Paper No.
MCI44

CORCON
17-20 September 2017
Mumbai, India

ROLE OF TETRAMETHYLAMMONIUM IODIDE ON CONTROL OF MICROBIOLOGICALLY INFLUENCED CORROSION OF MILD STEEL USED IN OIL AND NATURAL GA INDUSTRIES

Jitendra Girase

Chemistry Research Laboratory,
Department Of Chemistry, R.J. College Of Arts, Science and Commerce,

ABSTRACT

Corrosion behaviour of mild steel was investigated by exposing mild steel coupons in Barr's medium inoculated with *Desulfovibrio desulfuricans*, sulphate reducing bacteria (SRB). Considerable loss in weight and deterioration of the microstructure of mild steel surface was observed during the investigations. Coupons were further exposed to culture media containing different concentrations of tetramethylammonium Iodide. The corrosion behavior of mild steel was measured by weight loss, corrosion potential and potentiodynamic polarization techniques. The surface analysis was performed by scanning electron microscopy (SEM). The corrosion current densities of both anodic and cathodic coefficients decreased in the presence of inhibitor, hence the inhibitor is of mixed type. The inhibitor exhibited its best performance at 500 ppm concentration. The inhibitor obeyed the Langmuir adsorption isotherm phenomenon since it is obtained as a straight line graph.

Keywords: SRB, Corrosion Potential, Mixed Type Inhibitor.

INTRODUCTION:

Metal in its natural state is in the form of ore and it is present in combination with other elements. To strip away these elements and produce pure metal, a large amount of energy is required. As the energy content of metals and alloys get higher, they become unstable and hence discharge the additional energy. The process by which the metal reverts to its lower energy state is termed corrosion [1]. Corrosion is the interaction between the metallic material and its environment leading to the deterioration of the metal [1]. Although assessment of the cost of corrosion is difficult, corrosion's annual cost worldwide is estimated to exceed U.S. $ 1.8 trillion, which translates to 3-4% of the gross domestic product of industrialized countries [1]. Therefore, there is a need to explore new strategies to prevent corrosion management techniques.

Microbiologically influenced corrosion is the deterioration of metals by corrosion processes that occur directly or indirectly as a result of metabolic activity of microorganisms [2]. The corrosion influenced by micro-organisms is called biocorrosion. The attachment of bacteria, release of metabolites and formation of biofilms change the electrochemical conditions at the metal/solution interface accelerating the corrosion process [3-5]. The major responsibility for biocorrosion is attributed to SRB, since there is H_2S release during its metabolism, a reactive, toxic and corrosive agent [6, 7]. The SRB create serious damage to the petrochemical industry resulting from the formation of biofilms on the metal surface [8, 9].

Generally coatings, paints and use of organic compounds provide corrosion mitigation. The organic compounds especially, heterocyclic compounds containing heteroatoms like S, N, O, Se with loosely bound lone pair of electrons and compounds with π electrons, undergo adsorption on the metal surface and protect the material from the aggressive environments. Various workers have used organic compounds for corrosion inhibition of metals like copper, iron, aluminium, mild steel, and stainless steel at different concentrations in acidic, basic and salt solutions [10-20]. Mild steel is used in various engineering applications like chemical and pharmaceutical industry [21, 22], food and beverage industry [23], petrochemical industry [24-26], oil and water pipelines [27], ship and naval structures [28-29]. Protection of the structural plants of the various industries will save leakage of the pipeline, on line and off line structures and also life and economy. In present study, the inhibition property of the organic compound tetramethylammonium iodide towards microbiologically influenced corrosion (MIC) of mild steel by Desulfovibrio desulfuricans in Barr's medium was investigated. Surface coverage and microbial action by tetramethylammonium iodide over mild steel substrates in corrosive environment was studied using SEM.

EXPERIMENTAL PROCEDURE:

METALS AND ALLOYS:

Mild Steel coupons having composition (C: 0.16%, Si: 0.10%, Mn: 0.40%, P: 0.013%, S: 0.02% and remaining as iron) have been used as working electrode in the present investigation.

CHEMICALS:

Chemicals used in corrosion test solutions and corrosion inhibitors were obtained from Merck (India), Loba Chemie (India). All these chemicals were of AR grade and were used without any further purification.

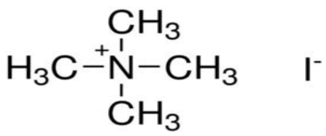
BACTERIA:

The bacteria used in the present study were obtained from National Collection of Industrial Micro-organisms (NCIM), Biochemical Science Division, National Chemical Laboratory, Pune-411088, Maharashtra.The bacterium used in the present study was Desulfovibrio desulfuricans. Composition of the culture medium is given below:

Name of the Organism	NCIM No.	Medium used
Desulfovibrio desulfuricans.	2047	Barr's medium (sulfur bacteria) K_2HPO_4 0.05g, NH_4Cl 0.19g, $CaSO_4$ 0.29g, Sodium lactate 0.79g, $MgSO_4.7H_2O$ 0.29g, Ferrous Ammonium Sulfate 0.05g, Distilled Water 100 cm^3 (medium is sterilized for three consecutive days at 121°C for 20 min. and the final pH was adjusted to 7.0-7.5).

BIOCIDE:

The biocide tetramethylammonium iodide is added in to the test solution. The chemical structure of tetramethylammonium iodide is as follows:

Inhibitor	Molecular Structure.
Tetramethylammonium iodide.	

SAMPLE PREPARATION:

For weight loss experiments, rectangular shaped coupons (1 cm X 3 cm) were sheared from sheets of mild steel and flag shaped specimens with 1 cm^2 working area were used for electrochemical experiments. The surface of specimens was prepared by sequential polishing with 1/0, 2/0, 3/0, 4/0 grade emery papers. Each sample was polished with the next higher grade in a right angle to the first. During the polishing of mild steel surface, the emery paper was impregnated with a dilute solution of paraffin wax in kerosene oil. All specimens were washed with triple distilled water and degreased with 95% ethyl alcohol. Specimens were dried and stored over silica gel in vacuum desiccators.

IMMERSION TEST:

Specimens were weighed on an electronic balance (Shimadzu Type BL22OH, least count 0.001g) before and after immersion tests. After removing the specimens from the test solution, the corrosion products were removed from the surface with the help of brush. Generally duplicate experiments were performed in each case and the mean value of the weight loss was recorded.

ELECTROCHEMICAL MEASURMENTS:

The variation of corrosion potential of mild steel was measured against saturated calomel electrode in absence and presence of various concentrations of inhibitors. The time dependence of open circuit potential (OCP) for different experiments was recorded for one-hour exposure periods. Then same sample was used for potentiodynamic polarization (PD) experiments. The polarization studies were carried out in unstirred solutions. For electrochemical polarization studies (corrosion potential and potentiodynamic polarization) flag shaped specimens with sufficiently long tail were cut from the mild steel sheet. These samples were polished as described earlier, leaving a working area of 1 cm^2 on both sides of the flag and a small portion at the tip for providing electrical contact. The rest of the surface was coated with enamel lacquer including side edges. The test specimen was connected to the working electrode holder through the tip of the tail. About 50 ml of the corrosive medium was taken in a mini corrosion testing electrochemical cell.

Electrochemical measurement system, DC 105, containing software of DC corrosion techniques from M/S Gamry Instruments Inc., (No. 23-25), Louis Drive, Warminster, PA- 18974, USA was used for performing corrosion potential and polarization experiments. The electrochemical studies were performed in a three electrodes Pyrex glass vessel with mild steel coupons as working electrode, saturated calomel electrode as reference electrode and spectroscopic grade graphite rod as counter electrode.

SCANNING ELECTRON MICROSCOPIC ANALYSIS:

The composition and surface morphology of corrosion product on mild steel sample after 240 hours(10 days) immersion in the Barr's medium containing *Desulfovibrio desulfuricans* in the absence and presence of tetramethylammonium iodide was studied by a scanning electron microscopy (SEM).

RESULTS AND DISCUSSION:

WEIGHT LOSS MEASUREMENT:

Weight loss data of mild steel in Barr's medium inoculated with *Desulfovibrio desulfuricans* in the absence and presence of various concentrations of inhibitor were obtained and are given in Table-1. Inhibition efficiencies (IE %) were calculated by formula as:

$$(IE\ \%) = [W_0 - W]/W_0 X\ 100$$

Where W_{corr} and W_o are the weight loss of mild steel in the presence and absence of inhibitor, respectively. The results show that the inhibition efficiencies increase with increasing inhibitor concentration. The results obtained from the weight loss measurements are in good agreement with those obtained from the electrochemical methods.

Inhibitor	Conc. (ppm)	Weight Loss (mg)	Surface Coverage (θ)	Inhibition Efficiency (IE %)
Blank Barr's medium inoculated with *Desulfovibrio desulfuricans*	-	190	-	-
Tetramethylammonium iodide	100	121	0.3621	36.31
	300	72	0.6210	62.10
	500	50	0.7368	73.68

Table-1: Weight loss data for inhibition of corrosion of mild steel exposed to Barr's medium inoculated with *Desulfovibrio desulfuricans* with different concentration of tetramethylammonium iodide.

ADSORPTION ISOTHERM

The surface coverage values $\boldsymbol{\theta}$, (defined as $\boldsymbol{\theta}$ =IE %/100), increases with increasing inhibitor concentration as a result of adsorption of more inhibitor. The corrosion inhibition efficiency was calculated by using the following equation: Inhibition efficiency (IE %) = $\frac{\mathbf{100}(i_{0-i})}{i_0}$, Where I_o and I are the corrosion current densities in the absence and presence of inhibitor in the solution, respectively.

C (PPM)	θ	IE%
100	0.3631	36.31
300	0.6210	62.10
500	0.7368	73.68

Table 3. Adsorption parameters of tetramethylammonium iodide.

It is observed that the adsorption behavior of tetramethylammonium iodide obeys the Langmuir's adsorption isotherm as it gives straight line when graph of C(ppm)/ θ is plotted against C(ppm) as shown in Fig 1. It was proposed that adsorption of tetramethylammonium iodide occurs by physisorption and chemisorption. Thus the surface of inhibitor layer formation on the mild steel is the combination of both, physisorption and chemisorptions.

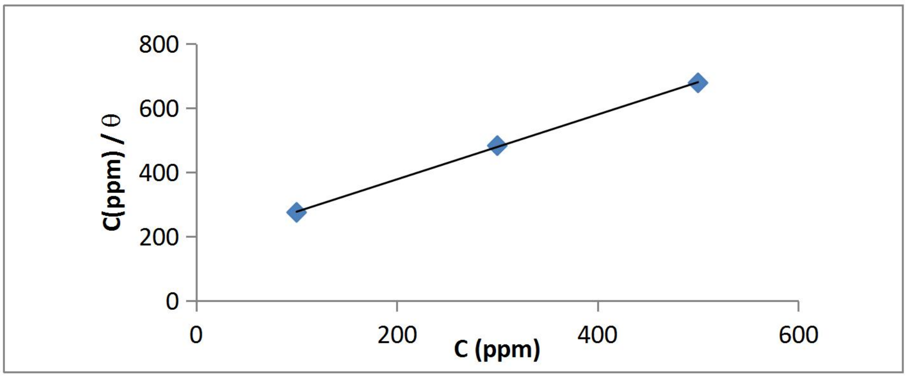


Fig. 1: Adsorption Isotherm of tetramethylammonium iodide.

OPEN CIRCUIT POTENTIAL (OCP) MEASUREMENT:

The electrochemical behavior of mild steel in 1M HCl was studied by monitoring change in corrosion potential (E_{corr}) with time. The change in open circuit potential of mild steel in absence and presence of various concentrations of inhibitor tetramethylammonium iodide in Barr's medium is shown in fig. 2.The change in open circuit potential of mild steel in absence and presence of inhibitors were measured after 10 days exposure in Barr's medium inoculated with *Desulfovibrio desulfuricans* for period of 1h with sample period of one data per second. The potential attained steady state after exposure of 0.5h. The steady state potential is an equilibrium state at which $I_{ox.}$ is equal to $I_{red.}$ In the presence of various concentrations of inhibitors the steady state potential of mild steel shifts more towards positive value. This is due to adsorption of inhibitors on metal surface resulting in passivation of metal.

The influence of various concentration (100, 300, and 500 ppm) of tetramethylammonium iodide on open circuit potential of mild steel in Barr's medium is given in fig. 2. It is obvious from figure that, it exhibit good inhibition performance at 100 ppm and above. Inhibition efficiency increased with increase in concentration of tetramethylammonium iodide.

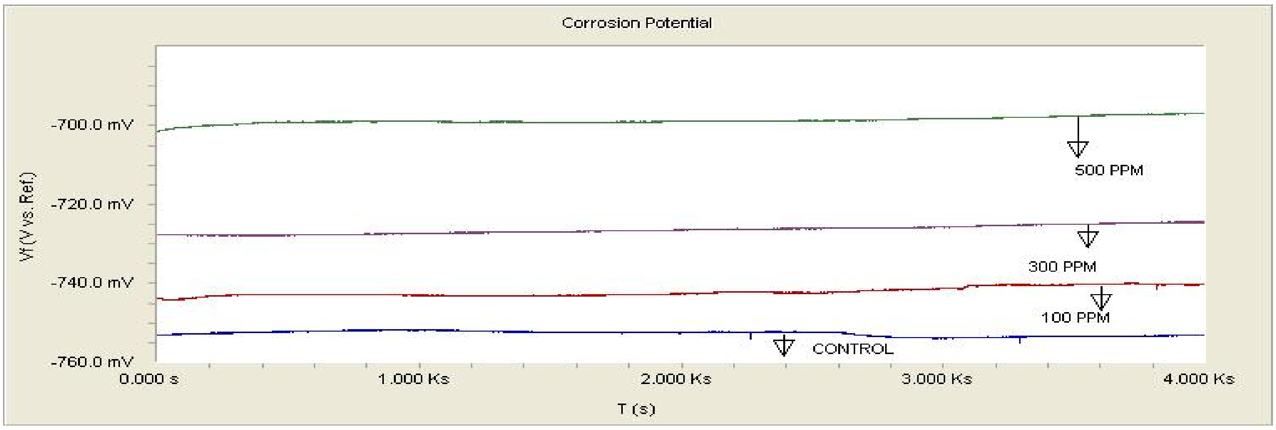


Fig.2.. Corrosion potential of mild steel exposed to the solution of Barr's medium with different concentrations of tetramethylammonium iodide.

POTENTIODYNAMIC POLARIZATION MEASUREMENT:

Fig. 3 depicts typical potentiodynamic polarization curves for mild steel in Barr's medium solution in the absence and presence of different concentrations of tetramethylammonium iodide at 30^{0}C. It could be observed that extent of damage to mild steel surface was less, the rate of corrosion was reduced considerably in the presence of inhibitors. There was a good protective film adsorbed on metal surface, which acted as a barrier and was responsible for the inhibition of corrosion.

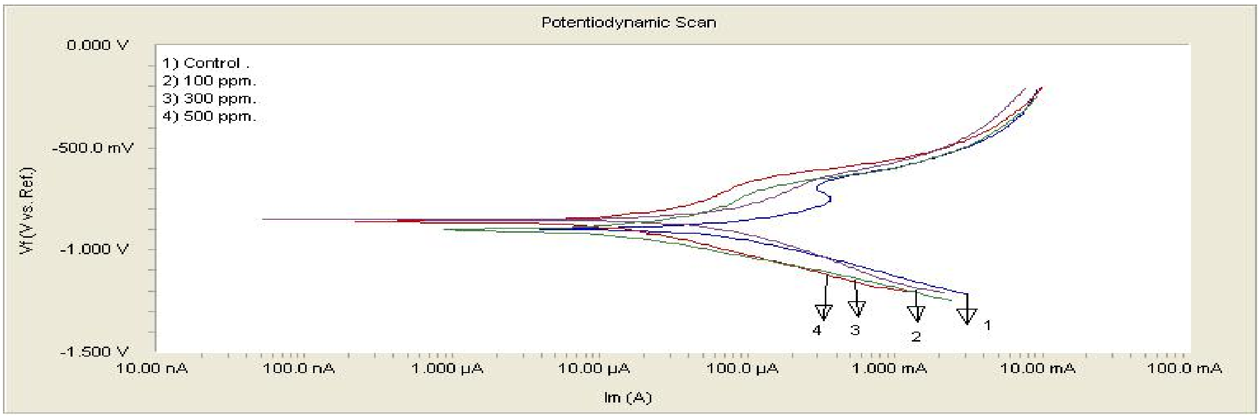


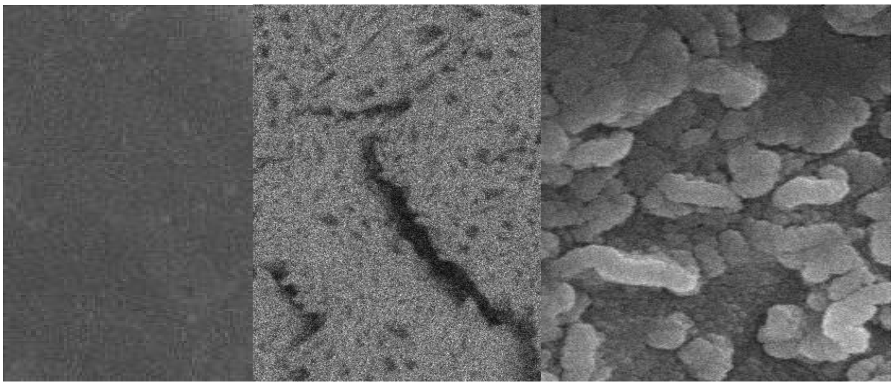
Fig.3. Potentiodynamic polarization curve of mild steel exposed to Barr's medium inoculated with Desulfovibrio Desulfuricans with different concentrations of tetramethylammonium iodide.

Conc. (ppm)	β_a (V/dec.) e^{-3}	β_c (V/dec.) e^{-3}	I_{corr} (µA.cm^2)	E_{corr} (mV)	%IE
Control	299.7	250.0	26.00	-868.0	-
Tetramethylammonium iodide.					
100	219.8	174.1	16.56	-902.0	36.30
300	218.3	199.0	9.85	-861.0	62.00
500	138.6	167.0	6.84	-829.0	74.00

Table .4.Electrochemical Parameters for Inhibition of corrosion of mild steel exposed to 1M HCl with different concentration of Tetramethylammonium iodide.

SCANNING ELECTRON MICROSCOPIC (SEM) ANALYSIS:

SEM micrographs obtained from unexposed and exposed specimen coupons in Barr's medium inoculated with *Desulfovibrio desulfuricans* for 240 hours in the absence and presence of 500 ppm tetramethylammonium iodide are shown in Fig. 4. The accelerating voltage for SEM scanning was 10KV. It is obvious from fig.4b that in the presence of *Desulfovibrio desulfuricans* there was severe pitting, exfoliation and localized corrosion. In the presence of inhibitor a smooth surface covered with thin biofilm was observed. The results obtained from weight loss and electrochemical measurements were further supported by SEM analysis.



a) b) c)

Fig. 4: SEM of mild steel: a) Polished and without inhibitor. b) After immersion in Barr's medium inoculated with *Desulfovibrio desulfuricans* without inhibitor. c) After immersion in Barr's medium inoculated with *Desulfovibrio desulfuricans* with 500 ppm of tetramethylammonium iodide.

CONCLUSIONS

1. The result obtained by gravimetric analysis, provided good agreement with the result obtained by electrochemical studies.

2. It revealed that tetramethylammonium iodide was acting as a very good corrosion inhibitor of mild steel in Barr's medium.

3. The inhibition efficiency increased with increasing concentration of inhibitor. In the present investigation, 500 ppm solution of tetramethylammonium iodide showed nearly 75% corrosion inhibition. Tetramethylammonium iodide is mixed type of inhibitor.

4. The SEM examination showed the formation of protective surface film of inhibitor molecules on the surface of mild steel and obeyed the Langmuir adsorption isotherm.

REFERENCES:

[1] B. Little, P. Wagner, F. Mansfeld, "An overview of microbiologically influenced corrosion", Electrochim. Acta, 1992, 37, pp. 2185–2194.

2] B. Jiang, C. Du, X. Li, A. Gong, "Development of typical microbiologically influenced corrosion research", Petrochem. Corros. Prot. 2008, 25, pp. 1–4.

[3] H. Venzlaff, D. Enning, J. Srinivasan, K.J.J. Mayrhofer, A.W. Hassel, F. Widdel, M. Stratmann, "Accelerated cathodic reaction in microbial corrosion of iron due to direct electron uptake by sulfate-reducing bacteria", Corros. Sci. 2013, 66, pp. 88– 96.

[4] W. Iverson, "Direct evidence for the cathodic depolarization theory of bacterialcorrosion" Science , 1966, 151,pp. 986–988.

[5] R.A. King, J.D.A. Miller, "Corrosion by the sulphate-reducing bacteria", Nature, 1971,233, pp. 491–492.

[6] W.P. Iverson, “Corrosion of iron and formation of iron phosphide by Desulfovibrio desulfuricans”, Nature, 1968, 217, pp. 1265–1267.

[7] F. Kuang, J. Wang, L. Yan, D. Zhang, “Effects of sulfate-reducing bacteria on the corrosion behavior of carbon steel”, Electrochim.Acta, 2007,52,pp. 6084–6088.

[8] I.B. Beech, C.W.S. Cheung, “Interactions of exopolymers produced by sulphate reducing bacteria with metal ions”, Int. Biodeter. Biodegr. 1995,35,pp. 59–72.

[9] H.T. Dinh, J. Kuever, M. Muszmann, A.W. Hassel, M. Stratmann, F. Widdel, “Iron corrosion by novel anaerobic microorganisms”, Nature, 2004,427, pp. 829–832.

[10] K. Mori, H. Tsurumaru, S. Harayama, “Iron corrosion activity of anaerobic hydrogen-consuming microorganisms isolated from oil facilities”, J. Biosci. Bioeng. 2010,110,pp. 426–430.

[11] J.A. Hardy, “Utilisation of cathodic hydrogen by sulphate-reducing bacteria”,Brit. Corros. J. 1983,18 , pp. 190–193 .

[12] I. Betova, M. Bojinov, O. Hyökyvirta, T. Saario, “Effect of sulphide on the corrosion behaviour of AISI 316L stainless steel and its constituent elements insimulated Kraft digester conditions”, Corros. Sci. 2010, 52, pp. 1499–1507.

[13] M.S. Wiener, B.V. Salas, M. Quintero-Núñez, R. Zlatev, “Effect of H2S on corrosion in polluted waters: a review”, Corros. Eng. Sci. Technol. 2006,41, pp.221–227.

[14] A. Davoodi, M. Pakshir, M. Babaiee, G.R. Ebrahimi,” A comparative H2S corrosion study of 304L and 316L stainless steels in acidic media”, Corros. Sci.2011, 53, pp.399–408.

[15] B.W.A. Sherar, I.M. Power, P.G. Keech, S. Mitlin, G. Southam, D.W. Shoesmith,”Characterizing the effect of carbon steel exposure in sulfide containing solutions to microbially induced corrosion”, Corros. Sci.2011, 53, pp. 955–960.

[16] F. Li, M. An, G. Liu, D. Duan,” Effects of sulfidation of passive film in the presence of SRB on the pitting corrosion behaviors of stainless steels”, Mater. Chem. Phys. 2009,113, pp. 971–976.

[17] S.L. Johnston, G. Voordouw, “Sulfate-reducing bacteria lower sulfur-mediated pitting corrosion under conditions of oxygen ingress”, Environ. Sci. Technol.2012, 46, pp. 9183–9190.

[18] H. Ma, X. Cheng, G. Li, S. Chen, Z. Quan, S. Zhao, L. Niu,” The influence of hydrogen sulfide on corrosion of iron under different conditions”, Corros. Sci.2000, 42, pp . 1669–1683.

[19] D. Starosvetsky, J. Starosvetsky, R. Armon, Y. Ein-Eli, “A peculiar cathodic process during iron and steel corrosion in sulfate reducing bacteria (SRB) media”, Corros. Sci. 2010, 52,pp. 1536–1540.

[20] A.P. Yadav, A.Nishikata,T.Tsuru,“Electrochemical impedance study on galvanized steel corrosion under cyclic wet–dry conditions—influence of time of wetness”,Corros.Sci. 2004,46, pp.169–181.

[21] E.Ilhan-Sungur, A.Çotuk, “Microbial corrosion of galvanized steel in a simulated recirculating cooling tower system”, Corros. Sci. 2010, 52,pp.161–171.

[22] J.Yu, Y.Chen, H.Yang, Q.Huang,”Theinfluencesoforganicadditivesonzincelectrocrystallization from KCl solutions”, Electrochem.Soc.1999,146, pp.1789–1793.

[23] K. Boto,”Organic additives in zinc electroplating”, Electrodep.Surf.1975,3, pp.77– 95.

[24] S. Beloglazov, M.Myamina, A.Gribankova,” Application of Antipyrine Derivative as an Inhibitor Against Myxomycete Corrosion and Steel Hydriding in a Water Salt Medium” [P],RU Patent 2359068,2009.

[25] M.Moradi, J.Duan, X.Du,”Investigation of the effect of 4,5-dichloro-2-n-octyl- 4-isothiazolin-3-one inhibition on the corrosion of carbon steel in Bacillus sp. inoculated artificial seawater”Corros.Sci.2012, pp. 338–345.

[26] R. Steen, F.Ariese, B.Hattum, J.Jacobsen, A.Jacobson,”Monitoring and evaluation of the environmental dissipation of the marine antifoulant 4,5- dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) in a Danish Harbor”, Chemosphere,2004, 57 ,pp. 513–521.

[27] J. Duan, X.Zhai, M.Myamina, “A Kind of Antibacterial and Anticorrosion Zinc Coating for Marine Engineering Material “[P],CN Patent 201210189394.0,2012.

[28] Yu Linizhou Duan, WeiZhao, Yanliang Huang, BaorongHou,”Characteristics of hydrogen evolution and oxidation catalyzed by Desulfovibrio caledoniensis biofilm on pyrolytic graphite electrode”, Electrochim.Acta, 2011, 56, pp.9041– 9047.

[29] M. Li,S.Luo,Y.Qian,W. Zhang,L.Jiang,J.Shen,”Effect of additives on electrodeposition of nanocrystalline zinc from acidic sulfate solutions”,J. Electrochem. Soc.2007,154,pp.567–571.