standard electrode potentials.

Cathode (Reduction) Half – Reaction	**Standard Potential E^0 (volts)**
$Li^+ + e^- \longleftrightarrow Li$	-3.05
$K^+ + e^- \longleftrightarrow K$	-2.93
$Ca^+ + e^- \longleftrightarrow Ca$	-2.87
$Na^+ + e^- \longleftrightarrow Na$	-2.71
$Mg^{2+} + 2e^- \longleftrightarrow Mg$	-2.37
$Al^{3+} + 3e^- \longleftrightarrow Al$	-1.66
$Ti^{2+} + 2e^- \longleftrightarrow Ti$	-1.63
$Zn^{2+} + 2e^- \longleftrightarrow Zn$	-0.76
$Cr^{3+} + 3e^- \longleftrightarrow Cr$	-0.74
$Fe^{2+} + 2e^- \longleftrightarrow Fe$	-0.44
$Cd^{2+} + 2e^- \longleftrightarrow Cd$	-0.40
$Ni^{2+} + 2e^- \longleftrightarrow Ni$	-0.25
$Sn^{2+} + 2e^- \longleftrightarrow Sn$	-0.14
$Pb^{2+} + 2e^- \longleftrightarrow Pb$	-0.13
$2H^+ + 2e^- \longleftrightarrow H_2$	-0.00
$Cu^{2+} + 2e^- \longleftrightarrow Cu$	+0.34
$Fe^{3+} + e^- \longleftrightarrow Fe^{2+}$	+0.77
$Ag^+ + e^- \longleftrightarrow Ag$	+0.80
$Hg2^2 + 2e- \longleftrightarrow 2Hg$	+0.85
$F_2 + 2e^- \longleftrightarrow 2F^-$	+2.87

iii) Concentration of the metal in its pure form:
This study finds that the extent of impurities present in a metal increases the heterogeneity of atomic spread. This implies that galvanic cells develop on the basis of these impurities with distinct anodic and cathodic area definitions incidental to potential difference in the metal. Consequently, the higher the percentage of impurity present in a metal, the faster is the rate of corrosion of the anodic metal. It is evident that the corrosion resistance of a metal may be improved by enriching its structural matrix with atoms of other metals with low corrosion rates. These interstitial atoms could be deemed as impurities which may increase or reduce the mechanical properties of such metals.

iv) Physical state of the metal:
The structural state of any metal that is subjected to unevenly distributed mechanical stresses are noticed to undergo rapid corrosion processes. Studies have shown that in most homogenously arranged metals (pure metals), the areas under stress tend to be anodic and deplete with corrosive tendencies. Consequently, it has been shown that the visible presence of caustic embrittlement on stressed parts such as bends, joints and rivets in boilers are due to corrosion on the basis of uneven distribution of stress profiles [4].

v) Nature of the Oxide film:
The natural conditions of metals that react with their immediate environments to form oxides is a well understood in earth mineral processing. Thus, metals such as Mg, Ca and Ba form oxides whose volumes are less than the volume of the primary metal when exposed to such environments. Since these are natural tendencies, the resulting oxide film will be permeable, thus permitting the diffusion of oxygen into the structural matrix of the metal to bring about further corrosion. Conversely, studies have shown that metals like AI, Cr and Ni form oxides whose volume is greater than that of the metal and the nonporous oxide film so formed will protect the metal from further corrosion.

v) Solubility of the products of corrosion:
Corrosion studies dealing with various range of solubility is crucial to the development of engineering materials in the sense that metals whose corrosion product is soluble in the corroding medium tend to corrode faster. Conversely, if the corrosion product is insoluble in the corroding medium, then the protective film formed tends to suppress corrosion [5].

B. Prevalent environmental conditions

It is common knowledge in corrosion study that the nature of the environment influences the rate of corrosion of metals in the following ways:

i) Temperature: The study finds that the rate of chemical reactions and the rate of diffusion of ions between the electrodes increase with rising temperature. Hence, corrosion in metals increases with increase in temperature. This implies that a passive metal may become active at a higher temperature due to structural realignments of its atomic and molecular level conditions [6].

ii) Humidity: Some metals corrode faster upon increase in humidity; for instance, atmospheric corrosion of iron is slow in dry air but increases rapidly in the presence of moisture. This is due to the fact that moisture acts as a solvent which dissolves oxygen in the air to furnish the electrolyte that is essential for setting up a corrosion cell. Consequently, rusting of iron increases when the relative humidity of air progresses from 60% to 80%.

iii) Effect of pH: It should be noted that acidic scale of pH level described how acidic or alkaline a substance is. Instructively, acidic solution will increase the corrosion rate of chemical reaction. This account for the reason why most corrosion studies are carried out in the presence of acidic mediums.

iv) Nature of the electrolyte: The nature and type of electrolyte also influences the rate of corrosion. As a result, if the electrolyte consists of silicate ions, for instance, they form insoluble silicates and prevent further corrosion from happening. Conversely, if chloride ions are present, they diminish the protective film and the surface is exposed for further corrosion. In addition, if the conductance of the electrolyte is more, the corrosion current is easily conducted and hence the rate of corrosion is increased [7].

III. DETERMINATION OF AVERAGE LIFE SPAN OF ORGANIC COATING USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

In furtherance of the foregoing, the main objective of this investigation is to predict the positive extent to metals for deployment in marine locations could be selected on the basis of their corrosion imprints. In order to achieve this, the phenomenon that an organic inhibitor can prevent corrosive action in acidic electrolytic medium by exposing same to controlled electrical energy (circuit) interference, must be tested for consistency. Thus, by making the organic coating a circuit component, the flow of electric energy can be determined alongside its resistance or impedance to the flow of current. By design, EIS systems captures the resistivity of the organic coated surface to the flow of electrical signal and interprets this resistance as an impedance and thereafter compares its value with predetermined data in its registry; these are referred to as equivalent circuit models [8].

Table 2: equivalent impedance circuits

Equivalent Element	Admittance	Impedance
R	1/R	R
C	jωC	1/jωC
L	1/jωL	jωL
W (infinite Warburg)	Y0√(jω)	1/Y0√(jω)
O (finite Warburg)	Y0√(jω)Coth(B√(jω))	Tanh(B√(jω))/Y0√(jω
Q (CPE)	Y0(jω)α	1/Y0(jω)α

Source: Gamry Instruments [8]

As indicated in the circuit elements in Table 1 above, equivalent circuit models define electrical signal parameters such as resistivity, capacitance, inductance and angular velocity; and interprets the EIS obtained data by conversion to these parameters. Thus, programing of the operational dynamics of EIS schemes for predictive determination of materials' corrosion signatures for deployment in marine environment involves calculation of depths of coating, wear rates, adhesivity, life span of the organic coating, etc. Further, it has been observed that EIS has been used to investigate degradation of coated metals exposed to various environmental conditions [9]; however, Zou and Thierry observed that the prevalent method at that time was limited by the unavailability of a scanning impedance technique that could overcome the problems of size characterization and cell geometry of the material's surface.

In view of these identified drawbacks in the Zou and Thierry study, a more recent investigation by Lu *et al.* [10] agreed with our findings on the applicability of organic coatings in the retardation of corrosion signatures. Although the Lu *et al.* studies was premised on a chemical technology background, their findings are very material to the position of this paper and as such shall be significantly relied upon alongside the findings in Siongo *et al.* [11], under the following subsections.

IV. METHODS ANALYSIS AND DISCUSSIONS

The application of EIS as a manufacturing probe parameter in determination of the deployability of metals for various fabrications and applications in marine environments, derives significance in method analysis incidental to the conditions of preparation and application of the organic coating on the metal. As reported in Lu *el al.*, which is also agreeable with Siongo *et al*, but with modifications in this paper; the laboratory controlled combination of hydroxyl acrylic resin, butyl acetate, organic tin catalyst and N75 isocyanate provided the paste like paint for homogenous protection of the metal surface. From Lu *et al's* method of preparation, it is indicated that an addition of the N75 isocyanate grade was progressed in NCO/OH ratios of 0.8, 1.0, 1.2 and 1.4.

It should be stated that this ratio adjustment created the same mixture but with different structural peculiarities and mechanical characteristics on account of the various proportional ratios. The coupons specimen used in the adopted Lu *et al.*, investigation was made of mild steel material with dimensional configurations of 80mm x 30mm x 3mm (grade of Q235, C:0.17, - 024%. Si:0.17 - 0.37%; Mn:0.35 -0.65%; S $<$ 0.030%; p $<$ 0.030%. These coupons were made to undergo abrasive action for surface
de-rusting after which the coupons were washed and rinsed in ethanol and acetone to remove any interlaced surface impurities.

Further, a double blind coating was applied and allowed to settle for about 24 hours under ambient room temperature after which samples were heat treated for 12 hours at 60^oC regulated temperature with coating thickness of $60\underline{+}10\mu m$. It should be noted that this chemical combination and subsequent curing and heat treatment of the painted coupon produced a complex compound of acrylic resin and *hexamethylene diisocyanate (HDI) biuret* as shown below in Fig 1.

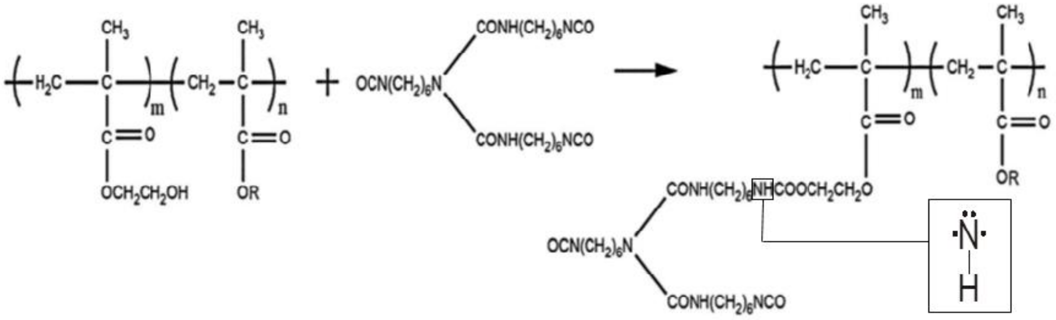

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Fig 1: The chemical reaction chain of acrylic resin and hexamethylene diisocyanate (HDI) biuret
Source: Lu *et al.* [10] with illustrative modification as shown in the N-H link

As could be observed in Fig. 1 above, the *OH* at the lower link of the acrylic resin chain loses the valence electron of its *H*-atom to the upper molecule of isocyanate resulting the N-H bond as the structural link between the acrylic resin and isocyanate molecule. Thus, H-N orbital hybridization analysis indicate bond dissociation energy of 390 kJ/mol with a bond length of 1.01 Å [12].

i) Characterization of the Experimental Setup

The electrolyte for the characterization assessment of the experiment utilized NaCl in a cell arrangement having three probe electrodes including graphite electrodes, saturated calomel electrode and the coating specimen coupons. Further, the experiment was designed to incorporate the use of counter electrode, reference electrode and confirmatory/deployment electrode, respectively. The confirmatory electrode has a work area of 1.00cm^2 of immersion impact in 3.5wt % NaCl solution. However, as suggested, a Faraday cage was used to conduct the EIS measurement to avoid *Columbic fields deflections* in reading outputs. Consequently, the EIS measurement frequencies range from 0.1 Hz to 100 KHz with the amplitude set at 10 mV.

ii) Impedance Data and Equivalent Electrical Circuits

It should be noted that the EIS signal output on the test electrode returns values that are further analyzed on the basis of individual parameters or requirements for the test. For the purpose of the support investigation reported in this paper, we shall concentrate on the analysis of the result of impedance data that was generated in Lu *et al.* and the structural characteristics of the organic coatings as advanced in Siongo *et al.*

IV. IMPEDANCE RELATIVITIES IN THE PREDICATION OF MATERIAL VIABILITY FOR DEPLOYMENT

We observe that the use of electrochemical measurements of degradation potentials of organic coating agents is well discussed in several literatures [13]. Consequently, Lu *et al* deployed the use of Bode and Nyquist plots to determine the range of impedance spectra and the conclusion of their assessment agrees with the views of Nematollahi *et al.* [14] that the organic coating agents act as a pure capacitor in the initial days of immersion; however, after some time, the inhibitor property of the coating diminished for the NCO/OH ration of 0.8. Consequently, the Nyquist plot indicates a content protection of the coating for the NCO/OH ratio of 1.0, 1.2 and 1.4.

Further, the ratio NCO/OH =1.4 was shown to possess the highest inhibitor performance, which implies high impedance measurement at low frequency testing which indicated a modulus as high as *10^{11}ohms/cm^2* in current resistivity. For that of NCO/OH ratio of 1.2, the recorded impedance is *10^{9}ohms/cm^2*. In view of this, studies have shown that where impedance measurement are in excess of *10^{9}ohms /cm^2*, then the materials has high inhibitor efficiency.

A. Water Absorption in Relation to Mechanical Properties of the Organic Coating

It was observed that there is the need to determine the water absorption level of the coating in order to understand its adhesive strength. Thus, the determination of this quality of the organic coating would require a critical expression for water absorption ratio as follows:

$$W(\%) = \frac{M_t - M_o}{M_o} 100\% \qquad \ldots\ldots 2$$

where, W = water absorption ratio
M_o = weight of dry coating film
M_t = weight of immersion time t

A computation of parameters of exposed section of the coupons' organic coating to electrolytic environment can be evaluated using equation (2). The period of such exposure is 120 hours and is indicated the following table and accompany graph.

Table 3: water absorption rate and coating permeability

% of H_2O absorption	Time, t (hrs)	NCO/OH concentration ratios			
		1.4	1.2	1.0	0.8
0.0%	0	0	0	0	0
0.1%	20	25	25	25	25
0.2%	40	45	45	45	45
0.3%	60				
0.4%	70	70	70	70	70
0.5%	95	95	95	95	95
0.6%	120				

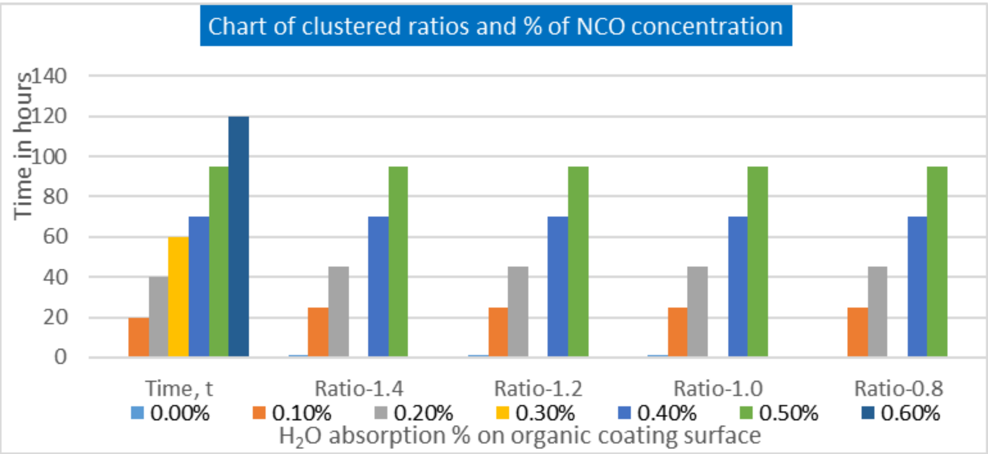

Fig 2: chart of clustered ratios and % of NCO concentration

V. DISCUSSIONS

From Table 3 and Fig 2 above, *continuous balancing gravimetric method* was used in the simulation of the chart and the indication is that in all the coating specimen, water absorption was less than 0.45 wt% as the green bar shows. This result also agrees with the findings in Lu *et al.* which imply that as NCO/OH ratio increases, the absorption of water by the organic coating also decrease due to increase in the rate of adhesivity of the N-H thin film barrier.

The implication of this phenomenon to materials selection is that a material to be selected for deployment in marine environment must during the period of testing show very low or no water absorption. Further, it should be noted that this absorption result would be different if the electrolyte is fresh water that does not contain active chemical combinations or ions, as found in aqueous NaCl or brine environment. Therefore, materials engineers and testing officials ought to be cognizant of this fact. It should be added that at NCO/OH ratio of 1.4 water absorption from the simulation indicate approximately 0.15% wt % water permeation. Implying that the corrosive electrolyte upon direct contact with the external thin film of ratio 1.4 organic coating, degrades by 15% of its thickness. However, the investigation data shows that when this ratio is intercalated at ratio 0.8, water absorption rose up to about 0.45wt% of coating thickness. Thus implying that wettability of coating increased when the NCO active inhibitor is decreased in the metal coating arraignment.

The practical inference from the foregoing is that the predictability for suitability of materials for deployment in marine environment during materials selection process should consider metals with external surface integrity. Such metals must possess significantly high chemical combinations or reactivity index with the active ingredient of the chosen organic coating. The manufacturers or suppliers' catalogues and handbooks could be useful in this regard, as the metal's composition including the primary metal constituents are provided in such sources. The foregoing thus implies that metals that show higher chemical bonding with the organic coating should be preferred, since their adhesivity also promotes impermeability of the coating profile. It should also be stated that impedance device with calibrated positive material identification (PMI) features could also be used to determine materials compositions and structural combination or reactivity possibilities with organic coating.

VI CONCLUSION

The study has significantly considered the use of EIS in the predictive evaluation and determination of metals with sufficient surface coating integrity for deployment in marine environment as fabrication and structural support members for platforms, topsides and various industrial utilities. The chemical combinations and conditions necessary for corrosion to occur have been discussed and the practical relativities of the evaluation which bordered on experimental inferences, deductions and simulations were performed.

Thus, the sequence of chemical reactions resulting the nitrogen-hydrogen composed thin film and how nitrogen attaches with four atoms of the host metal has been discussed. This phenomenon increases the bond strength of the nitrogen-metal interface and characteristically result strong coating adhesivity as the NCO/OH higher ratio introduces more N-atoms by reason of the N-H thin film. The study has observed that the structural composition of the resultant interface has bond energy of 391 KJ/mol and bond length of 1.01Å for the N-H chain.

Conclusively, we have posited that increase in NCO/OH ratios characteristically imply decrease in bond length on account of closer atomic nucleic attraction on the valence electrons. These decreased bond lengths directly increase the dissociation energies thus making water permeability very difficult and enhancing the ability of the coating to resist water permeability. The overall effect is an increased adhesivity of the organic coating on the metal, on account of high and penetrating adsorption of the thin N-H film which acts as barrier between the metal surface and the bulk of the coating material. Although the investigation did not consider the scanning election microscopic result of the specimen coupons after the film is removed, it is believed that the chemo-structural reactivity between the four lone pair of the nitrogen electrons would have a surface re-orientation effect on the valence electrons of the engaging atoms of the metal. This is hoped to improve the material's surface integrity even when the organic coating agent has been removed.

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