Review on Benzotriazole As Anti-corrosive Agents

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Abstract: This article presents an overview of the studies on the adsorption of 1,2,3 benzotriazole (BTA) and its derivatives on copper, zinc and some of their alloys from aqueous solutions, and their corrosion inhibition capability in neutral and acidic media. It examines the effect of these organic corrosion inhibitors (CIs) on the formation of surface layers, their composition and the effectiveness of their protective action that were investigated by corrosion, electrochemical and other physicochemical methods. Considerable attention has been given to BTA itself, the wide range of corrosive media in which it can be an effective CI, an analysis of the reasons for its successful application in the practice of anticorrosion protection of copper and its alloys, as well as the new prospects of its usage and increasing its inhibition efficiency.

The inhibition of corrosion of zinc and copper–zinc alloys by BTA has been discussed. It has been shown that the protection is based on the formation of sparingly soluble complexes of copper and zinc with BTA. Examples of improving the effectiveness of their protection with mixed CIs are given. The review notes the almost complete absence of studies of BTA derivatives for the protection of Zn, which could also be very useful for improving the corrosion protection not only of zinc but also galvanized steel.
Key Words: Benzotriazole, Anti corrosive Agent, Copper, Zinc, Alloys

I. INTRODUCTION:

Benzotriazole

Benzotriazole are a class of heterocyclic organic compound having a ring system containing three nitrogen atoms and fused benzene ring shows wide range of biological activities. [1]

Physical properties:

Molecular formula	$C_6H_5N_3$
Molecular weight	119.1240
Melting point	98.5-100°C
Nature	White to brown crystalline powder
Density	1.36 g/cm^3
Solubility	in water g /100 ml is 2 (moderate)
CAS Registry Number	95-14-7
UV absorbance	286 nm

Uses: Prevention of rust and other corrosive effects on metals. Also used as Antifungal & Anti-Hypertensive. [11]

Corrosion:

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxides, Hydroxides, or sulphides. It is the gradual destruction of material (usually metals) by chemical and/or electrochemical reactions with their environment. In the most common use of word, it is mean Electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulphates. Rusting, the formation of iron oxides or salts of original metal, and result in distinct colouration.

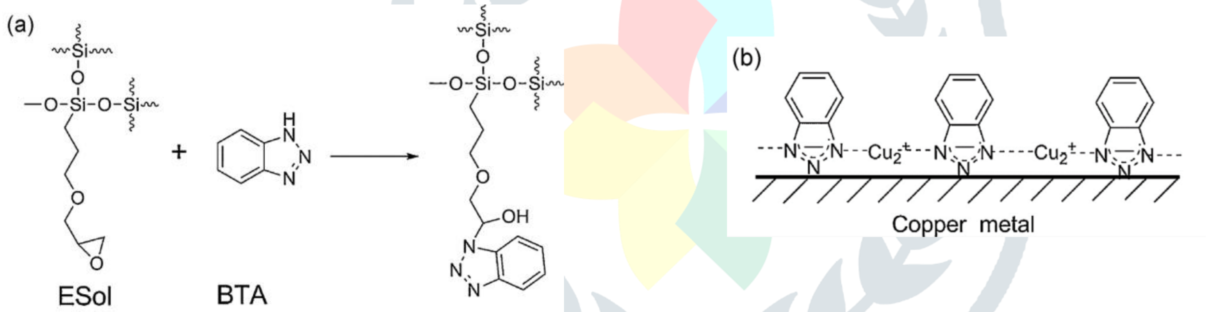
Anti-corrosive Agents:

Anti-corrosion refers to the protection of metal surfaces from corroding in high risk (corrosive) environment.The ability of corrosion inhibitors (CIs) to protect a wide range of metals and alloys, and even more so in various corrosive media and under diverse conditions, would certainly be a very valuable property. However, it is hardly easier to imagine such CIs than to believe in the existence of a cure for all diseases and for different people. In other words, their search can be very useful, but the attainment of the goal, at least in a foreseeable future, is apparently impossible. Hence the inaccuracy of the term "universal inhibitor of metal corrosion", which was more of an advertising nature than reflected the true possibilities of using such an anti-corrosion protection.

The name "multifunctional CIs", implying that they are able to protect various metals and alloys and to effectively operate under various conditions and in various media, seems more correct. Of course, it is better to refer this term not to individual compounds but to a class of chemical compounds. In it one can find CIs that protect metals in aqueous solutions with various compositions, corrosive atmospheres and natural gas, acid and alkaline media, or hydrocarbons. They can be volatile (VCI) or non-volatile. [12]

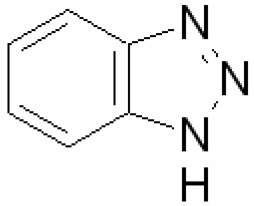
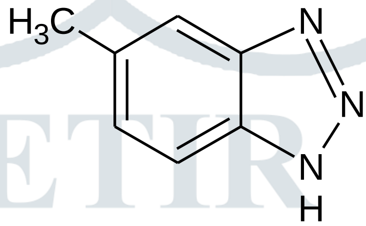
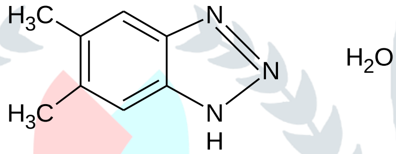
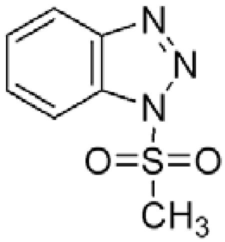
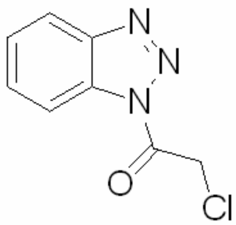
II. REVIEW OF LITERATURE

- **Shusen Peng, Wenjie Zhao *et al.*** has said that IR results demonstrate that BTA reacted with ESol through a 1:1 addition reaction of N H to epoxy group. The water contact angle of the ESol coating increases with an increase in the amount of BTA. SEM and adhesion tests reveal that BTA could improve the adhesion of ESol to copper surface. Moreover, the best protection was achieved when the amount of BTA equals to the molar number of epoxy group in the ESol coating according to the results of electrochemical measurements and salt spray test. [2]



- **Srikanth *et al*.,** have synthesized a various composition of few copolymers of N-acryloyloxymethyl benzotriazole and N-methacryloyloxymethyl benzotriazole with methyl methacrylate and glycidylmethacrylate. They extended his study to exploit the adhesive behaviour of methacrylate and the corrosion inhibiting behaviour of benzotriazole on mild steel in 0.1 M HC1 medium. Photo-cross linking properties of new photoresist materials based on the copolymers of 3-methacryloyloxystyry1-4'-methylphenyl ketone with methyl methacrylate have been synthesized and reported. They also developed the copolymers of 4-methacryloyloxypheny1-3',4'-dimethoxystyryl ketone with methyl methacrylate. The photocrosslinkable cinnamoyl methacrylamide polymers containing bromo, N,N-dimethylamino and benzo substituted chalcone moiety were also reported by Selvam *et al*.

- **Ayman Ababneh, Mashal Sheban *et. al.*** has developed corrosion protection systems for reinforced concrete structures under. carbonation attack. Benzotriazole (BTA) and BTA derivatives were used as two separate protection systems: inhibition and pickling protection systems. The experiments were performed in Simulated Concrete Pore (SCP) solutions with and without severe carbonation attack. Electrochemical techniques, i.e. potentiodynamic polarization and electrochemical impedance were used to assess the steel corrosion protection systems. The potentiodynamic polarization studies showed a reduction in the corrosion rate and a shifting in the corrosion potential to more noble potential for the steel specimen in the simulated carbonated concrete solution. In addition, a large increase in the steel interfacial resistance was observed by Electrochemical Impedance Studies (EIS) due to the formation of steel-BTA derivative complex on the surface. BTA derivatives provided a good protection for the steel in SCP simulated carbonated concrete solutions. This study indicates the applicability of these compounds for steel corrosion protection in reinforced concrete structures. [3]

Synonyms	Abbr.	Molecular formula	Molecular structure	Manufactured by
Benzotriazole	BTA	$C_6H_5N_3$		Alfa Aesar
5-Methyl-1HBenzotriazole	MBTA	$C_7H_7N_3$		TCI America
5,6-Dimethyl-1HBenzotriazole monohydrate	DMBTA	$C_8H_9N_3.H_2O$		Alfa Aesar
1-Methanesulfonyl-1H-Benzotriazole	MSBTA	$C_7H_7N_3O_2S$		Sigma-Aldrich Co.
1-(α-Chloroacetyl)-1H-Benzotriazole	CABTA	$C_8H_6ClN_3O$		Sigma-Aldrich Co.

- **A.C.Jayasree and R.Ravichandran** has synthesised Benzotriazole and their inhibition behaviour on admiralty brass in artificial sea water were investigated by the weight-loss method and potentiodynamic polarisation methods. Benzotriazole derivatives were found to act as mixed type inhibitors. Solution analysis revealed the dissolution of both copper and zinc occurred in the presence of the inhibitors. The morphology of the brass after corrosion in the presence and absence of the BTA derivatives was examined using scanning electron microscopy (SEM). The percentage composition of the brass surface was analysed using energy dispersive X-ray analysis (EDAX). [4]

- **S. Ullah, A. M. Shariff *et al.*** investigated the corrosion inhibition and corrosion rates of copper alloys in sulphuric acid by benzotriazole (BTAH) and surfactants. Three types of surfactants namely sodium dodecyl sulphate (SDS), cetyle trimethyl ammonium bromide (CTAB) and X-Triton were used in the given research work. From the results, it was noticed that the rate of corrosion of copper decreased with an increase in concentration of inhibitor. Excellent results on corrosion inhibition of the copper alloys, in the tested acids, were achieved in the presence of benzotriazole and surfactants. It was observed that benzotriazole and surfactants inhibit the corrosion of copper significantly. The highest corrosion inhibition was materialized in post micellar concentration (PMC) of Triton X-100 and CTAB with 0.75 ppm benzotriazole in 1.5 M H2SO4. The maximum corrosion inhabitation achieved with Triton X-100 and CTAB was 5.41 and 5.44 mpy, respectively. Finally, the Linear Polarization Resistance (LPR) was used to investigate the corrosion resistance of optimized concentrations of surfactants and BTAH. The LPR results revealed that Triton X-100 causes significantly higher corrosion inhibition performance as compared to CTAB. [6]

- **P. MATHESWARAN *et al.*** has studied Benzotriazole as corrosion inhibition for mild steel in 1 N citric acid by weight loss method. The result showed that the corrosion inhibition efficiency of the compound was found to be varying with the temperature and acid concentration. Also it was found that the corrosion inhibition behaviour of benzotriazole is better when the concentration of inhibitor is increased. The kinetic treatment of the results shows first order kinetics. [7]

- **Agus Solehudin** has conducted Corrosion and inhibition studies on API 5LX65 carbon steel in chloride solution containing various concentrations of benzotriazole at temperature of 70oC using Electrochemical Impedance Spectroscopy (EIS). Corroded carbon steel surface with and without inhibitor have been observed using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Energy Dispersive Spectroscopy (EDS). The objectives of this research are to study the performance of benzotriazole as corrosion inhibitors. The experimental results of carbon steel corrosion in 3.5% NaCl solution containing 500 mg/l H2S at different BTAH concentrations showed that corrosion rate of carbon steel decreases with increasing of BTAH concentrations from 0 to 10 mmol/l. The inhibition efficiency of BTAH was found to be affected by its concentration. The optimum efficiency obtained of BTAH is 93% at concentration of 5 mmol/l. The result of XRD and EDS analysis reveal the iron sulphide (FeS) formation on corroded carbon steel surface without inhibitor. The EDS spectrum show the Nitrogen (N) bond on carbon steel surface inhibited by BTAH. [8]

- **Parook Feroz Khan *et al.*** has investigated the corrosion inhibition of benzotriazole on the copper surface in static environment. The evidence for the protection of copper in dynamic flowing environment is limited. Hence, we investigated the corrosion control of copper in 3.5% NaCl solution in the presence of benzotriazole by a rotating cage. The flow test was carried out at different velocities 0.5–3.0 m/s (100– 700 rpm). Copper showed accelerated corrosion activity with respect to the increase in the velocity in 3.5% NaCl test solution. However, benzotriazole added to the test solution reduced the corrosion attack on the copper. This clearly shows the adsorption of inhibitor on copper surface resulted in decreasing the mass loss by 4–5 times. The surface property was examined by using a scanning electron microscopy, atomic force microscopy and contact angle measurements. Adsorption of benzotriazole on copper surface follows the Langmuir adsorption isotherm. [9]

- **M.M. Mennucci *et al.*** has investigated, benzotriazole (BTAH), a well-known corrosion inhibitor for copper, has been evaluated as a possible corrosion inhibitor of a carbon steel (CA-50) used as reinforcement in concrete. BTAH was added to a simulated pore solution of an aged concrete with addition of 3.5 wt.% NaCl to imitate marine environments. The effect of BTAH in a concentration of 1.5 wt.% on the corrosion resistance of CA-50 carbon steel was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests. The improvement of the corrosion resistance due to BTAH addition was superior to that associated with nitrite in similar concentration, suggesting that BTAH is a potentially attractive alternative to nitrites for inhibiting corrosion of reinforcement steel in concrete. [10]

III. MECHANISM OF CORROSION INHIBITION:

The dissolution and film formation of brass in artificial sea water takes place via the reactions outlined below. In the initial corrosion stage, zinc forms ZnO as a result of

$$Zn + H_2O = ZnO + 2H+ + 2e^-$$

And copper forms Cu_2O as a result of

$$2Cu + H_2O = Cu_2O + 2H+ + 2e^-$$

Thus, a passive oxide film consisting of both Cu_2O and ZnO covers the surface. However, CuCl is formed on the surface (in the presence of chloride) by the reaction

$$Cu^+ + Cl^- = CuCl$$

which may ultimately result in the formation of $CuCl_2$ complex via

$$CuCl + Cl^- = CuCl_2$$

The effectiveness of BTA derivatives as corrosion inhibitors for brass can be gauged from the electrochemical behaviour of brass in artificial sea water. The nature of the interaction of inhibitor on the metal surface during corrosion inhibition has been deduced in terms of the adsorption characteristics. In most cases the adsorption of inhibitor from the corrosive medium is a quasi-substitution process.

$$\text{Inhibitor (sol}^n\text{)} + nH_2O \text{ (ads)} = \text{Inhibitor (ads)} + H_2O \text{ (sol}^n\text{)}$$

The BTA derivatives are chemisorbed on the metal surface and that this chemisorbed layer prevents adsorption of oxygen and oxide formation. The protective film is a 1:1 complex of Cu (I) and BTA. The film is probably polymeric, in which BTA bridges two copper atoms via N_1 and N_3 and the aromatic ring is aligned parallel to the metal surface. Formation Cu (II) complexes also can occur, but they do not be protective. Chadwick et al concluded that zinc is also incorporated into the surface film in significant quantities. BTA derivatives inhibits by a two-fold mechanism. The chemisorbed film has a hydrophobic backbone that limits the transport of hydrated aggressive ions to the metal surface. Once formed, the film stabilized Cu (I) ions by means of an electronic effect, network formation or both. It is well known that the inhibitive action of organic compound containing S, N and/or O is due to the formation of a coordinate type of bond between the metal and the lone pair of electrons present in the additive. The tendency to form coordinate bond and hence the extent of inhibition can be enhanced by increasing the effective electron density at the functional group of the additive. In aromatic or heterocyclic ring compounds, the effective electron density at the functional group can be varied by introducing different substituents in the ring leading to variations of the molecular structure. Based on the results, due to the presence of heteroatom such as N, O, S and electrons on aromatic nuclei. The higher inhibition efficiency of the organic compounds is due to the basis of donor-acceptor interactions between the electrons of the inhibitor and the vacant d-orbital of copper surface or an interaction of inhibitor with already adsorbed chloride ions. [4]

IV. Conclusion:

Conclusion: Based on previously discussed reviews on various articles, it can be said that Benzotriazole compounds can be used as copper corrosion inhibitors. The substituted benzotriazole derivatives showed good inhibition efficiency in artificial sea water. The potentiodynamic polarisation studies showed that the inhibitors were mixed type for brass in chloride solution. They decreased the anodic reaction rate more strongly than the cathodic reaction rate and rendered the open circuit potential more positive in artificial sea water. The benzotriazole derivatives easily adsorbed onto the brass surface at the corrosion potential and formed a protective complex with the Cu(I) ion, thereby reducing the susceptibility of brass to corrosion. [4][5]

V. Acknowledgement: We are very thankful to our Principal Dr. G. J. Khan to providing us enthusiastic academic environment and all necessary facilities required for this work.

VI. Reference:

1. B. V. Suma, N. N. Natesh and V. Madhavan, Benzotriazole in medicinal chemistry, Journal of Chemical and Pharmaceutical Research, 2011, 3(6):375-381.
2. Shusen Peng, Wenjie Zhao, He Li, Zhixiang Zeng, Qunji Xue, Xuedong Wu, 2013, The enhancement of benzotriazole on epoxy functionalized silica sol–gel coating for copper protection, Applied Surface Science 276: 284– 290.
3. Ayman Ababneh, Mashal Sheban, Muna Abu-Dalo and Silvana Andreescu, 2009, Effect of Benzotriazole Derivatives on Steel Corrosion in Solution Simulated Carbonated Concrete, Jordan Journal of Civil Engineering, Volume 3, No. 1.
4. A.C.Jayasree and R.Ravichandran, (2014), Anti-Corrosive effect of N-[(benzylidene hydrazino)-propyl]- benzotriazole and N-[(4-oxo-2-phenyl-1,3-thiazolidineimino)-propyl]-benzotriazole for admiralty brass in marine environment, Int.J.Curr.Microbiol.App.Sci 3(3): 515-526
5. M. M. Antonijevic and M. B. Petrovic, 2008, Copper Corrosion Inhibitors. A review, International journal of electrochemical science, Int. J. Electrochem. Sci., 3: 1 – 28
6. S. Ullah1, A. M. Shariff, M. A.Bustam1, M. Nadeem, M. Y. Naz and M. Ayoub, 2015, Study on Effect of Benzotriazole and Surfactants on Corrosion Inhibition of Copper Alloys in Sulphuric Acid, Int. J. Electrochem. Sci., (10) 8321 – 8333
7. P. MATHESWARAN and A.K. RAMASAMY, 2010, Influence of Benzotriazole on Corrosion Inhibition of Mild Steel in Citric Acid Medium, E-Journal of Chemistry, 7(3), 1090-1094
8. Agus Solehudin, 2012, Performance Of Benzotriazole As Corrosion Inhibitors Of Carbon Steel In Chloride Solution Containing Hydrogen Sulfide, International Refereed Journal of Engineering and Science, 4(1), 21-26
9. Parook Feroz Khan, Vaithianathan Shanthi, Rupesh K. Babu, Srinivasan Muralidharan, Rakesh Chandra Barik, 2015, Effect of benzotriazole on corrosion inhibition of copper under flow conditions, Journal of Environmental Chemical Engineering (3) 10–19
10. M.M. Mennucci, E.P. Banczek, P.R.P. Rodrigues, I. Costa, 2009, Evaluation of benzotriazole as corrosion inhibitor for carbon steel in simulated pore solution, Cement & Concrete Composites (31) 418–424
11. https://www.uni-tradebg.com/many-uses-of-benzotriazole/
12. https://en.m.wikipedia.org/wiki/Anti-corrosion/