

CORROSION PROTECTION OF MATERIALS BY NANOCOATING OF DECAHYDROBENZO[8]ANNULENE-5,10-DIPHENYLHYDRAZONE AND ALN FILLER

Rajesh Kumar Singh

Assistant Professor, Department of Chemistry
Jagdam College, J P University Chapra – 841301, India.

(Received on Date: 3rd August 2017

Date of Acceptance: 21st September 2017)

ABSTRACT

Stainless steel is an important metal for transport industries. Epoxy coating uses for the protection of this metal. But epoxy coating do not protection itself and base metal in longer periods. Corrosive pollutants interact with epoxy-coated stainless steel to activate chemical and corrosion reaction whereas weather changes also insist such type's reaction. They can alter their physical, chemical, mechanical and internal and external morphology of epoxy-coated stainless steel. Corrosive pollutants enter inside of epoxy-coating by osmosis and diffusion process and create acidic environment for them. Acids develop corrosion cell on the surface of metal so it produces galvanic, pitting, stress, crevice, blistering and embrillement corrosion. It develops swelling corrosion with epoxy-coating and make weaker c-c bond. It produces disbonding between stainless steel and epoxy-coating. When weather changes happens surrounding temperatures increase or decrease and the nature of pollutants and their concentrations also change such occurrences accelerate corrosion reaction. Nanocoating and filler techniques used for corrosion protection of epoxy-coated stainless steel in such hostile environment. Decahydrobenzo[8]annulene-5,10-diphenylhydrazone was synthesized a nanocoating materials and ALN applied as filler for corrosion protection of epoxy-coated stainless steel. The corrosion rates of epoxy-coated stainless steel were calculated by weight loss experiment. Electrode potential, corrosion current and current density were determined by potentiostat technique. Nanocoating and filler compounds performance were studied at different temperatures, weathers and times. Coating and filling works were completed by nozzle spray and chemical vapour deposition. Nanocoating and filler materials were formed a composite film barrier on the surface of epoxy-coated stainless steel. The composite film formation, thermal stability and nature of chemical deposition and bonding were studied by activation energy, heat of adsorption, free energy, enthalpy and entropy. The results of all thermal parameters, surface coverage areas and coating efficiencies were indicated that composite film formed by nanocoating and filler materials providing protection in corrosive medium and weather changes.

Keywords: Corrosive pollutants, corrosion, epoxy polymer, nanocoating, filler, surface coverage area, coating efficiency.

No: of Figures : 8

No: of Tables : 3

No: of References: 21

INTRODUCTION

The main killer [1] of material is acids, alkalis, salts, pollutants, effluents, biowastes, food wastes and agricultural wastes. Corrosion protection of materials is a major problem. It cannot be fully control but it can minimize by suitable techniques. It is necessary to design proper shape and size of materials [2]. The internal and external morphology of materials [3] were arranged in order ways. It is tried to make outer layer uniform [4]. Organic [5] and inorganic [6] materials used for corrosion protection in various hostile environments [7] but such types materials are not stable. After a few months or years they can disintegrate [8]. Metallic coatings [9] provide corrosion protection in ambient attack of pollutants. This coating facial appearance changes after certain times and corrosion problems start. Polymeric coating [10] applied in various aggressive environments to control the corrosion of materials. Such coating barrier faces corrosion [11] by corrosive pollutants. They can inter inside by osmosis or diffusion process [12] and corrode base metal. They can also create debonding into polymeric compounds. Paint coatings [13] use for the protection of outer layers in railways, construction, marine areas and others types of metallic and nonmetallic materials but these coatings are not stable in acidic and alkaline environment. Organic and inorganic inhibitors [14] use for control corrosion of materials as per working conditions. Nanocoating [15] provides good protective barrier whereas such coating develops porosities so

corrosive substances inter inside and accelerates corrosion reaction. Several types of nanocoating process are applicable in ambient of pollutants for the protection of materials [16] like top layer coating [17], composite coating [18], thermal barrier [19] coating and conversion coating. Top layer coating shaves materials for general corrosion whereas composite coating protects metals from uniform corrosion. Thermal barrier coating controls high temperature corrosion. Conversion coating checks atmospheric corrosion of materials. These types of coating do not provide long term corrosion protection due to porosities develop during coating which causes of corrosion. In this work decahydrobenzo[8]annulene-5,10-diphenylhydrazone used as nanocoating materials and their porosities were blocked by AlN filler.

Experimental

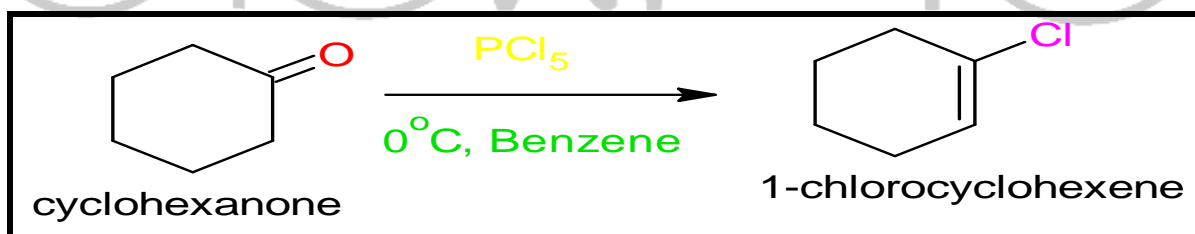
Coupons of epoxy-coated stainless steel kept in corrosive environment and their corrosion rate determined at different temperatures, times and weathers as mentioned 278^oK, 283^oK, 288^oK, 293^oK and 298^oK temperature and time fixed 24, 48, 72, 96 and 120 hours. Epoxy-coated stainless steel was nanocoated with decahydrobenzo[8]annulene-5,10-diphenylhydrazone and its corrosion rate calculated at above recorded temperatures and times. AlN filler used on

the surface of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and corrosion rate of material determined above mentioned temperatures and times. These results were obtained by the help of weight loss experiment. Potentiostat 173 model EG & PG Princeton used to measured corrosion potential, corrosion current, current density, anodic and cathodic polarization of epoxy-coated stainless steel, decahydrobenzo[8]annulene-5,10-diphenylhydrazone-epoxy-coated stainless steel and AlN-decahydrobenzo[8]annulene-5,10-diphenylhydrazone-epoxy-coated stainless steel. Plasma spray used for nanocoating purpose. The surface adherence properties studied by Arrhenius equation and Langmuir isotherm equation. The composite thin film barrier bonding formation studied by activation energy, heat of adsorption, free energy, enthalpy

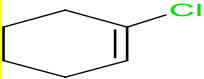
and entropy. The synthesis process of decahydrobenzo[8]annulene-5,10-diphenylhydrazone was given as:

Scheme1: Synthesis of 1-chlorocyclohexene

Cyclohexanone (80g) was added in dry benzene (150ml) and reaction mixture was poured drop wise into a cool solution of PCl_5 . The mixture was taken in two necks round bottle flask and stirred for further 3hours and during reaction temperature was maintained 0°C . The product was extracted from ethereal solution and was washed with 5% aqueous Na_2CO_3 then after dried with Na_2SO_4 and solvent removed by application of rotator vapour. The product was purified by column chromatograph by the use of silica gel in petroleum ether. After purification 87% of 1-chlorocyclohexene was obtained.



Physical properties of 1-chlorocyclohexene

	Molecular Formula	= C ₆ H ₉ Cl
	Formula Weight	= 116.58866
	Composition	= C(61.81%) H(7.78%) Cl(30.41%)
	Molar Refractivity	= 32.29 ± 0.4 cm ³
	Molar Volume	= 113.5 ± 5.0 cm ³
	Parachor	= 263.4 ± 6.0 cm ³
	Index of Refraction	= 1.480 ± 0.03
	Surface Tension	= 29.0 ± 5.0 dyne/cm
	Density	= 1.02 ± 0.1 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 12.80 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 116.039278 Da
	Nominal Mass	= 116 Da
	Average Mass	= 116.5887 Da
	M+	= 116.038729 Da
	M-	= 116.039827 Da
	[M+H] ⁺	= 117.046554 Da
	[M+H] ⁻	= 117.047652 Da
	[M-H] ⁺	= 115.030904 Da
	[M-H] ⁻	= 115.032002 Da

¹H NMR of 1-chlorocyclohexene

ChemNMR ¹H Estimation Estimation quality is indicated by color: **good**, **medium**, **rough**

Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2	1.96	1.96	cyclohexene
CH2	1.99	1.96	cyclohexene
		0.03	general corrections
CH2	1.74	1.65	cyclohexene
		0.09	general corrections
CH2	1.61	1.65	cyclohexene
		-0.04	general corrections
H	5.77	5.59	cyclohexene
		0.18	1-Cl cis from 1-ethylene

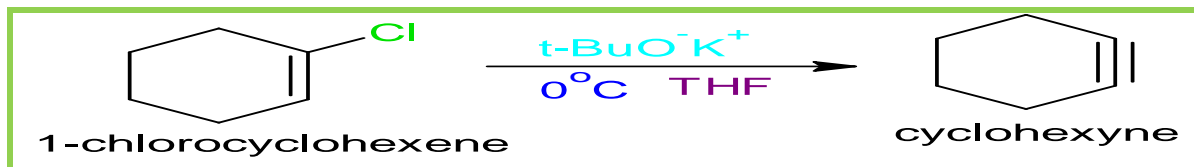
¹H NMR Coupling Constant Prediction

shift	atom index	coupling partner, constant and vector
1.96	3	5 7.1 H-CH-CH-H
		8 -1.0 H-CH>C=C>H
1.99	4	8 6.2 H-CH-C(sp ²)-H
		6 7.1 H-CH-CH-H
1.74	5	3 7.1 H-CH-CH-H
		6 7.1 H-CH-CH-H
1.61	6	4 7.1 H-CH-CH-H
		5 7.1 H-CH-CH-H
5.77	8	4 6.2 H-C(sp ²)-CH-H
		3 -1.0 H>C=C>CH-H

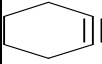
Scheme2: Synthesis of cyclohexene

1-Chlorocyclohexane (57g) was dissolved in THF and potassium t-butoxide (BuO⁻K⁺) was added (75g) at room temperature then after cyclohexene (70ml) was mixed into reaction mixture as trapping agent. After completion of reaction water was poured then it

quenched with brine solution and reaction mixture was extracted from ether. Finally, the compound was dried with sodium sulphate. Solvent was removed by rotator vapour and target product was purified by silica gel column chromatograph. After purification 83% yield of 1,2,3,4,4a,5,6,7,8,8b decahydrobipthalene was obtained.



Physical properties of cyclohexyne

	Molecular Formula	= C ₆ H ₈
	Formula Weight	= 80.12772
	Composition	= C(89.94%) H(10.06%)
	Molar Refractivity	= 25.79 ± 0.4 cm ³
	Molar Volume	= 91.7 ± 5.0 cm ³
	Parachor	= 217.9 ± 6.0 cm ³
	Index of Refraction	= 1.474 ± 0.03
	Surface Tension	= 31.8 ± 5.0 dyne/cm
	Density	= 0.87 ± 0.1 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 10.22 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 80.0626 Da
	Nominal Mass	= 80 Da
	Average Mass	= 80.1277 Da
	M+	= 80.062052 Da
	M-	= 80.063149 Da
	[M+H] ⁺	= 81.069877 Da
	[M+H] ⁻	= 81.070974 Da
	[M-H] ⁺	= 79.054227 Da
	[M-H] ⁻	= 79.055324 Da

¹H NMR of cyclohexyne

ChemNMR ¹H Estimation of cyclohexyne

Estimation quality is indicated by color: good, medium, rough

Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):

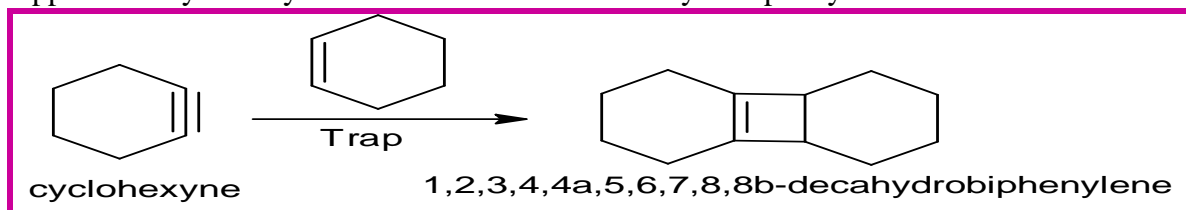
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2 1.96	1.96	1.37	methylene
		0.65	1 alpha -C+C-C
		-0.06	1 beta -C
CH2 1.96	1.96	1.37	methylene
		0.65	1 alpha -C+C-C
		-0.06	1 beta -C
CH2 1.44	1.44	1.37	methylene
		0.13	1 beta -C+C-C
		-0.06	1 beta -C
CH2 1.44	1.44	1.37	methylene
		0.13	1 beta -C+C-C
		-0.06	1 beta -C

1H NMR Coupling Constant Prediction

shift	atom index	coupling partner, constant and vector
1.96	3	5 7.1 H-CH-CH-H
		4 2.5 H-CH-C+C-CH-H
1.96	4	6 7.1 H-CH-CH-H
		3 2.5 H-CH-C+C-CH-H
1.44	5	3 7.1 H-CH-CH-H
		6 7.1 H-CH-CH-H
1.44	6	4 7.1 H-CH-CH-H
		5 7.1 H-CH-CH-H

Scheme3: Synthesis of decahydrobiphenylene

Cyclohexene solution poured into cyclohexyne and reaction mixture was stirred one hours then cyclohexene trapped with cyclohexyne to form an adduct of decahydrobiphenylene.



Physical properties of 1, 2,3,4,4a,5,6,7,8,8b-decahydrobiphenylene

Molecular Formula	= C ₁₂ H ₁₈
Formula Weight	= 162.27132
Composition	= C(88.82%) H(11.18%)
Molar Refractivity	= 50.88 ± 0.4 cm ³
Molar Volume	= 164.7 ± 5.0 cm ³
Parachor	= 398.2 ± 6.0 cm ³
Index of Refraction	= 1.529 ± 0.03
Surface Tension	= 34.1 ± 5.0 dyne/cm
Density	= 0.98 ± 0.1 g/cm ³
Dielectric Constant	= 2.79 ± 0.2
Polarizability	= 20.17 ± 0.5 10 ⁻²⁴ cm ³
Monoisotopic Mass	= 162.140851 Da
Nominal Mass	= 162 Da
Average Mass	= 162.2713 Da
M+	= 162.140302 Da
M-	= 162.141399 Da
[M+H] ⁺	= 163.148127 Da
[M+H] ⁻	= 163.149224 Da
[M-H] ⁺	= 161.132477 Da
[M-H] ⁻	= 161.133574 Da

H¹NMR of 1, 2,3,4,4a,5,6,7,8,8b-decahydrobiphenylene

ChemNMR ¹H Estimation

Estimation quality is indicated by color: good, medium, rough

Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	2.15	1.44	cyclohexane
		0.63	1 alpha -C=C from methine
CH	2.15	0.03	1 beta -C=C from methine
		1.44	cyclohexane
		0.63	1 alpha -C=C from methine
CH2	1.99,1.890000	0.03	1 beta -C=C from methine
		1.96	cyclohexene
CH2	1.99,1.890000	0.02	general corrections
		1.96	cyclohexene
CH2	1.41,1.310000	0.00	1.44 cyclohexane
		0.00	1 beta -C=C from methylene
CH2	1.41,1.310000	0.08	general corrections
		1.44	cyclohexane
		0.00	1 beta -C=C from methylene
CH2	1.65	1.65	cyclohexene
CH2	1.65	1.65	cyclohexene
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections

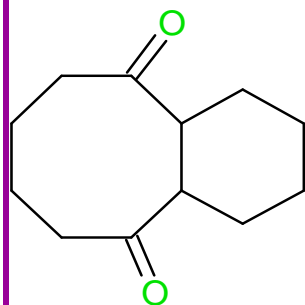
1H NMR Coupling Constant Prediction

shift	atom	index	coupling partner	constant and vector
2.15	7	8	7,0	H-C-CH
		9	7,0	H-C-CH
2.15	8	7	7,0	H-C-CH
		12	7,0	H-C-CH
1.94	3	diastereotopic	5	-12.4 H-C-CH
1.94	4	diastereotopic	7,1	-12.4 H-CH-CH
1.36	9	diastereotopic	7,1	-12.4 H-CH-CH
		10	7,0	H-CH-CH
1.36	12	diastereotopic	7,1	-12.4 H-CH-CH
		5	7,0	H-CH-CH
1.65	5	3	7,1	H-CH-CH
		6	7,1	H-CH-CH
1.65	6	4	7,1	H-CH-CH
		5	7,1	H-CH-CH
1.48	10	diastereotopic	9	-12.4 H-C-CH
		11	7,1	H-CH-CH
1.48	11	diastereotopic	12	-12.4 H-C-CH
		10	7,1	H-CH-CH

Scheme4: Synthesis of decahydrobenzo[8]annulene-5,10-dione

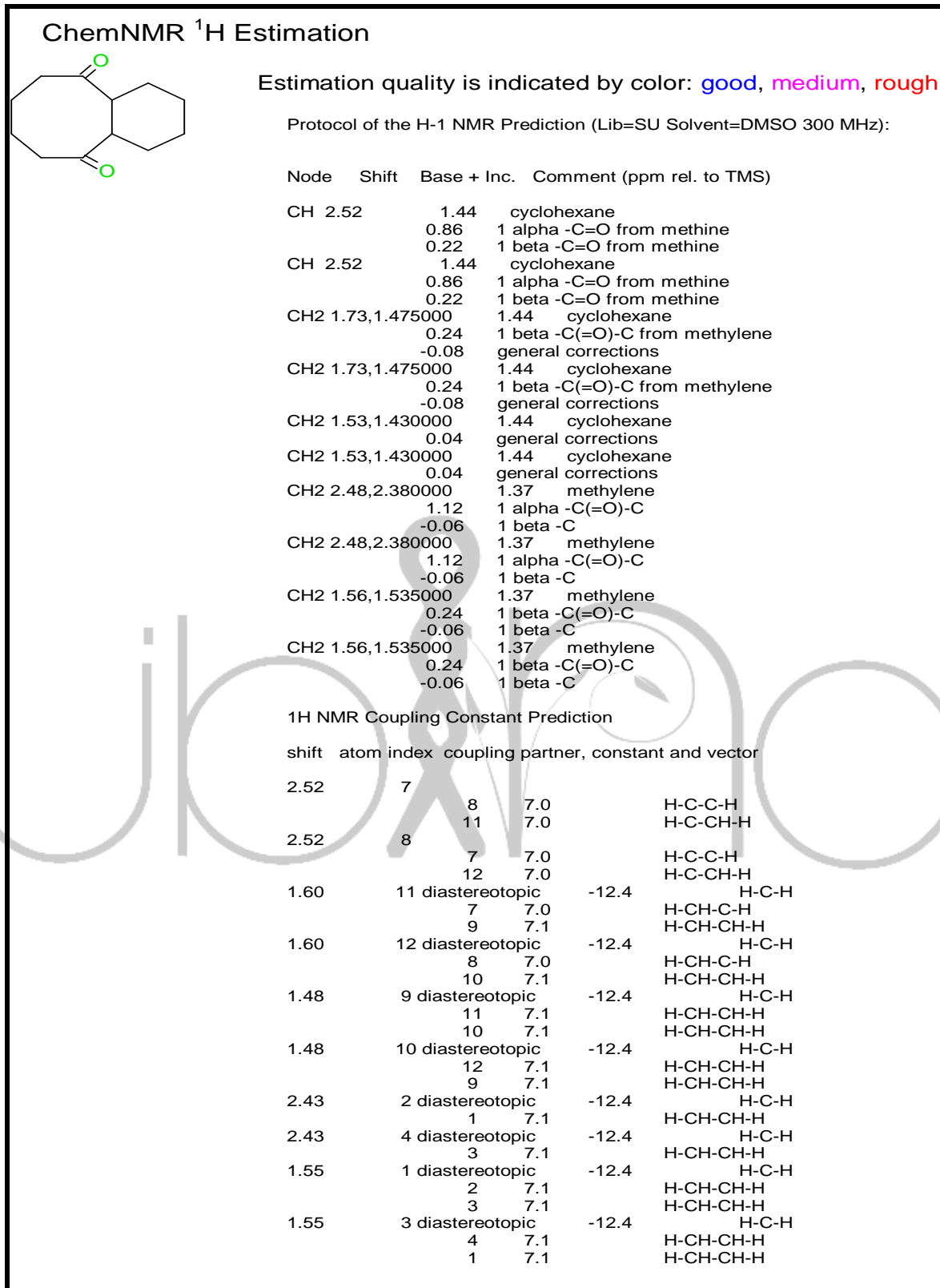
1,2,3,4,4a,5,6,7,8,8b-decahydrobiphenylene (78g) was taken and was dissolved with carbon tetrachloride. Sodium periodate (NaIO₄) (58g) was added into reaction mixture, then after methyl nitrile and water was added. The reaction mixture was stirred 24 hours at room temperature. The product was quenched with brine solution then adding sodium bicarbonate workup was completed with ether and ethereal solution dried with sodium sulphate. The target product was purified by silica gel column chromatograph and 76% yield of decahydrobenzo[8]annulene-5,10-dione was obtained.



Physical properties of decahydrobenzo[8]annulene-5,10-dione

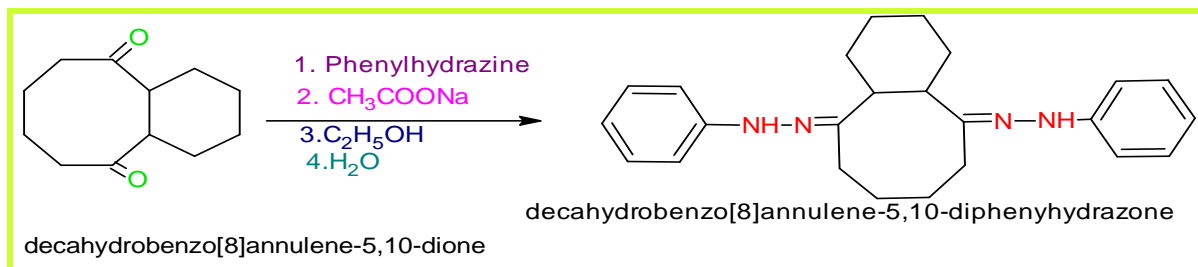
Molecular Formula	= C ₁₂ H ₁₈ O ₂
Formula Weight	= 194.27012
Composition	= C(74.19%) H(9.34%) O(16.47%)
Molar Refractivity	= 53.65 ± 0.3 cm ³
Molar Volume	= 186.8 ± 3.0 cm ³
Parachor	= 457.9 ± 6.0 cm ³
Index of Refraction	= 1.485 ± 0.02
Surface Tension	= 36.0 ± 3.0 dyne/cm
Density	= 1.039 ± 0.06 g/cm ³
Dielectric Constant	= Not available
Polarizability	= 21.27 ± 0.5 10 ⁻²⁴ cm ³
Monoisotopic Mass	= 194.13068 Da
Nominal Mass	= 194 Da
Average Mass	= 194.2701 Da
M+	= 194.130131 Da
M-	= 194.131228 Da
[M+H] ⁺	= 195.137956 Da
[M+H] ⁻	= 195.139053 Da
[M-H] ⁺	= 193.122306 Da
[M-H] ⁻	= 193.123403 Da

H¹NMR of decahydrobenzo[8]annulene-5,10-dione

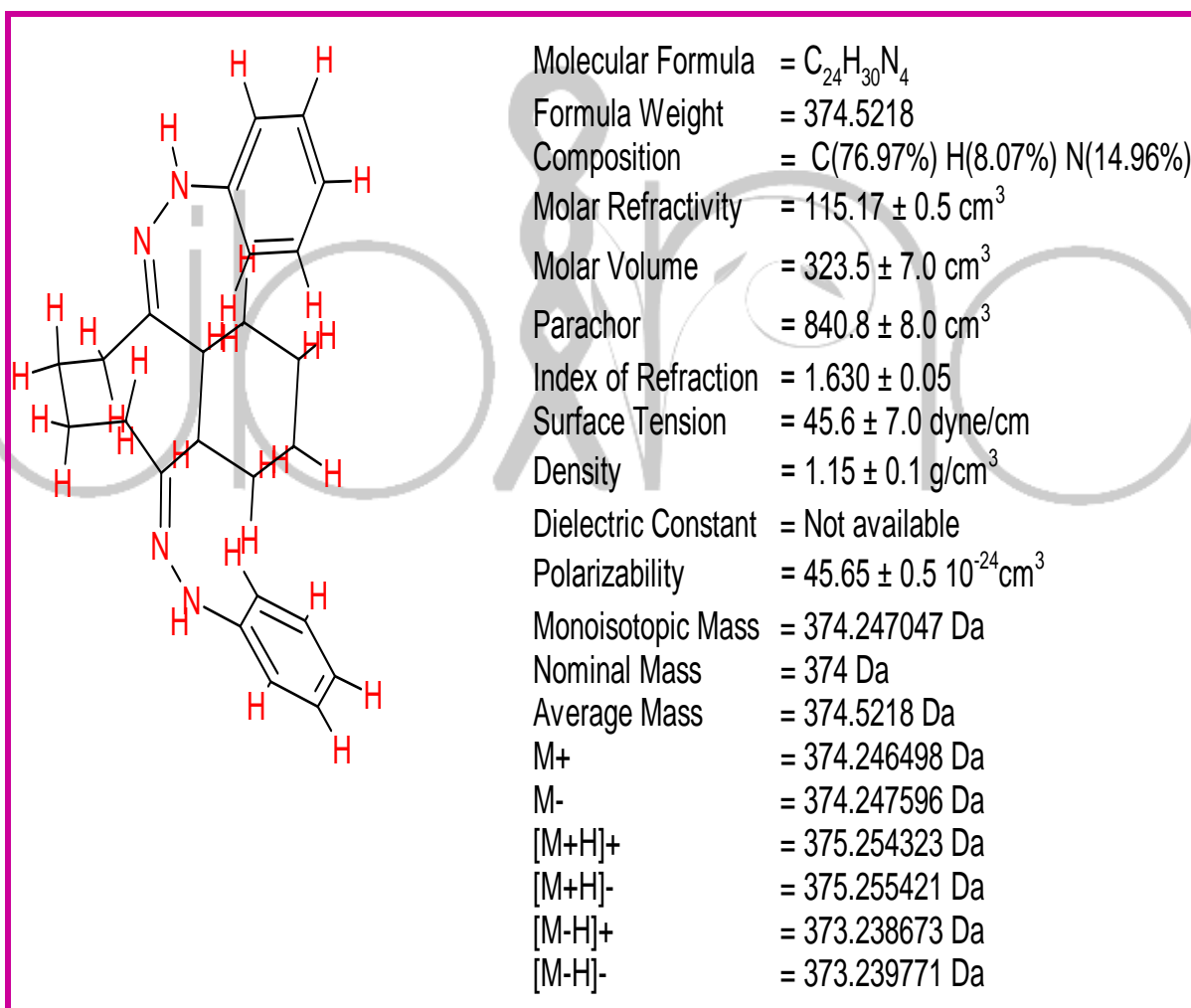


Scheme5: Synthesis of decahydrobenzo[8]annulene-5,10-diphenylhydrazone

20g of colourless phenylhydrazine hydrochloride and 25g of sodium acetate in 100ml water was taken and further added in a solution of 65g of decahydrobenzo[8]annulene-5,10-dione in a little ethanol. The mixture was shaken until a clear solution was obtained and a little more ethanol was added. The reaction mixture was heated on a water bath for 30 minutes and then it was cooled. Filter off the crystalline derivative and received 87% of decahydrobenzo[8]annulene-5,10-diphenylhydrazone.



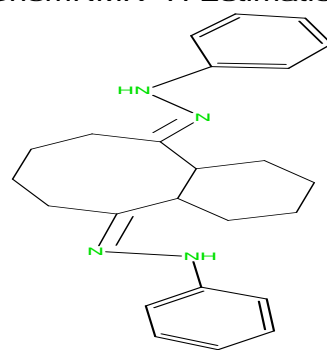
Physical properties of decahydrobenzo[8]annulene-5,10-diphenylhydrazone



¹H NMR of decahydrobenzo[8]annulene-5,10-diphenylhydrazone

ChemNMR ¹H Estimation

Estimation quality is indicated by color: **good**, **medium**, **rough**
 Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):

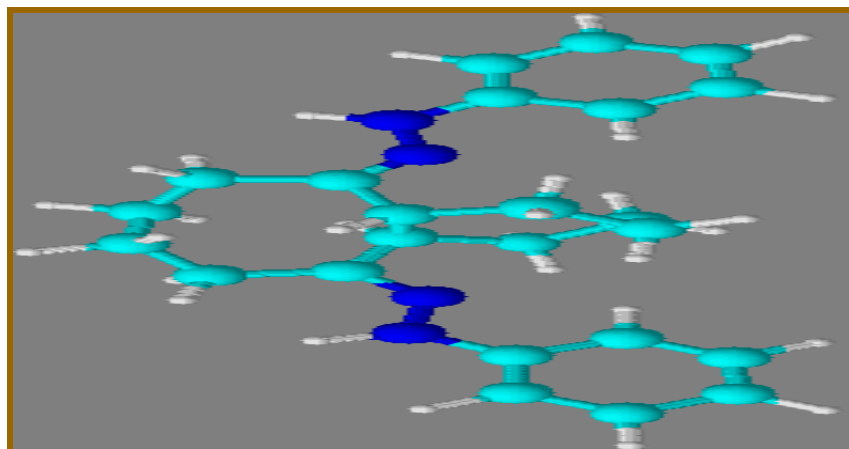


Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
NH	11.61	7.00	hydrazid
		3.40	1 -1.C ⁺ C ⁺ C ⁺ C ⁺ C ⁺ 1 from sec amine
		1.21	general corrections
NH	11.61	7.00	hydrazid
		3.40	1 -1.C ⁺ C ⁺ C ⁺ C ⁺ C ⁺ 1 from sec amine
		1.21	general corrections
CH	7.34	7.26	1-benzene
		0.10	1 -N=N=C
		-0.02	general corrections
CH	7.34	7.26	1-benzene
		0.10	1 -N=N=C
		-0.02	general corrections
CH	7.34	7.26	1-benzene
		0.10	1 -N=N=C
		-0.02	general corrections
CH	7.34	7.26	1-benzene
		0.10	1 -N=N=C
		-0.02	general corrections
CH	7.34	7.26	1-benzene
		0.30	1 -N=N=C
		-0.22	general corrections
CH	7.34	7.26	1-benzene
		0.30	1 -N=N=C
		-0.22	general corrections
CH	7.34	7.26	1-benzene
		0.30	1 -N=N=C
		-0.22	general corrections
CH	7.34	7.26	1-benzene
		0.30	1 -N=N=C
		-0.22	general corrections
CH	7.06	7.26	1-benzene
		-0.03	1 -N=N=C
		-0.17	general corrections
CH	7.06	7.26	1-benzene
		-0.03	1 -N=N=C
		-0.17	general corrections
CH	2.26	1.44	cyclohexane
		?	1 unknown alpha substituent(s) from methine
		?	1 unknown beta substituent(s) from methine
		0.82	general corrections
CH	2.26	1.44	cyclohexane
		?	1 unknown alpha substituent(s) from methine
		?	1 unknown beta substituent(s) from methine
		0.82	general corrections
CH2	1.74,1.485000	1.44	cyclohexane
		0.25	1 beta -C=N from methylene
		0.08	general corrections
CH2	1.74,1.485000	1.44	cyclohexane
		0.25	1 beta -C=N from methylene
		0.08	general corrections
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections
CH2	2.16,2.060000	1.37	methylene
		0.80	1 alpha -C=N
		-0.06	1 beta -C
CH2	2.16,2.060000	1.37	methylene
		0.80	1 alpha -C=N
		-0.06	1 beta -C
CH2	1.58,1.545000	1.37	methylene
		0.25	1 beta -C=N
		-0.06	1 beta -C
CH2	1.58,1.545000	1.37	methylene
		0.25	1 beta -C=N
		-0.06	1 beta -C

¹H NMR Coupling Constant Prediction

shift	atom index	coupling partner, constant and vector
11.61	14	
11.61	22	
7.34	16	
	17	7.5 H-C ⁺ C-H
	20	1.5 H-C ⁺ C ⁺ C-H
	18	1.5 H-C ⁺ CH ⁺ C-H
7.34	24	
	25	7.5 H-C ⁺ C-H
	28	1.5 H-C ⁺ C-H
	26	1.5 H-C ⁺ CH ⁺ C-H
7.34	20	
	19	7.5 H-C ⁺ C-H
	16	1.5 H-C ⁺ C ⁺ C-H
	18	1.5 H-C ⁺ CH ⁺ C-H
7.34	28	
	27	7.5 H-C ⁺ C-H
	24	1.5 H-C ⁺ C ⁺ C-H
	26	1.5 H-C ⁺ CH ⁺ C-H
7.34	19	
	20	7.5 H-C ⁺ C-H
	18	7.5 H-C ⁺ C-H
	17	1.5 H-C ⁺ CH ⁺ C-H
7.34	27	
	28	7.5 H-C ⁺ C-H
	26	7.5 H-C ⁺ C-H
	25	1.5 H-C ⁺ CH ⁺ C-H
7.34	17	
	16	7.5 H-C ⁺ C-H
	18	7.5 H-C ⁺ C-H
	19	1.5 H-C ⁺ CH ⁺ C-H
7.34	25	
	24	7.5 H-C ⁺ C-H
	26	7.5 H-C ⁺ C-H
	27	1.5 H-C ⁺ CH ⁺ C-H
7.06	18	
	19	7.5 H-C ⁺ C-H
	17	7.5 H-C ⁺ C-H
	20	1.5 H-C ⁺ CH ⁺ C-H
	26	1.5 H-C ⁺ CH ⁺ C-H
	16	1.5 H-C ⁺ CH ⁺ C-H
7.06	26	
	27	7.5 H-C ⁺ C-H
	25	7.5 H-C ⁺ C-H
	28	1.5 H-C ⁺ CH ⁺ C-H
	24	1.5 H-C ⁺ CH ⁺ C-H
2.26	7	
	8	7.0 H-C-C-H
	11	7.0 H-C-CH-H
2.26	8	
	7	7.0 H-C-C-H
	12	7.0 H-C-CH-H
1.61	11 diastereotopic	-12.4 H-C-H H-C-H
	7	7.0 H-CH-C-H
	9	7.1 H-CH-CH-H
1.61	12 diastereotopic	-12.4 H-C-H H-C-H
	8	7.0 H-CH-C-H
	10	7.1 H-CH-CH-H
1.48	9 diastereotopic	-12.4 H-C-H H-C-H
	11	7.1 H-CH-C-H
	10	7.1 H-CH-CH-H
1.48	10 diastereotopic	-12.4 H-C-H H-C-H
	12	7.1 H-CH-C-H
	9	7.1 H-CH-CH-H
2.11	2 diastereotopic	-12.4 H-C-H H-C-H
	1	7.1 H-CH-C-H
2.11	4 diastereotopic	-12.4 H-C-H H-C-H
	3	7.1 H-CH-C-H
1.56	1 diastereotopic	-12.4 H-C-H H-C-H
	2	7.1 H-CH-C-H
	3	7.1 H-CH-CH-H
1.56	3 diastereotopic	-12.4 H-C-H H-C-H
	4	7.1 H-CH-C-H
	1	7.1 H-CH-CH-H

XRD of decahydrobenzo[8]annulene-5,10-diphenylhydrazone



Results and Dissuasion

Automobile industries use epoxy-coated stainless steel body of transport vehicles. It comes in contact of H₂O, O₂(moist), CO₂ and SO₂ environment and weather change to produce chemical and electrochemical reaction which produce disintegration into materials and change their physical, chemical and mechanical properties. People expense bulk money for repairing and mentainance works. To control such types of corrosive problems, nanocoating and filler technique can be applied. For this work decahydrobenzo[8]annulene-5,10-diphenylhydrazone was used as nanocoating whereas AlN as filler. Corrosion protection phenomena were studied at 278⁰K, 283⁰K, 288⁰K, 293⁰K and 298⁰K temperature and time fixed 24, 48, 72, 96 and 120 hours.

Epoxy-coated stainless steel was exposed in above mentioned environments and temperatures and their corrosion rate was determined without and with coating of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN filler. The corrosion rate of metal was calculated in each case by equation $K=13.56 W/A D t$ and its values were recorded in table1. These nanocoating and filler compounds reduced the corrosion rate of metal, it was clearly noticed in figure1 plotted between K(mmpy) versus t(hours).

Table1 Corrosion rate of epoxy-coated stainless steel by nanocoating of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN filler at different temperatures and times used as nanocoating and filler compounds in H₂O, O₂(moist), CO₂ and SO₂ environment and weather change

NC	Temp(⁰ K)	278 ⁰ K	283 ⁰ K	288 ⁰ K	293 ⁰ K	298 ⁰ K	C(mM)
	Times (hrs.)	24	48	72	96	120	

NC(0)	K _o	425	628	738	977	1021	00
	logK _o	2.628	2.797	2.868	2.989	3.001	
NC(3)	K	177	89	58	45	32	50
	logK	2.247	1.949	1.763	1.653	1.505	
	log(K/T)	1.692	1.401	1.223	1.120	0.980	
	θ	0.58	0.85	0.92	0.95	0.97	
	log(θ/1-θ)	0.146	0.781	1.069	1.347	1.489	
	%CE	58	85	92	95	97	
NC(AIN)	K	129	65	44	35	26	20
	logK	2.110	1.812	1.643	1.544	1.414	
	log(K/T)	1.555	1.265	1.103	1.011	0.889	
	θ	0.69	0.89	0.94	0.96	0.98	
	log(θ/1-θ)	0.361	0.937	1.197	1.429	1.582	
	%CE	69	89	94	96	98	

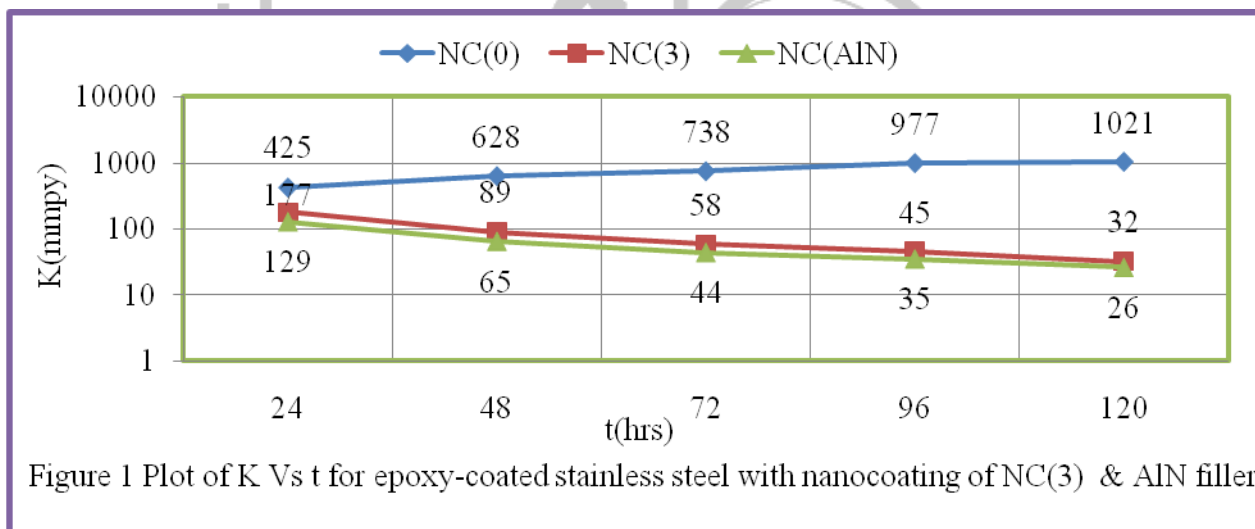


Figure 1 Plot of K Vs t for epoxy-coated stainless steel with nanocoating of NC(3) & AlN filler

The corrosion rate of epoxy-coated stainless steel studied at different temperatures with nanocoating of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN filler and their values recorded in table1. Graph plotted between logK versus 1/T in figure2 indicated that corrosion rate increased without coating but their values decreased with nanocoating of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN filler in H₂O, O₂(moist), CO₂ and SO₂ environment.

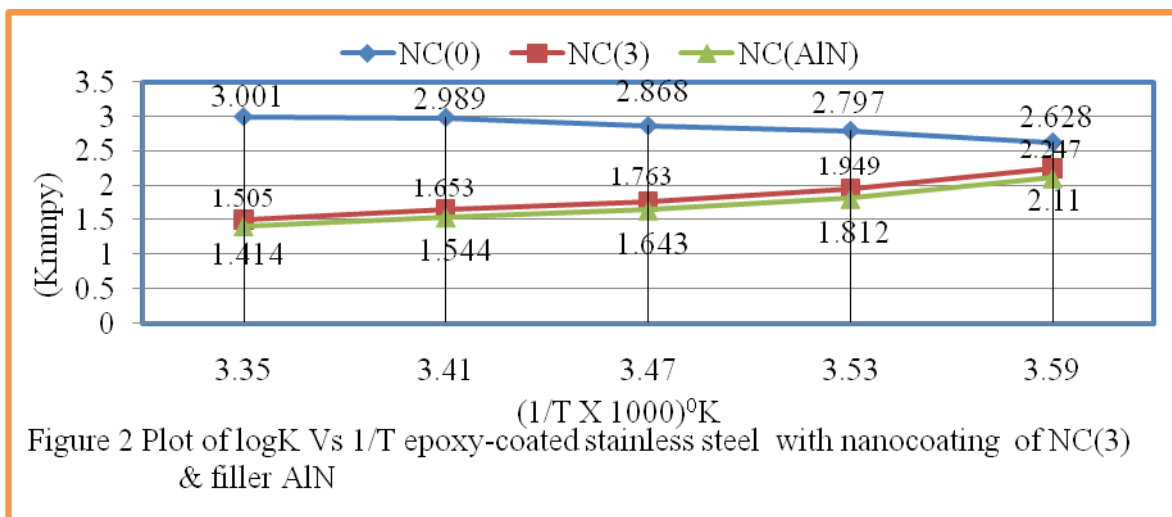
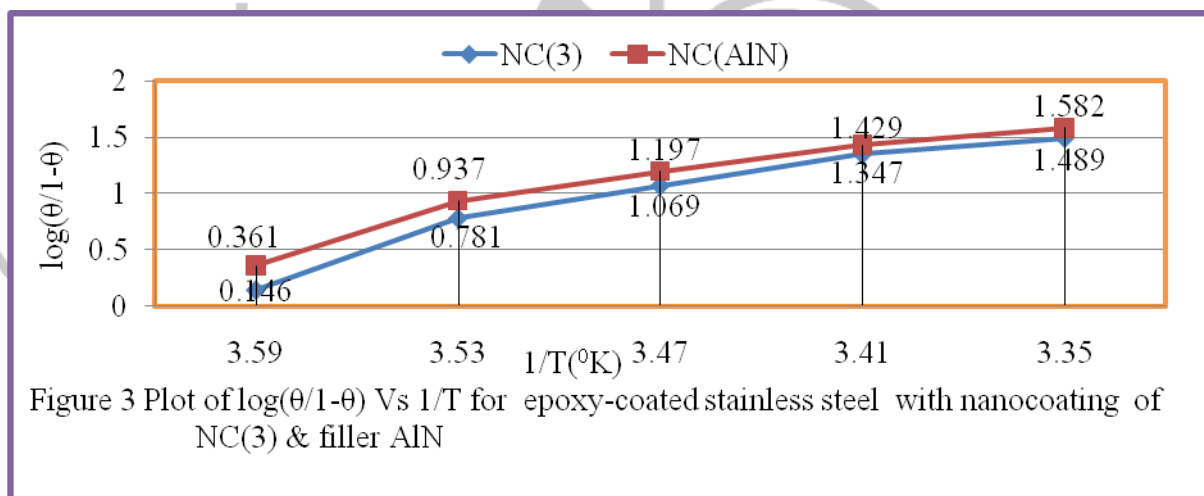


Figure3 plotted between $\log(\theta/1-\theta)$ versus $1/T$ for nanocoating of decahydrobenzo[8]annulene-5,10-diphenylhyrazone and AlN filler and their values were written in table1. The results of these compounds indicated that nanocoating and filler compounds produced adsorption effect on the surface of base material. The filler compound enhanced stability of nanocoating of decahydrobenzo[8]annulene-5,10-diphenylhyrazone. They formed stable coating barrier which provided protection of material in corrosive medium.



Surface coverage area occupied by decahydrobenzo[8]annulene-5,10-diphenylhyrazone and AlN filler were calculated by equation $\theta = (1-K/K_0)$ and their values were mentioned in table1. Figure4 show plot between surface coverage area (θ) versus T ($^{\circ}K$) which indicated that surface accommodation capacity increased as temperature rising from 278 to 298 $^{\circ}K$ with nanocoating and filler compounds.

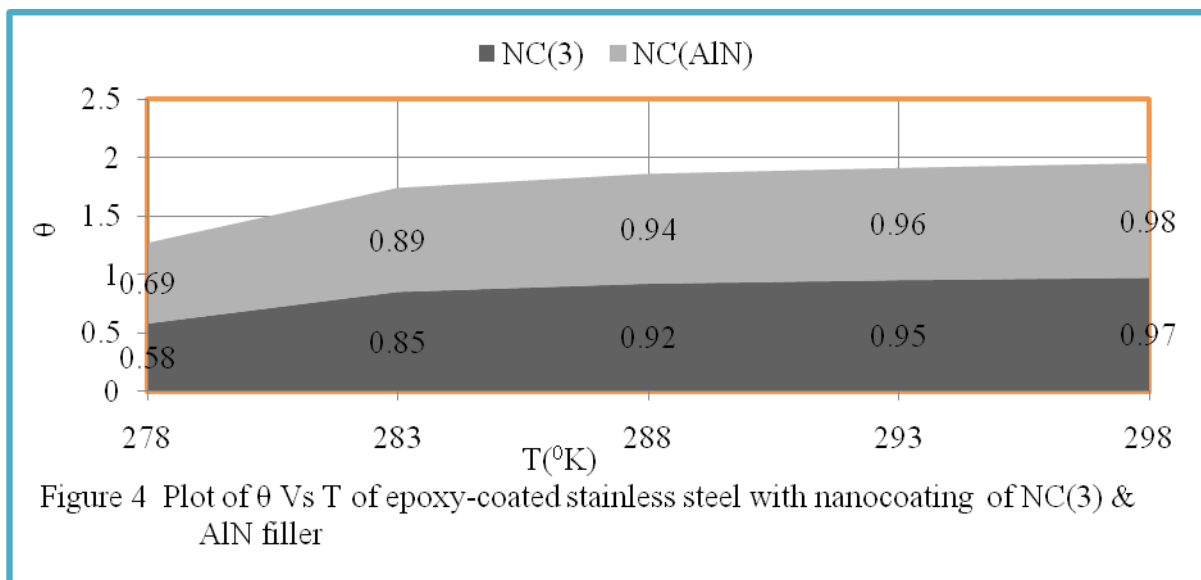


Figure 4 Plot of θ Vs T of epoxy-coated stainless steel with nanocoating of NC(3) & AlN filler

Percentage coating efficiencies produced by nanocoating decahydrobenzo[8]annulene-5,10-diphenylhyrazone and AlN filler were determined by equation $\%CE = (1-K/K_0) \times 100$ and their values are recorded in table1. Percentage coating efficiency versus temperatures plotted in figure5 indicates that coating efficiency increased with nanocoating and filler compounds. But filler compound enhanced more coating efficiency with respect of nanocoating materials. Table1 and figure5 confirmed that nanocoating and filler compounds produced good inhibition properties in H₂O, O₂ (moist), CO₂ and SO₂ environment.

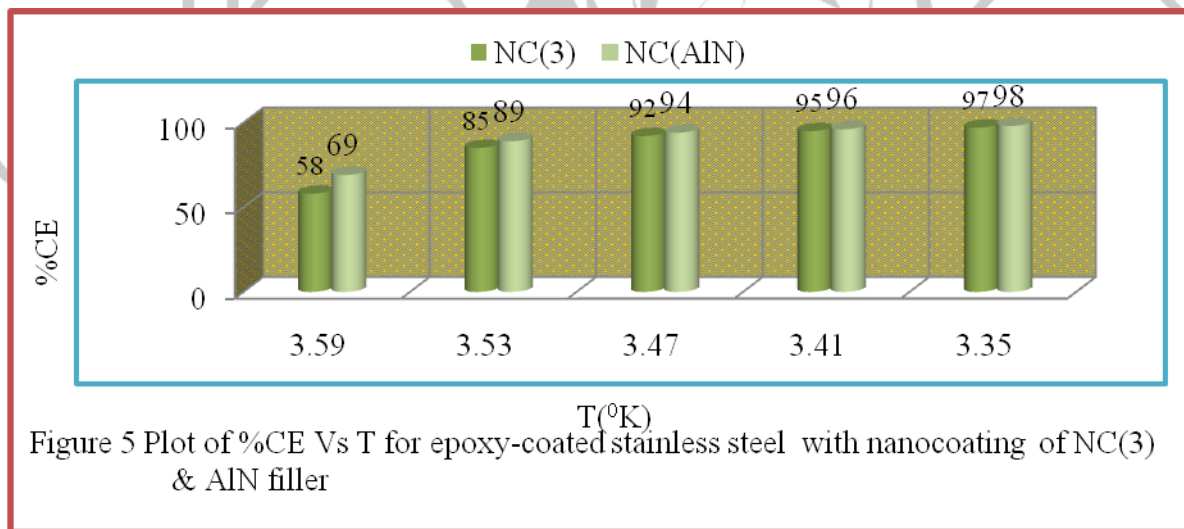


Figure 5 Plot of %CE Vs T for epoxy-coated stainless steel with nanocoating of NC(3) & AlN filler

Activation energy of decahydrobenzo[8]annulene-5,10-diphenylhyrazone and AlN were calculated by Arrhenius equation $d/dT(\ln K) = A e^{-E_a/RT}$ and figure2 and their results were written in table2. Figure2 is a straight line for Arrhenius plot between $\log K$ versus $1/T$. The

results of table2 and figure2 indicate that without coating activation energy increased but its values reduced with nanocoating and filler compounds. These results show that nanocoating and filler compounds formed chemical bond on the surface of base material.

Heat of adsorption produced by decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN was calculated by equation $\log(\theta/1-\theta) = \log(AC) - (q/2.303RT)$ and figure 3 plotted between $\log(\theta/1-\theta)$ versus $1/T$ heat of adsorption found to be negative sign which indicated coating and filler materials adsorbed on the surface of epoxy-coated stainless steel by chemical bonding.

Free energy of nanocoating and filler compounds were determined by equation $-\Delta G = -2.303\log RT$ and their values are given in table 2. Both compounds gave negative values of free energy. This sign confirm that nanocoating is an exothermic process and their values were decreased as temperatures increased. Free energy both compounds were shown they attached with material by chemical bonding. Both compounds formed complex barrier which stopped osmosis or diffusion.

Enthalpy and entropy of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN were calculated by transition state equation $K =$

$R T / N h \log (\Delta S^\# / R) \times \log (-\Delta H^\# / R T)$ and figure 6 and their values were expressed in table 2. Both values found to be negative which indicated that nanocoating was an exothermic process which generated chemical bonding with material. The entropy of values nanocoating and filler compounds were shown that they accommodated on the surface of base material in ordered manners. It observed that enthalpy and entropy of nanocoating and filler compounds were decreased as temperature raising from 278 to 298°K so the coating barrier developed by these materials were more stable in high temperature and corrosive medium. Entropy of AlN indicated that filler compounds occupied in matrix of decahydrobenzo[8]annulene-5,10-diphenylhydrazone. On the basis of above mentioned thermal results it is found that used nanocoating and filler compounds were generated chemical bonding on the surface of epoxy-coated stainless steel.

Table 2 Thermal parameters of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN on nanocoating on the surface of epoxy-coated stainless steel

Thermal parameters	278 ⁰ K	283 ⁰ K	288 ⁰ K	293 ⁰ K	298 ⁰ K
NC(0)Ea	180	191	192	197	195
NC(3) Ea	156	134	110	109	101
NC(3)q	-5.97	-48.62	-68.35	-83.89	-92.06
NC(3)ΔG	-261	-236	-221	-209	-197
NC(3)ΔH	-118	-97	-84	-75	-66
NC(3)ΔS	-105	-94	-88	-83	-78
θ NC(3)	0.58	0.85	0.92	0.95	0.97
NC(AlN)Ea	148	127	113	103	95
NC(AlN)q	-15.86	-57.69	-74.87	-90.85	-96.32
NC(AlN)ΔG	-254	-230	-214	-202	-193

NC(AIN) Δ H	-112	-92	-77	-68	-62
NC(AIN) Δ S	-102	-91	-84	-79	-76
θ NC(AIN)	0.69	0.89	0.94	0.96	0.98

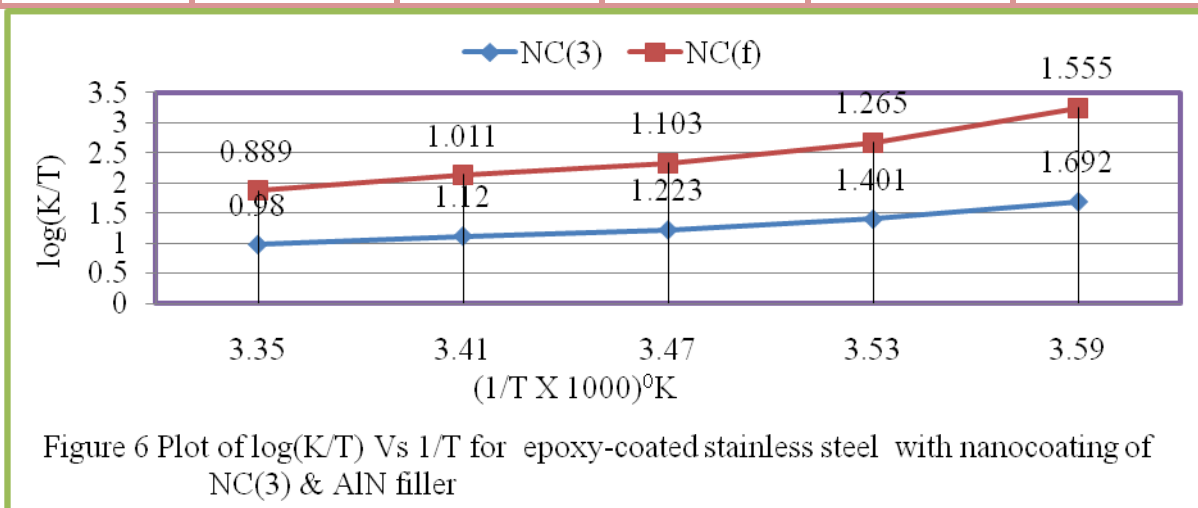


Figure 6 Plot of log(K/T) Vs 1/T for epoxy-coated stainless steel with nanocoating of NC(3) & AlN filler

It was observed that activation energy, heat of adsorption, free energy, enthalpy and entropy of decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN were reduced as temperatures increased. These results also confirmed that surface coverage area (θ) enhanced as thermal parameters and temperatures increased as depicted in figure7.

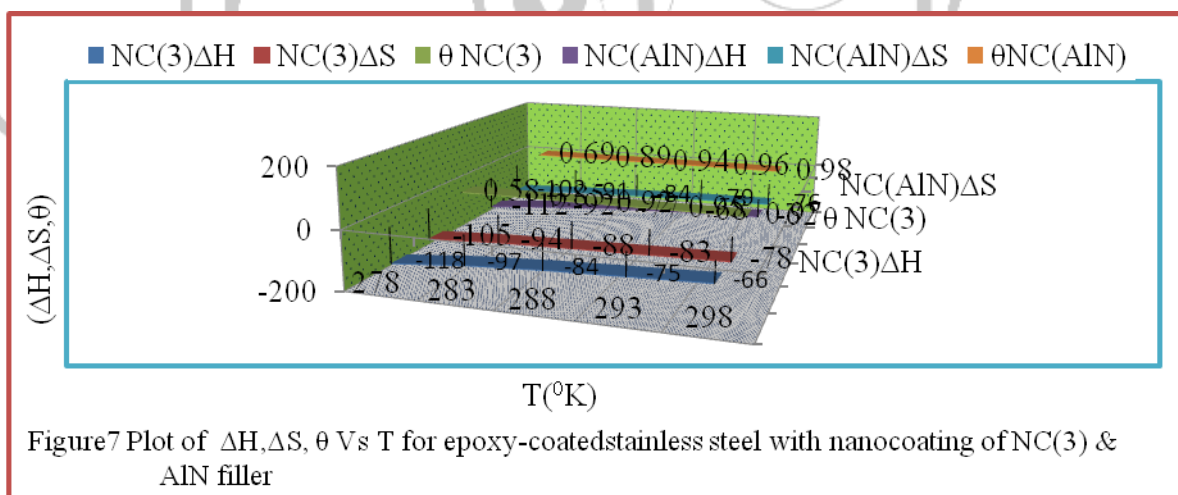


Figure7 Plot of Δ H, Δ S, θ Vs T for epoxy-coated stainless steel with nanocoating of NC(3) & AlN filler

Potentiostat results for decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN were recorded by equation $\Delta E/\Delta I = \beta_a \beta_c / 2.303 I_{corr} (\beta_a + \beta_c)$ and their results were written in table3. Figure8 plotted between ΔE (electrode potential) versus I (corrosion current density) is known as Tafel graph.

The corrosion rate of epoxy-coated stainless steel were calculated by equation $C. R (mmpy) = 0.1288 I_{corr} (mA /cm^2) \times Eq .Wt (g) / \rho (g/cm^3)$. In the Tafel plot of figure8 it was noticed that without coating corrosion potential and corrosion current density values were high but nanocoating

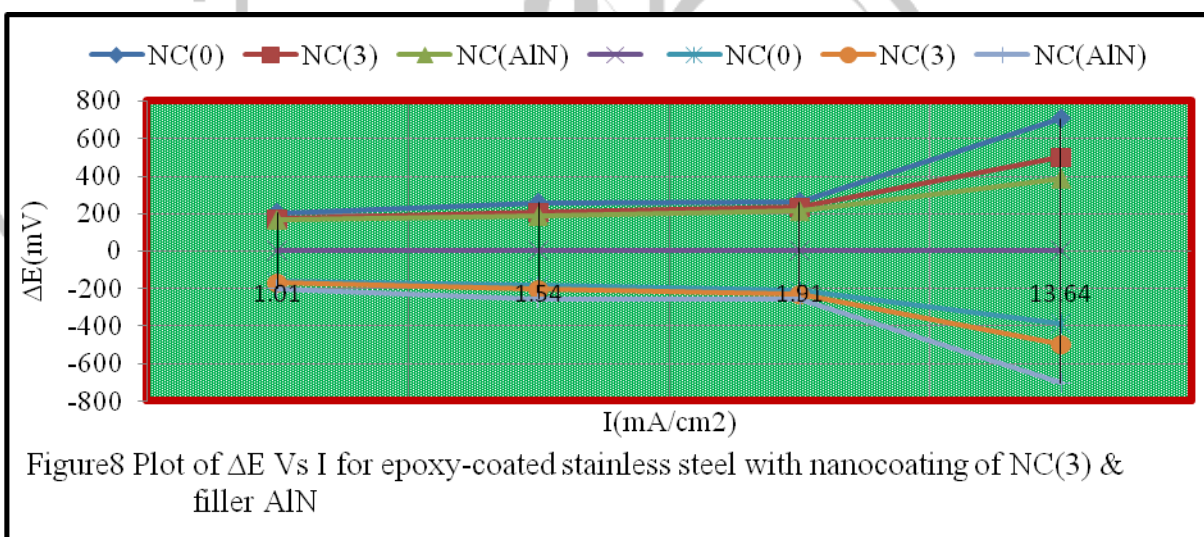
and filler compounds reduced these values.

It was also observed that without coating anodic polarization enhanced but after nanocoating and filler cathodic

polarization raised and anodic polarization reduced. These compounds minimized corrosion rate and enhanced surface coverage area and coating efficiency.

Table3 Potentiostat polarization results of nanocoating decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN filler for epoxy-coated stainless steel

NC	ΔE (mV)	ΔI	β_a	β_c	I_{corr} (mA/cm ²)	K (mmpy)	θ	%CE	C(mM)
NC(0)	-704	187	295	197	13.64	417	0	0	0.0
NC(3)	-260	28	49	300	1.97	60	0.86	86	50
NC(AlN)	-255	25	40	310	1.51	46	0.89	89	20



Conclusion

The results were obtained by weight loss, potentiostat and thermal parameters were shown that nanocoating decahydrobenzo[8]annulene-5,10-diphenylhydrazone and AlN filler were formed a composite protective barrier. It is stable in corrosive medium, different temperatures and weathers. It works as

repeller for particulates materials. The nanocoating compound adhered on the surface of epoxy-coated stainless steel by chemical bonding. The filler compound nanoparticles enter into porosities of nanocoating material and enhance internal binding force. They can increase surface coverage area and coating efficiency. It observed that nanocoating

decahydrobenzo[8]annulene-5,10-diphenylhydrazone low doses covered more surface area. The values of activation energy, heat of adsorption, free energy, enthalpy and entropy indicate that nanocoating is an exothermic reaction.

Acknowledgement

Author thanks the founding agency of UGC, New Delhi for the providing financial support for this work. Author expresses his regards the HOD of IIT-Dhanbad and Ranchi University, Ranching for providing laboratory facilities.

REFERENCES

Bhadra S, Singh N K and Khashtgir D (2011), Polyaniline based anticorrosive and anti-molding coating, Journal of Chemical Engineering and Materials Science Vol.2(1) 1-11.

Szabo T, Molnar-Nagy L, and Telegdi J (2011), Self-healing microcapsules and slow release microspheres in paints, Progress in Organic Coatings, 72, 52-57.

Wen N T, Lin C S, Bai C Y, and Ger M D (2008) Structures and characteristics of Cr (III) based conversion coatings on electrogalvanized steels, Surf. Coat. Technol, 203, 317.

Boerio F J, Shah P (2005), Adhesion of injection molded PVC to steel substrates, J of Adhesion 81(6) 645-675.

Deveci H, Ahmetti G and Ersoz M, (2012), Modified styrenes: Corrosion physico-mechanical and thermal properties evaluation, Prog. Org. Coat. 73 1-7.

Genzer J (2005), Templating Surfaces with Gradient Assemblies, J of Adhesion 81 417-435.

Leon-Silva U, Nicho M E (2010), Poly(3-octylthiophene) and polystyrene blends thermally treated as coating for corrosion protection of stainless steel 304, J. Solid State Electrochem, 14 1487-1497.

Baier R E (2006) Surface behaviour of biomaterials: Surface for biocompatibility, J. Mater. Sci. Mater. Med. 17 1057-1062.

Rao BVA, Iqbal M Y and Sreehar B (2010), Electrochemical and surface analytical studies of the self assembled monolayer of 5-methoxy-2-(octadecylthiol) benzimidazole in corrosion protection of copper, Electrochim, Acta, 55 620-631.

Liu X Y, Ma H Y and Hou M Z (2009), Self-assembled monolayers of stearic imidazoline on copper electrodes detected using electro chemical measurement, XPS, molecular simulation and FTIR, Chinese Sci. Bull. 54 374-381.

Liao Q Q, Yue Z W and Zhou Q (2009), Corrosion inhibition effect of self-assembled monolayers of ammonium pyrrolidine dithiocarbamate on copper, Acta Phys. Chin. Sin. 25 1655-1661.

Zhang D Q, He X M and Kim G S (2009), Arginine self-assembled monolayers against copper corrosion and synergistic effect of iodide ion, J. Appl. Electrochem 39 1193-1198.

Sahoo R R and Biswas S K (2009), Frictional response of fatty acids on steel, J. Colloid Interf. Sci. 333 707-718.

Raman R and Gawalt E S (2007), Selfassembled monolayers of alkanolic acid on the native oxide surface of SS316L by solution deposition, Langmuir, 23 2284-2288.

Li D G, Chen S H and Zhao S Y (2006), The corrosion Inhibition of the self-assembled Au and Ag nanoparticles films on the surface of copper, Colloid. Surface. A 273 16-23.

Cristiani P, Perboni G and Debenedetti A (2008), Effect of chlorination on the corrosion of Cu|Ni 70|30 condenser tubing, Electrochim. Acta 54 100-107.

Cristiani P (2005), Solutions fouling in power station condensers, Appl. Therm. Eng. 25 2630-2640.

Videla H and L K Herrera (2009), Understanding microbial inhibition of corrosion, Electrochem Acta, 39 229-234.

Bibber J W (2009), Chromium free conversion coating for zinc and its alloys, Journal of Applied Surface Finishing, Vol. 2(4) 273-275.

Ghareba G S and Omanovic S (2010), Interaction of 12-aminododecanoic acid with a carbon steel surface: Towards the development of 'green' corrosion inhibitors, Corrosion Sci. 52 2104-2113.

