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Development of New Alternative Environmental-Friendly Passivatorfor Zinc Coated Sheets

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Abstract

Commercially available Tri-chromium and chrome-free passivator were evaluated with respect to their white rust resistance to the salt environment. The study also focused to evolve new environmental-friendly passivator for zinc-coated sheets. The corrosion behavior and mechanism of passivated samples are studised by electrochemical techniques. From electrochemical corrosion studies, the corrosion rates of commercial available chrome free passivator, tannic acid (t) and cerium+tannic acid passivated samples were identified as (2 to 3), 1.4, and 0.4 mpy, respectively. Cerium+tannic acid passivated samples exhibited a better corrosion resistance than commercial chrome-free or tannic acid passivated samples.

1. Introduction

Steel sheets are galvanized because the coated zinc layer confers sacrificial anode cathodic protection (SACP) to steel besides acting as a physical barrier to the ingress of corrosive constituents such as moisture, oxygen, chlorides, sulphates, etc. to the steel surface [1-5]. The corrosion resistance or, in other terms, the service life of a galvanized coating is directly proportional to its thickness [6-7]. As a barrier layer, a continuous zinc coating physically separates the steel from the corrosive environment [8]. On the other hand, by galvanic protection, zinc acts as a sacrificial anode and corrodes preferentially to protect the underlying steel at voids, scratches and cut edges of the coating. The sacrificial properties of zinc can been seen in a galvanic series where the potential of zinc is less noble than steel in most environments at ambient temperatures. In practice, this means that steel exposed at a coating defect or at a cut edge will not rust until the nearby zinc is consumed [6, 9-11].

Although zinc affords excellent corrosion protection to steel in a galvanized sheet by means of both barrier and galvanic protection, yet it is itself susceptible to corrosion even in mildly humid and moist environments. Under humid conditions, the zinc surface soon develops patches of a white, powdery corrosion product which is often referred to as “white rust” or a “storage stain” [4, 5, and 12]. Storage stains are so called because the phenomenon is frequently observed and encountered within the folds of finished galvanized coils/ sheets under storage where moisture accumulation and/or condensation takes place readily. If the zinc is protected against its own corrosion, then the longevity of the galvanized steel sheet is greatly enhanced. This is where the chemical treatments, termed “passivation” or “conversion” coatings, assume an important role in improving the performance of a hot dip galvanized sheet [3 and 4].

The continuous galvanizing lines (CGLs) of Rourkela Steel Plant (RSP) produce hot dip galvanized (HDG)sheets, which find wide application in construction and packaging segment. Currently, the CGLs of RSP use hexavalent chromium (CrVI) based chromic acid passivation treatment for hot dip zinc coating to confer resistance against formation of white rust and storage stains. The hexavalent chromium (CrVI) based passivators present numerous advantages: (1) high corrosion resistance for the galvanized sheet, (2) self-healing properties of the passivate film which endow it with good resistance to weathering damage, and (3) relatively low cost due to wide availability of raw materials. However, despite all these advantages, there is major drawback and restriction to the use of CrVI, owing to its toxicity and environmental hazard [6 and 9].

In recent years, much of passivator research has been focused towards the substitution of CrVI based chromic acid treatment on zinc-coated sheets with environmental-friendly trivalent chromium (CrIII) and other Cr-free alternative passivation treatments. An increasing number of customers are also now demanding these environmental-friendly solutions, whilst maintaining and even increasing their requirements in terms of white rust resistance of HDG sheets [12-17].

In the present work, it is therefore proposed to develop a new alternative environmental-friendly passivator for zinc-coated sheets as a replacement to conventional CrVI chromic acid passivator.

2. Experimental Work

2.1. Materials

Hot dip galvanized unpassivated sheet of 0.35mm thickness from Rourkela steel plant was collected for the studies.

2.2. Passivation Chemicals

Commercially available tri-chromium and chrome-free passivator were collected from the commercial supplier parties and the details of the passivators are listed in Table -1 and 2. Laboratory developed passivators are also listed in the table.

Table 1. *Details of Tri-chromium passivator.*

S.No.	Supplier of the passivator	Passivator	Chemical ID
1	GRowell	HB 203C 29041-1	T1
2	GTZ chemicals	Chemdite 831 TCP	T2
3	GTZ chemicals	Chemdite 83 TCP	T3
4	Surtec chemicals	Surtec 541	T4
5	ChemetalRai	Grade TP 10606/7	T5
6	ChemetalRai	Grade TP 10724/7	T6

Table 2. *Details of Chrome-free passivator.*

S.No.	Supplier of the passivator	Passivator	Chemical ID
1	GTZ chemicals	Chemdite 821 NCP	F1
2	GTZ chemicals	Chemdite 82 NCP	F2
3	Surtec chemicals	Surtec 641 A	F3
4	Surtec chemicals	Surtec 641 B	F4
5	Salt and Chemicals	Zipac 303	F5
6	---	Tannic Acid	t
7	---	Citric+Tannic acid	C+t

2.3. Chemcial Analysis of the Passivator

To find out the chromium percentage and to verify the presence of hexavalent chromium, Inductive couple plasma analysis and wet chemical analysis were carried out on the collected passivator (Table-3). The analysis of the test solutions was conducted using a Perkin Elmer Model Optima 2100 DV Inductively-Coupled Plasma Optical Emission Spectrometer (ICP-OES). Commonly chrome based passivator observed as brownish orange to muddy yellow in the form of fine colloidal suspension. Therefore, for analytical purposes, the fine suspended particulate matter were digested (dissolved) using mineral acid before subjecting to instrumental analysis in ICP-OES. Metal ion release rate for Cr was computed for each passivator.

2.4. Process Parameter

Process conditions were charted out for carrying out the passivation treatment in the laboratory. The details laboratory trails are shown in Table-4.

Table 3. *Chromium content by wet chemical/ Inductive coupled plasma (ICP) analysis.*

Passivator	% of Tri-chromium
Growel – HB 203C (T1)	10.5
GTZ– Chemdite 831 TCP (T2)	5.9
GTZ– Chemdite 831 TC(T3)	5.8
Surtech – 541 (T4)	11.1
ChemtelRai – Grade TP 10606/7 (T5)	5.5
ChemtelRai – Grade TP 10124/1 (T6)	11.4

Table 4. *Process parameters for passivation treatment.*

Chemicals	**Sample ID**	**Process parameters**					
		Conc	**Temp °C**	**pH**	**time (sec)**	**Drying °C**	**Pre treatment**
Tri Chromium Passivator							
T1	T1	120ml/l	25	1.8	60		
T2	T2	6%	25	2.56	2	80 to 90	Unikleen 46- 50g/l 5min immersion, temp 30°C
T3	T3	6%	25	2.56	2	80 to 90	---do---
T4	T4-1	12.5%	70	1.7	20	AIR dry	Alkaline degreasing
	T4-2	12.5%	70	1.7	90	AIR dry	---do---
T5	T5-1	10%	25	2.3		60 to 80	
	T5-2	20%	25	2.3		60 to 80	
T6	T6-1	10%	25	2.3		60 to 80	
	T6-2	20%	25	2.3		60 to 80	
Chrome Free passivator							
F1	F1	10%	25	2.1	2	80 to 90	Unikleen 46 etc..
F2	F2	10%	25	2.1	2	80 to 90	Unikleen 46 etc..
F3	F3-1	10%	25	2.6	60	Hot air	Alkaline degreasing
	F3-2	12%	25	2.6	20		---do---
	F3-3	12%	25	2.6	60		---do---
F4	F4-1	5%	25	2.6	60		---do---
	F4-2	10%	25	2.6	20		---do---
	F4-3	10%	25	2.6	60		---do---
F5	F5-1	6%	25	2-3	20	Hot air	---do---
	F5-2	12%	25	2-3	20	Hot air	---do---
Tannic acid	t	tannic acid - 40 g/L; HNO_3 (63%)-5 ml/l	50 - 70	3-5	20	Hot air	---do---
Citric+tannic	C+t	$Ce(NO_3)_3$, -0.4 mol/l; H_2O_2 (30%) -25 to35 ml/l; tannic acid -4 g/l.	25	2.5-3	20	Hot air	---do---

2.5. Salt Fog Exposure

The unpassivated HDG sheets were initially sheared into rectangular coupons of size 90 x 110 mm. Both chrome-free and tri-chromium passivation treatment were carried out according the process conditions listed in the Table-4. Three test coupons were employed for the purpose. Prior to testing, the sheared edges of sheet coupons were masked with molten wax to eliminate the edge effects on coupon corrosion during salt fog exposure. The test coupons were subjected to accelerated corrosion testing under 5% salt fog with an intermittent spraying cycle of 20 min in an hour and a fog fall-out rate of 1-2 ml per 80 cm^2 per hour. The test was conducted in accordance with ASTM standard B-117 and the skyward surfaces of the coupons were exposed to the fog at 15^o from the vertical. The initiation and progressive coverage (in area%) of white rust on skyward surfaces of test coupons was visually and periodically estimated and recorded during the course of the test exposure.

2.6. Electrochemcial Polarization Studies

2.6.1. Tafel Polarization

For investigating the corrosion performance of the passivated zinc coated sheets TafelExrapolation experiments were performed in 3.5% NaCl solution using a computer controlled Multichannel potentiostat Princeston Applied Research Model VersaSTAT MC. A standard PAR model K0235 flat electrochemical corrosion testing cell with a platinum (Pt) wire mesh counter electrode and a silver-silver chloride [Ag, AgCl/ KCl (saturated); Eo = +0.197 V versus SHE] reference electrode were conjunctively employed for the experiments. The passivated zinc coated sheets test specimens were subsequently clamped on to the corrosion testing cell to form the working electrode such that only a specimen surface area of 1 cm^2 was exposed to the test solution. The three-electrode corrosion cell was then annexed to the potentiostat by means of appropriate electrical connections. Before commencing the experiment, the open circuit potential (OCP) of the working electrode was monitored for stability for 60-120 seconds. The experiment was conducted at the potential scan rate of 1mV/s using Versastudio® test program. The polarization plots, thus obtained, between the potential (V) and current density (A/cm^2) were analyzed to evaluate the electrochemical parameters such as equilibrium corrosion potential (E_{corr}), corrosion current density (I_{corr}), Anodic Tafel slope, CathodicTafel slope and corrosion rate. Three specimens were tested for each passivation treatement to ensure reproducibility of the test results. Only the average values for each grade of steel are reported here.

2.6.2. Electrochemical Impedance Spectroscopy

The passivated zinc coated sheets were subjected to electrochemical impedance spectroscopy (EIS) in 3.5% NaCl solution in order to characterize the impedances of the films formed on steels. For the EIS experiments, the same standard flat electrochemical corrosion testing cell with a Pt wire mesh counter electrode and a silver-silver chloride reference electrode was used. The passivated zinc coated sheets specimens were mounted in the corrosion testing cell to expose a surface area of 1 cm^2 to the test solution. The three-electrode corrosion cell was electrically connected to computer controlled Multichannel potentiostatPrinceston Applied Research Model VersaSTAT which has inbuilt frequency response analyzer (FRA) for effecting AC impedance measurements.

The impedance spectra generated in the form of complex plane Nyquist impedance plots were regressed and modeled with their equivalent electrical circuit, R(QR) using ZSimpwin® software, developed by PAR, to compute the charge transfer resistances (in $\Omega.cm^2$) and capacitances (in F/cm^2) of the films.

3. Results and Discussion

3.1. Microstructure Characterization

Figure 1 shows the optical mictrotructure of the passivated and unpassivated zinc coated sheets. As tri-chromium passivator is principally nitrates which play the part of oxidizers of zinc, the localized pH increase leads to the precipitation of trivalent chromium as oxides or hydroxides, which gives rise to films of considerably lower thickness and crack pattern as shown in the Figure 1. From Chemcial analysis of the collected passivator it is clear that the passivator do not contain any hexavalent chromium.

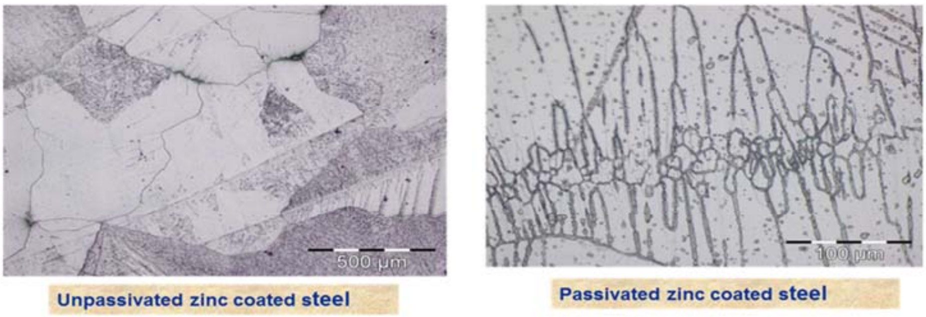

Figure 1. *Microstructure of unpassivated and passivated zinc coated sheets.*

3.2. Salt Fog Corrosion

Table-5 and 6show the time for initiation of white rust on tri-chromium and chrome free passivated HDG steel coupons in corrosive test environment of 5% salt fog with varying treatment conditions. The graphs in Figure 2 and 3 depict the kinetics of white rust initiation and growth on the coupons with progressing period of exposure. Figure 4 shows photograph of typical with and without white rust formation of Zinc coated sheets passivated sheets after 100h salts spray exposure. It may be noticed from the graphs that the white rust formation initiates only after a distinct incubation period, which is a measure of corrosion resistance afforded by the passivation film. It is clear from Table-5, the trichromium passivation conditions such as T2, T4-2, T5-1, T5-2 and T6-1 found to exhibit visual signs of white rust only after 90-96 hours of exposure where as other process parameters exhibit mottled appearance with spots of white rust after only 10-18 hours of exposure. It is pertinent to mention that the adequacy of chromate passivation treatment is adjudged from the ability of the passivated HDG sheet to withstand 100 hours of salt fog exposure without any incidences of white rust. Similarly, from Table 6 it can be concluded that F1, F5-2, Tannic acid and Cerium+tannic acid passivator better resistance to white rust formation under of 5% salt fog environment.

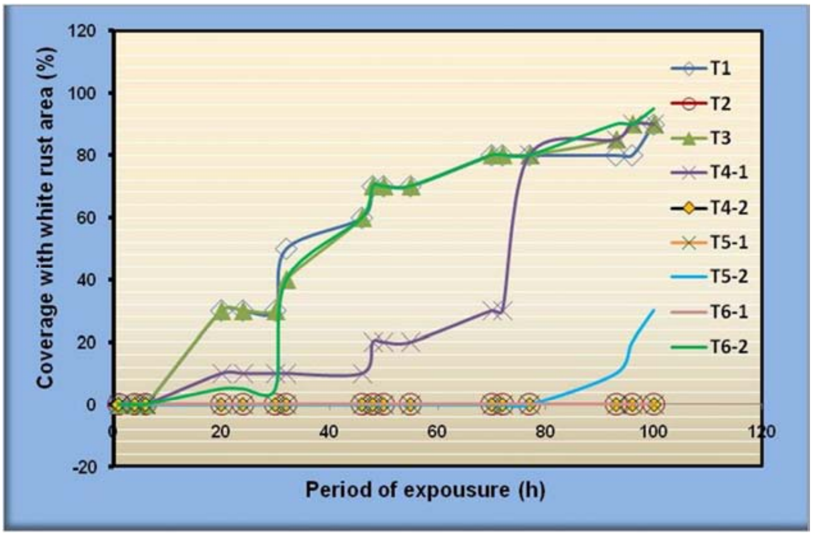

Figure 2. *Rusting pattern of Tri-chromium passivated HDG sheets.*

Table 5. *Time to initiation for white rust on tri-chromium passivated HDG coupons under 5% salt fog exposure.*

Passivators	Sample ID	Time to initiation of white rust (hours)
GRowell	T1	10-20
GTZ chemicals	T2	---
GTZ chemicals	T3	10-20
Surtec chemicals	T4-1	10-20
	T4-2	---
ChemetalRai	T5-1	---
	T5-2	90-93
ChemetalRai	T6-1	---
	T6-2	20-24

Table 6. *Time to initiation for white rust on chrome-free passivated HDG coupons under 5% salt fog exposure.*

Passivators	Sample ID	Time to initiation of white rust (hours)
GTZ chemicals	F1	---
GTZ chemicals	F2	50-55
Surtec chemicals	F3-1	10-20
	F3-2	10-20
	F3-3	10-20
Surtec chemicals	F4-1	10-20
	F4-2	30-32
	F4-3	30-32
Salt and Chemicals	F5-1	50-55
	F5-2	---
Tannic acid	t	93-96
Citric+tannic	C+t	---

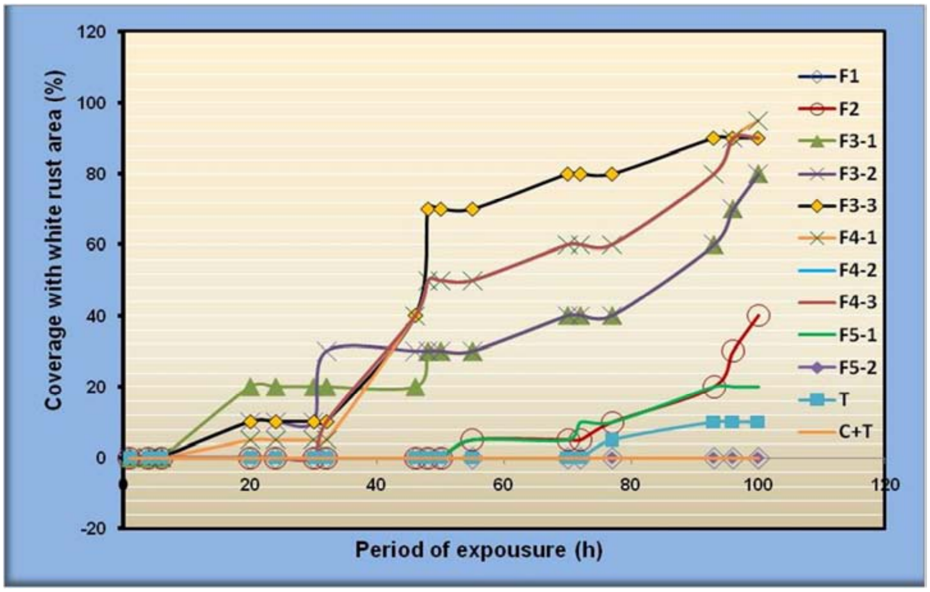

Figure 3. *Rusting pattern of Chrome-free passivated HDG sheets.*

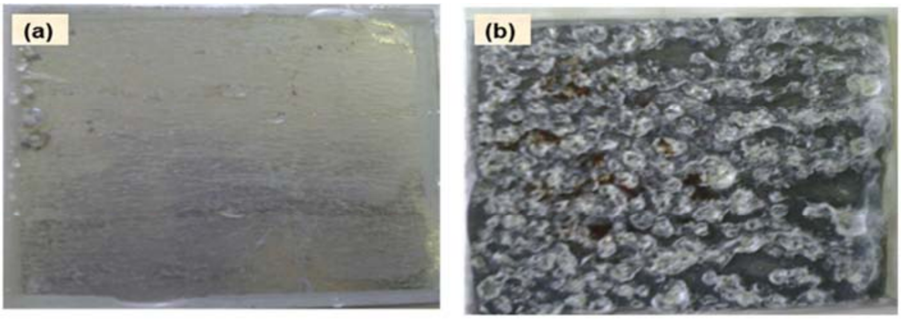

Figure 4. *Zinc coated passivated sheets after 100h salts spray exposure (a) without white rust (b) Rusted sheets.*

3.3. Electrochemical Corrosion Studies

3.3.1. Tafel Polarization Studies

Figure 5 shows the typical Tafel polarization curves of tri-chromium and chrome free passivated samples for in 3.5% NaCl solution. The calculated corrosion data for the above tri-chromium passivation treatment are shown in Table-7 along with the hexavalent chromium passivation corrosion data. The corrosion current density of the samples treated by hexavalent chromium passivated sample was 5.2μA/cm^2, whereas the corrosion current density of the tri-chromium passivated samples were about 1 to 2μA/cm^2. The corresponding corrosion rate of hexavalent chromium passivated sample was around 3 mpy. Tri-chromium passivated samples exhibited a better corrosion rate of 0.5 to 1 mpy. The results suggested that tri-chromium treatment has better corrosion reistance that that of hexavalent chrome passivation. Tri-chrome passivation showed passive layer in the tafel polarization graph (Figure 5) suggesting that barrier coating characteristics [11 and 12]. Hence, the tri-chromium passivation efficiency depends on the thickness of the passive/barrier layer.

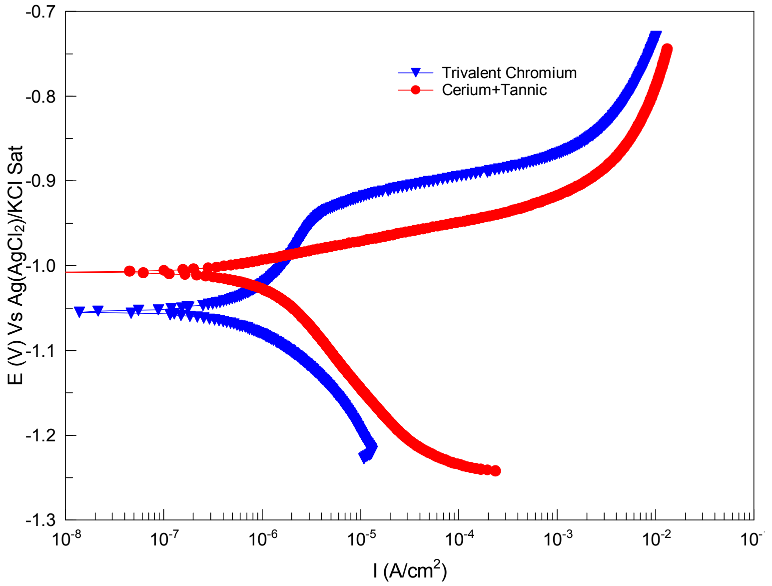

Figure 5. *Typical TafelExra-Polarisation graph of Tri-chromium and Chrome-free passivated HDG sheets.*

The mechanism of protection of hexavalent chromium is different from that of the trichromium. Hexavalent chromium has self-healing properties, they react with zinc and forms a complex film namely, zinc-chromate on the surface of the zinc coated sheets. Therefore, the quantity/concentration of hexavalent chromium passivation required is very less in the order of 1 to 2 g/l. Whereas, tri-chromium protection depends mainly on the barrier layer, so the amount of concentration must be higher (12 to 30 g/l) [6, 7, and 13].

The electrochemical corrosion data for the chrome free passivated samples, derived from the tafel polarization technique, are shown in Table-8. The corrosion current density of the samples treated by commercial available chrome free passivator (F1 and F5) and tannic acid (t) was 4 to 5μA/cm^2 and 2.8μA/cm^2 respectively, whereas the corrosion current density of the samples passivated by cerium+tannic acid was 0.7μA/cm^2. The corresponding corrosion rates of commercial available chrome free passivator (F1 and F5) tannic acid (t) and cerium+tannic acid passivated samples were identified as (2 to 3), 1.4, and 0.4 mpy, respectively. Cerium+tannic acid passivated samples exhibited a better corrosion resistance than commercial chrome-free or tannic acid passivated samples.

Table 7. *Tafelpolarisation parameters of tri-chromium passivated HDG steels.*

Passivator	Treatment	Corrosion Potential (mV)	Corrosion current (μA/cm^2)	Corrosion rate	Break down Potential E_{pit}
Hexavalent Cr	CrVI	-871	5.16	3.1	
T1	T1	-925	12.0	7.2	---
T2	T2	-943	1.8	1.1	---
T3	T3	-928	1.8	3.4	---
T4	T4-1	-938	12.0	7.4	---
	T4-2	-988	5.8	2.1	---
T5	T5-1	-1055	0.9	0.5	- 930
	T5-2	-990	1.0	0.6	- 910
T6	T6-1	-925	3.5	2.2	---
	T6-2	-930	6.3	3.7	---

3.3.2. Electrochemical Impedance Spectroscopy Studies

Figure 6 shows the typical Nyquist and Bode plots of the tri-chromium and chrome free passivated samples tested in 3.5% NaCl solution. The Nyquist spectra are composed of two capacitive loops. Two time constants can be distinguished well from Bode plots. The impedance tended to increase when the sample was passivated in trichromium passivation conditions such as T2, T4-2, T5-1, T5-2 and T6-1 compared to other parameters and similarly for chrome-free passivation such as, F1, F5, tannic acid and cerium+tannic acid in the range of mid-low frequencies. Figure 6(c) shows the equivalent circuit representing the impedance spectra for samples tested in 3.5% NaCl solution. The circuit is based on the following contributions: R_s represents the solution resistance, R_f is the conversion coating resistance, R_t is the resistance of corrosion products on the samples surface, C_c is the conversion coating capacitance, and C_{dl} is the double layer capacitance. Thus, the total impedance of equivalent circuit can be expressed by the following equation [18, 19 and 20]:

$$Z = R_s \frac{R_f}{R_f Y_{0,c}\,(j\omega)^{a1} + \frac{1}{1+\frac{R_t}{R_f[1+R_t Y_{0,d1}(j\omega)^{a2}]}}} \rightarrow \tag{1}$$

where the parameters $Y_{0,\,c}$ and a_1 are related to C_c; $Y_{0,\,dl}$ and a_2 are related to C_{dl}. The parameters in Eq. (1) were obtained by fitting the impedance spectra on the basis of the equivalent circuits of Figure 6(c), and the results are listed in Table-9 and 10. Tri-chromium passivation shows the higher coating film resistance (R_f), substantiate that the corrosion prevention is through barrier coating.

Table 8. *Tafelpolarisation parameters of of chrome-free passivated HDG steels.*

Passivator	Treatment	Corrosion Potential [mV]	Corrosion current [μA/cm^2]	Corrosion rate [mpy]
F1	F1	-970	4.5	2.2
F2	F2	-990	6.5	3.8
F3	F3-1	-932	10.0	6.0
	F3-2	-942	8.0	4.8
	F3-3	-964	7.3	4.4
F4	F4-1	-967	17.0	9.9
	F4-2	-973	18.0	11.0
	F4-3	-963	41.0	24.0
F5	F5-1	-992	4.3	3.5
	F5-2	-966	5.9	2.5
Tannic	t	-953	2.8	1.4
C+T	c+t	-1006	0.7	0.4

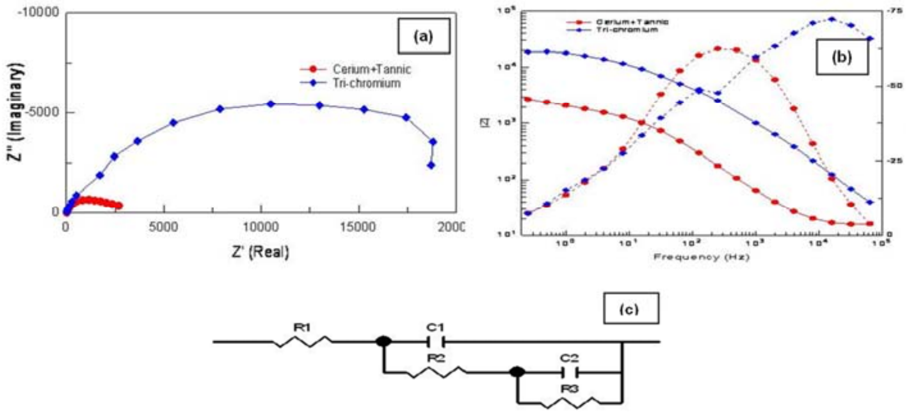

Figure 6. *Typical Electrochemical impedance plot of Tri-chromium and Chrome-free passivated HDG sheets (a) Nyquist Plot (b) Bode plot (c) Equivalent circuit.*

Table 9. *Electrochemical Impedance spectroscopy parameters of tri-chromium passivated HDG steels.*

Passivator	Treatment	Coating Resistance (R_s) [Ω.cm^2]	Coating Capacitance (C_1) x10^{-6} [F/cm^2]	Coating Resistance (R_1) [Ω.cm^2]	Double layer Capacitance (C_2) x10^{-6} [F/cm^2]	Charge Transfer Resistance(R_2) [Ω.cm^2]
T1	T1	18.7	1.8	1100	35	2100
T2	T2	9.6	0.04	5600	0.04	6800
T3	T3	11.5	3	460	57	600
T4	T4-1	9.8	0.11	790	2.1	710
	T4-2	16.2	2.6	3200	22	2200
T5	T5-1	24.5	0.12	11740	1.9	8195
	T5-2	69.0	0.19	8000	3.2	8650
T6	T6-1	13.6	1.4	6243	55	5968
	T6-2	13.8	1.5	1685	38	1120

Table 10. *Electrochemical Impedance spectroscopy parameters of chrome-free passivated HDG steels.*

Passivator	**Treatment**	**Coating Resistance (R_s) [Ω.cm^2]**	**Coating Capacitance (C_1) x10^{-6} [F/cm^2]**	**Coating Resistance (R_1) [Ω.cm^2]**	**Double layer Capacitance (C_2) x10^{-6} [F/cm^2]**	**Charge Transfer Resistance(R_2) [Ω.cm^2]**
F1	F1	38.9	0.42	1135	3.9	1213
F2	F2	18.6	0.46	1010	0.87	706
F3	F3-1	13.1	2.4	515	245	375
	F3-2	13.2	2.3	836	162	436
	F3-3	13.7	3.1	611	206	350
F4	F4-1	13.0	2.0	393	591	138
	F4-2	13.9	1.9	200	2.1	201
	F4-3	13.5	2.3	196	4.5	325
F5	F5-1	15.3	3.1	372	9.9	509
	F5-2	13.9	4.3	1251	5.8	1671
Tannic	t	17.6	7.8	1632	9.7	1052
C+T	c+t	19.6	4.8	2485	69.8	2165

4. Conclusions

Cerium+tannic acid passivated samples exhibited a better corrosion resistance than commercial chrome-free or tannic acid passivated samples. Hence, Cerium+tannic acid can be a potential alternative environment friendly passivatorfor existing hexavalent chromium passivator.

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