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Presentation of a New Organic Inhibitor as Temporary Protection of Steel Corrosion

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Abstract

The use of temporary corrosion protective is one of the best ways against the corrosion of steels that can be easily removed from the metal surface after treatment. In this research, *N,N'*-(3,3',4,4'-Benzophenonetetracarboxylic)-3,3',4,4'-diimido-bis-(aminonaphthalene-4-sulfonicacid) (BTDIAS) was synthesized as a new organic corrosion inhibitor. This sulfonated compound added to the base oil with a concentration of (2-100)ppm. The efficiency of sulfonated compound as organic corrosion inhibitor is evaluated by weight loss method and surface photography. The solutions of sulfonated compound(BTDIAS) (2-100)ppm in base oil were used on the low carbon steel surfaces, as a temporary corrosion protector. The samples were tested in a humidity chamber based on standard method (ASTM D-2247). The samples containing (5-30) ppm sulfonated compound showed the best corrosion resistance.

Keywords: Temporary corrosion protective, Sulfonated compound, corrosion inhibitor, Base oil, Low carbon steel.

1. Introduction

Metals corrosion is an important and inevitable problem responsible for a variety of damages in industry. Corrosionis a permanent problem depends on the type of the metal and environmental conditions, which cannot be removed completely. So, corrosion prevention become necessary and essential [1-4]. There are several different methods for the prevention of metal surface corrosion of which the use of corrosion inhibitors is the best method to protect metals against corrosion [5-12]. With regard to the fact that many of the pieces, tools, and metallic products are required to be kept for a long time in a warehouse, some materials named oil-based temporary protective coatings are usually used along with corrosion inhibiting materials to prevent corrosion [13,14]. The corrosion inhibitors are usually effective in low concentrations and reduce the metal reaction with the environment [15-17]. They are generally divided into three main groups of inorganic, organic, mixed material inhibitors[7].The organic inhibitors are generally compound containing heteroatomswith high electron density and high basic properties such as O, N, S, and P [18-24]which adsorbed by the metal producing disturbances in the two anodic and cathodic reactions leading to corrosion control[25,26]. A variety of studies have examined the relation between the inhibitor molecular structure and its efficiency [27,28]. The most effective organic inhibitors are compounds whose molecular structure consists of aromatic rings, π bonds, factorial groups, space factors, and electron density in electron donor atoms [29-31]. Many efforts have been made over years

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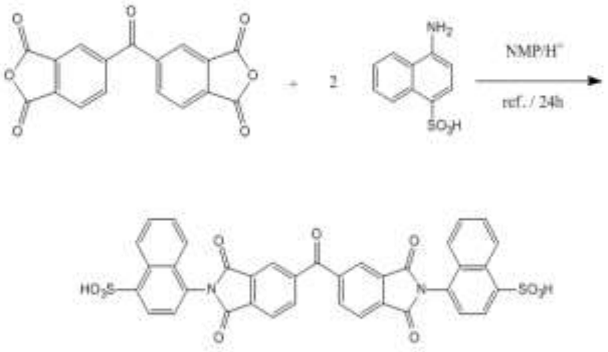
to find corrosion inhibitors of organic origin in varied corrosive environments [32,33] including compounds like 2-Amino-3-mercapto-propionic acid,5-(3,4,5-Trimethoxybenzyl) pyrimidine-2,4-diamine [34], 3-(4-Oxo-3,4-Dihydro-quinazolin-2-yl)-acrylic acid [35], 5-Phenyl-1,3,5,6,8-pentahydro-pyrimido[4,5] pyrimidine-2,4,7-trione[36], (2-Oxo-2-phenothiazine-10-yl-ethylamino)-acetic acid [37]. There aretwo steps related to the action of corrosion inhibitors including transfer of the inhibitor to the metal surface and adsorption of the inhibitor by the metal surface to increase or decrease thecathodic or anodic reactions and reduction of the penetration speed of the reactor to the metal surface and formation of a protective film on the metal surface to reduce corrosion [37-39]. At the time of metal contact with the inhibitor, the electrons are transferred from the inhibitor heteroatom to the metal surface affecting the chemical adsorption of the inhibitor molecule to the metal replacing water molecule [40-45].On the other hand, sulfonated compounds are among the bestcorrosion inhibitor materials that the addition of a negligible percentage of them to the base oil in the temporary protective coating formulation is applicable. Therefore, in this paper anew organic compound including imido sulfonicacid groups as inhibitor was synthesizedand used as a temporary corrosion protective coating to coat a simple carbon steel surface to evaluate its corrosion inhibitory effects in a 100% moist environment.

2.Experimental

2.1. Materials

The chemical composition of low carbon steel specimens carried out by elemental analysis quantumetry: C = 0.053 wt%; Si = 0.013 wt%; Mn = 0.192 wt%, P = 0.010wt%, S = 0.006 wt%;Cr = 0.006 wt%; Ni = 0.270wt%; Al = 0/054 wt%, Co = 0/008 wt%; Cu = 0/011 wt%; V = 0/002 wt%; Nb = 0/003 wt%; Ca = 0/001 wt%; As = 0/006 wt%; MO < 0.002 wt%; Zr< 0.002 wt%; W < 0.010wt%; Ti< 0.001 wt%; B < 0.001 wt%; Bi < 0.002 wt%; Sn< 0.001 wt%; Pb< 0.003 wt% and the remaining left out portion is iron, specimenswhich were used to determined their weight loss is (1 cm× 2 cm).All low carbon steel was mechanically polished using sand papers with 200-1200 grade to remove surface contaminants. They were degreased in absolute ethanol, dried in acetone and stored in moisture-free desiccators prior to use. *N,N*'-(3,3',4,4'-Benzophenone tetracarboxylic)-3,3',4,4'-diimido-bis-(aminonaphthalene-4-sulfonic acid) (BTDIAS) was synthesized by dissolving 3,3',4,4'-Benzophenone-tetra carboxylic dianhydride(0.16 g, 0.50 mmol), 1-aminonaphthalene-4-sulfonic acid(0.23 g, 1.00 mmol) and 5 ml of *N*-Methyl-2-Pyrrolidone (NMP)in presence of 0.2 mlof acetic acid were placed in a 25ml two-neck round-bottom flask and stirred for 24 hours at 120℃. The product was poured in to 50 ml of distilled water and then the solvent was evaporated in vacuum. The obtained sediment was filtered and washed with water and dried toobtained BTDISA in 88% yield and a decomposing temperature of 320 ℃ (Scheme.1). Pureorganic compounds are not usually impressive adequately for corrosion control. Therefore for prepare the temporary protective solutions, the BTDIAS (as anticorrosion factor) was added to the base oil(Table 1). Then, thehomogenous mixture were used to coat the steel surface to placed in moist chamber according to ASTM D-2247 standard.Finallysamples were removed from the chamber washed according to the standard method ASTM G_1-03[46] and were studied to characterize the efficiency of protector.



Scheme. 1. Synthesis of BTDIAS compound.

Table 1. Physical properties of mineral base oils.

Test Number	Test Name	Results	Reference standard
1	Appearance	Clear	Visual
2	Flash point, ◦C	218	ASTM D92
3	Pour point, ◦C	-6/86	ASTM D97
4	Cloud point, ◦C	0/09	ASTM D97
5	Viscosity at 40 ◦C, $mm^2 s^{-1}$	108/4	ASTM D445
6	Water and sediment, vol.%	0/02	ASTM D2273
7	Foaming characteristic, ml	0	ASTM D892
8	Viscosity apparent, mpa s^{-1}	-	ASTM D2602

2.2. Weight loss study

Due to its simplicity and high validity, the non-electrochemical weight reduction is considered as a useful method to determain the rate of corrosion and the efficiency and performance of corrosion inhibitor. The rate of corrosion in terms of mpy unit (mils / year) were determined based on (eq.1).

Mils/year (mpy)= 534W/AT.K (eq.1)

(1 mils = 1000 inch)

Where W is weight difference of the sample(mg); A is surface area($inch^2$); T is corrosive time (hr) and K is density coefficient (g/cm^3).

The protection equation (eq.2) is also used to study the performance of corrosion inhibitor, where the protection percentage shows effectiveness of the inhibitor coating in preventing corrosion.

$$\eta = \frac{W-Wo}{Wo} \times 100 \qquad (eq.2)$$

Where Wo is also the weight difference of the sample without coating before and after being placed in the moisture chamber and W is also the weight difference of the coated sample before and after being placed in the moisture chamber. The values related to protection percentage and rate of corrosion of the raw samples,base oil coated samples and inhibitor coated samplesare showed in Tables (2-5).

Table 2. Results of corrosion test of the raw sample (A) and the oil coated sample (B).

Samples code	Weight loss (mg)	Corrosion rate ($mg\ cm^{-2}h^{-1}$)	η (%)
After 180 hours			
A	9.8	8.937	0.00
B	2.2	8.025	66.15
After 260 hours			
A	14.1	10.287	0.00
B	4.5	8.207	50.00
After 300 hours			
A	21.7	15.83	0.00
B	7.1	8.633	45.80

***η*(%)**: ProtectionPercentage

Table 3. The results of corrosion tests for the formulated samples coated with an oil and inhibitor (SC_1-SC_7); completion time of the reaction is 180 hours.

Samples code	Inhibitor concentration (ppm)	Weight loss (mg)	Corrosion rate ($mg\ cm^{-2}\ h^{-1}$)	η (%)
SC_1	2	2.07	1.887	78.91
SC_2	5	1.67	1.522	82.99
SC_3	10	0.70	0.852	90.14
SC_4	20	0.20	0.731	90.91
SC_5	30	0.07	0.244	96.97
SC_6	50	1.13	1.380	84.04
SC_7	100	1.40	1.705	80.28

***η*(%)**: ProtectionPercentage

Table 4. The results of corrosion tests for the formulated samples coated with an oil and inhibitor (SD_1-SD_7); completion time of the reaction is 260 hours.

Samples code	Inhibitor concentration (ppm)	Weight loss (mg)	Corrosion rate (mg cm^{-2} h^{-1})	η (%)
SD_1	2	3.47	2.532	75.41
SD_2	5	1.77	1.613	81.97
SD_3	10	0.73	0.893	89.67
SD_4	20	0.33	0.609	92.59
SD_5	30	0.27	0.487	94.07
SD_6	50	1.27	1.542	82.16
SD_7	100	1.50	1.826	78.87

η**(%)**: ProtectionPercentage

Table 5. The results of corrosion tests for the formulated samples coated with an oil and inhibitor (SE_1-SE_7); completion time of the reaction is 300 hours.

Samples code	Inhibitor concentration (ppm)	Weight loss (mg)	Corrosion rate (mg cm^{-2} h^{-1})	η (%)
SE_1	2	3.73	2.727	73.52
SE_2	5	1.90	1.735	80.61
SE_3	10	0.53	0.974	88.15
SE_4	20	0.50	0.913	88.89
SE_5	30	0.13	0.487	93.94
SE_6	50	1.33	1.623	81.22
SE_7	100	2.23	2.039	77.21

η**(%)**: ProtectionPercentage

3. Results and discussion

3.1. Infrared spectroscopy

FT-IR spectrum of BTDIAS compound is presented in Figure (1). A strong and flat peak is observed in the region of 3193-3535 cm^{-1} related to SO_3H groups and the characteristic peaks of symmetric C=O stretching and asymmetric C=O stretching of the imide group were clearly visible at around 1722 and 1770 cm, respectively. The assignment of the stretching of the imidering was at 1367 cm^{-1}.

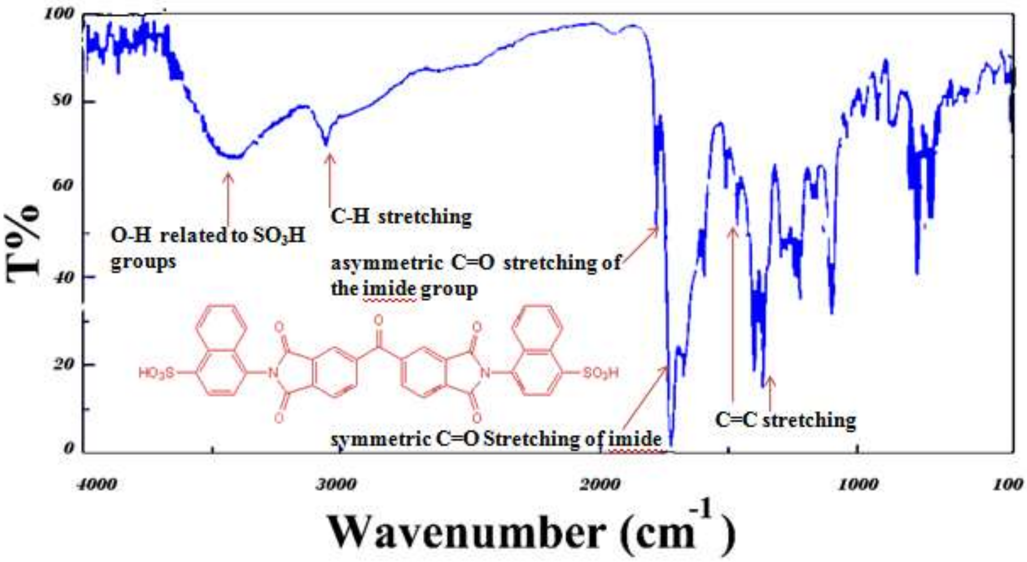


Fig. 1. FT-IR spectrum of BTDIAS.

3.2. Surface Analysis

The results of inhibitor performance werecompared with non-protectedsample, as shown in microscopic image of different samples, Figure.2

Figure (2b) clearly shows that the samples without coating are almost corroded completely due to their direct contact with corrosive environment.Figure (2c) shows that using of oil coating generate a barrier against moisture and oxygenand improved temporary protection and a reduction of corrosion was observed by using BTDIAS through replacing of water molecules of metal surface,Figures (2d, 2e, 2f).These Figuresshow that the surface protection dependsoninhibitor concentration. The optimized concentration is around 30 ppmwhich shows significantcorrosion protection.By increasing the inhibitor concentration due to the higher affinity of water absorption sample corrosion was increased.

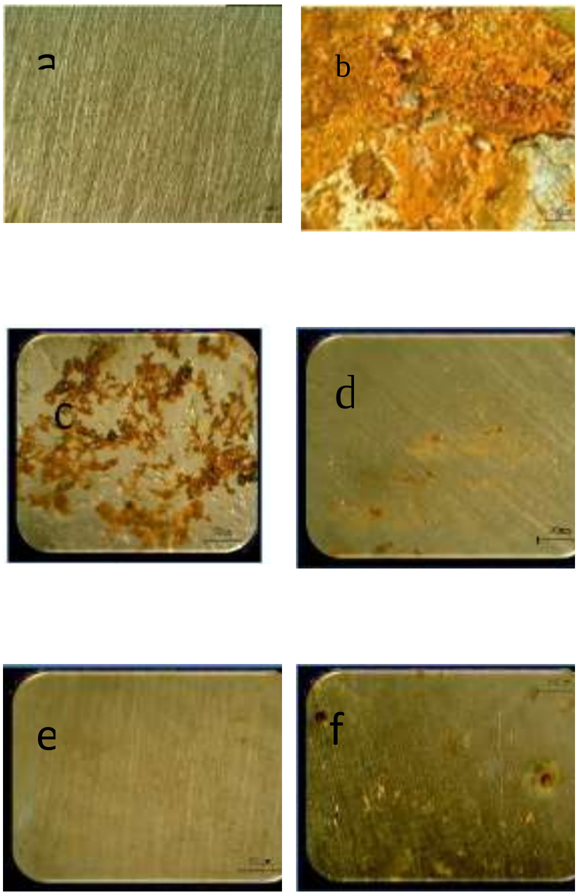


Fig. 2. Surface pictures of raw low carbon steel before corrosion (a), (b) the sample without coating after 300 hours, (c) the sample coated with oil after 300 hours, (d) The sample with 2 ppm inhibitor after 300 hours, (e) the sample with 30 ppm inhibitor

after 300 hours, (f) the sample with 100 ppm inhibitor after 300 hours.

The major performance of a corrosion inhibitor coating is to provide a barrier between the metal surface and the corrosive environment. Oils intensely reduce electrical conductivity over the surface. Although the oils contain hydrophobic long-chain alkyls, they are not able to replace water molecules entrapped between them and the metal surface and this is the reason that makes the inhibitors necessary for complete protection. It has been clearly specified that the adsorption process of the inhibitor over metal results from the presence of heteroatoms (oxygen, nitrogen, and sulfur), etcin its structure (Figure 3). According to Figures(2b, 2c, 4, 5) and Table (2), the samples with oil coatingreveale higher resistance compared to the sample without coating. Although these hydrophobic coatings prevent reaching oxygen to the metal surface, and they are not able to replace the metal surface water, therefore, the entrapped water molecules acceleratethe metal surface corrosion therefore the inhibitors used in coatings formulation to overcome the defect. The results(Tables (3-5), Figures (2d, 2e, 2f, 6)),show that the addition of small amount of the inhibitor to the base oil, significantly improved anticorrosion properties.Corrosion inhibitors usuallycreate chemical resistance against water penetration. Chemical bonds are form where the metal acts as an electron donor andthe power of chemical bond related with the metal structure, which depends to Van Der Val orbitals remaining on the metal surface and unoccupied orbitals. In fact, when anticorrosion compounds exist in humidity conditions, they develop a solubility power in the oily layer from their non-polar area. Moreover, these compounds have smallcontactangle with the metal surface and can be displacedunder water drops and create continuous film on the metal surface and repel water.

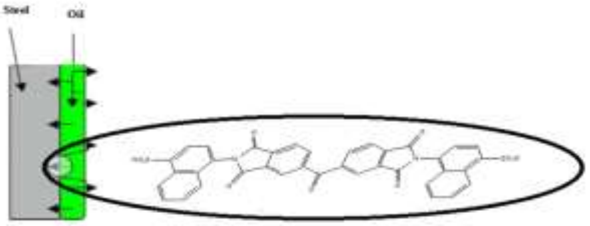


Fig. 3. Adsorption organic corrosion inhibitor (BTDIAS) and oil on the low carbon steel surface.

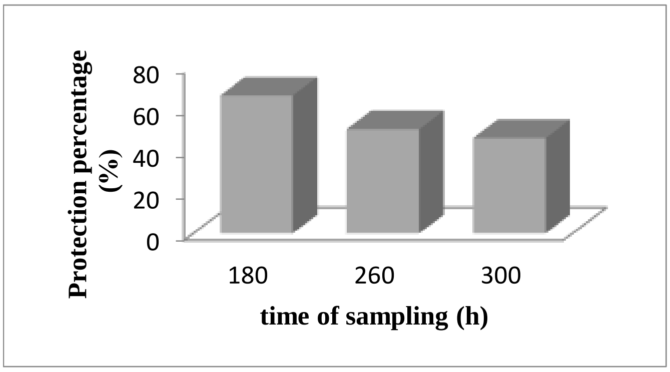


Fig. 4. Rate of oil coating protection in terms of time of sampling.

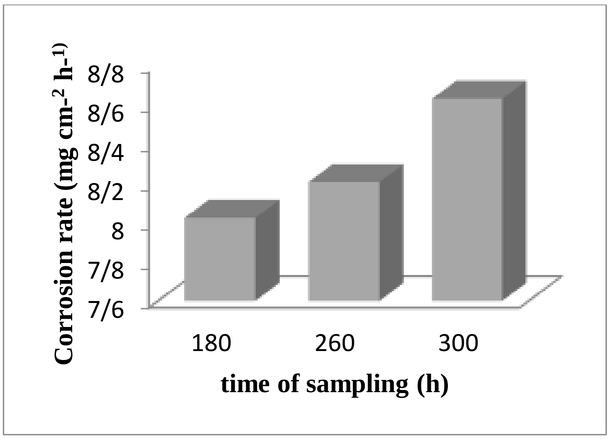


Fig. 5. Rate of oil coating corrosion in terms of time percentage of sampling.

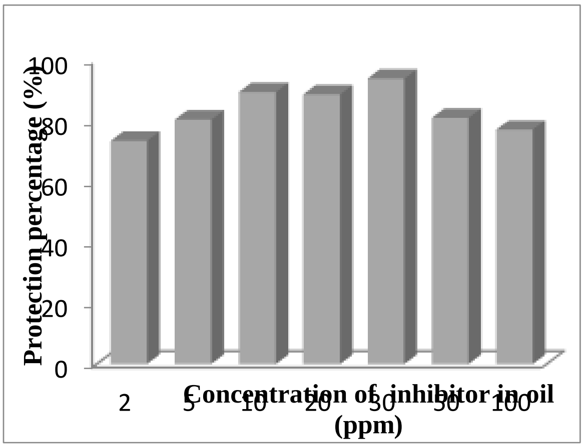


Fig. 6. Rate of protection in terms of percentage of the effective material in oil over 300 hours.

4. Conclusion

Herein, the BTDIAS as anacidic organic inhibitor containing different heteroatom was synthesized and added to the base oil in different concentration (2-100) ppm. To study the corrosion and protection of the metal surface according to ASTM D-2247, a chamber with a 100% humidity was used. Mass reduction of the sample and surface photography were used to study the corrosion inhibition property. The 30 ppm concentration as optimal concentration shows the best resistance and performance against corrosion. Higher concentrations show a reverse effect due to water absorption and polarization of the surface.

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