



**ENHANCED SYNERGISTIC EFFECTS OF TRISODIUM 2-HYDROXYPROPANE-1,2,3-TRICARBOXYLATE ON THE INHIBITION EFFICIENCY OF 5-METHYL BENZOTRIAZOLE SYSTEM ON BRASS IN AQUEOUS ENVIRONMENT**

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**ABSTRACT**

The corrosion inhibition of brass in 3% NaCl in the presence of 5-methyl benzotriazole (MBT) and Trisodium 2-hydroxypropane-1,2,3-tricarboxylate (TSPC) has been investigated using mass loss method, electrochemical techniques and solution analysis. Analysis of results revealed that of MBT inhibits 71% at optimum concentration(150 ppm). The addition of TSPC with MBT enhanced the inhibitive effect upto 90% and showed a synergism of inhibition. Potentiodynamic

polarization results suggested that the MBT and the mixture of MBT and TSPC behave as mixed type inhibitors. The results of solution analysis by atomic adsorption spectroscopy showed that the mixture of MBT and TSPC effectively controlled the dezincification of brass. EDX analysis was used to determine the nature of the protective film formed on the metal surface.

**KEYWORDS :** Brass, 5-methyl benzotriazole, Trisodium 2-hydroxypropane-1,2,3-tricarboxylate .

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## 1. INTRODUCTION

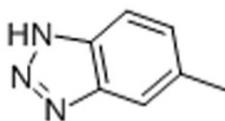
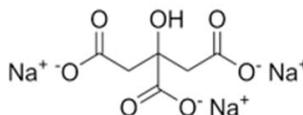
Brass is widely used for pipe and electrical fittings, screws, musical instruments, ornamental metal work and many others, due to its malleability, acoustic properties, bright gold-like appearance, etc. In spite of its important application, brass suffers from corrosion in aqueous environments containing corrosive ions such as chloride and sulfate. Dezincification of brass is one of the well-known and common processes by means of which brass loses its valuable physical and mechanical properties leading to failure of structure. One of the most important methods in the corrosion protection of brass was the use of organic inhibitors containing heterocyclic atoms such as oxygen, nitrogen, sulphur. Among these azoles are known as one of the best corrosion inhibitors for copper and its alloys in a wide range of environments<sup>[1-2]</sup>. One potential method to cost-effectively increase the corrosion inhibition efficiency is to employ the combination of inhibitors. The synergistic inhibition effect of combination of inhibitors has been studied by a number of authors<sup>[3-4]</sup>. It also found that the pitting inhibition might be due to the formation of a mixed layer of tin in citric acid concentrations higher than  $10^{-2}$  M oxide and tin citrate complexes on the electrode surfaces.

The present work is devoted to the investigation of the corrosion behavior of brass in NaCl medium. Further, the study was extended to understand the effect of MBT, TSPC and synergistic effect of MBT and TSPC in the corrosion inhibition of brass. The inhibition effect has been studied by the weight loss method and some electrochemical methods. Solution analysis was carried out to find out the concentration of Cu and Zn leached out from the brass using atomic absorption spectroscopy. The composition of brass surface was analyzed using energy dispersive X-ray analysis (EDAX).

## 2. Experimental Details

The chemical composition (weight percent) of the brass plate used in these tests was 65.3% Cu, 34.44% Zn, 0.1385% Fe, 0.0635% Sn and the rest Pb, Mn, Ni, Cr, As, Co, Al and Sr as analyzed by optical emission spectrophotometer. The brass specimens were polished mechanically with SiC papers (120 -1200 grit), washed with double distilled water and degreased in acetone. The solutions were prepared from AR chemicals using DD water.

The structure of MBT and TSPC is given in "Fig.1" and "Fig.2" respectively.

**“Fig.1” Structure of MBT****“Fig.2” Structure of TSPC**

### 2.1. Weight Loss Method

Weight loss measurements were carried out using brass specimen of size 4 x 1 x 0.4 cm. The specimens were immersed in 100 ml of 3% NaCl solution with and without inhibitors at room temperature for 24 h. The Corrosion rate CR and Inhibition efficiency IE were calculated using the following equation.  $C = (534 \times W) / (D \times T \times A)$  where A is the area, T the immersion time, W the weight loss and D the density of the specimen.

### 2.2. Potentiodynamic polarization study

The potentiodynamic polarization studies were carried out with brass strips having an exposed area of 1 cm<sup>2</sup>. The cell assembly consisted of brass as working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge. Polarization studies were carried out using a potentiostat/galvanostat and the data obtained were analyzed. The working electrode was immersed in a 3% NaCl solution and allowed to stabilize for half an hour<sup>[5]</sup>. Each electrode was immersed in a 3% NaCl solution in the presence and absence of optimum concentrations of the inhibitors to which a current of 1.5 mA cm<sup>-2</sup> was applied for 15 min to reduce oxides. The cathodic and anodic polarization curves for brass specimen in the test solution with and without inhibitor were recorded at a sweep rate of 1 mV s<sup>-1</sup>. The inhibition efficiencies of the compounds were determined from corrosion currents using the Tafel extrapolation method.

### 2.3. Electrochemical Ac Impedance Studies

AC impedance measurements were conducted at room temperature in the frequency range of 100 kHz to 1 mHz and the results were analysed.

## 2.4. Solution Analysis

During the anodic polarization, the metal dissolution takes place releasing considerable amount of metal ions from the material. Hence, the solution were analysed to determine the leaching characteristics of the brass alloys. The solution left after polarization measurements were analysed for copper and zinc by atomic absorption spectrometer to measure the metal ions leached out from the alloys. The solutions containing the optimum concentration of the inhibitor were chosen. A blank was chosen for comparison. The dezincification factor (z) was calculated by

$$z = \frac{[(Zn/Cu)_{sol}]}{[(Zn/Cu)_{alloy}]}$$

where the ratio (Zn/Cu)<sub>sol</sub> is determined from solution analysis and (Zn/Cu)<sub>alloy</sub> the ratio of weight-percent in the alloy <sup>[6]</sup>.

## 2.5. Surface Analysis

The composition of the brass surface after polarization measurements was analysed using energy dispersive X-ray analysis (EDAX).

## 3. RESULTS AND DISCUSSION

### 3.1. weight loss method

The inhibition efficiency (IE) of the inhibitors MBT, TSPC and the combination of MBT and TSPC in controlling the corrosion of brass immersed in 3% NaCl solution for a period of one day is shown in Table 1, 2 and 3 respectively. It can be shown from the data that MBT shows maximum of 71% IE at 150 ppm, whereas TSPC alone is found to be corrosive (negative IE). When MBT (150 ppm) is combined with different concentration of TSPC, it is found that the IE increases with the concentration of TSPC. Interestingly, their combination shows 90% IE. In the absence of MBT, the rate of transport of TSPC towards the metal surface is slower than the rate of the corrosion process on the metal surface. Hence acceleration of corrosion (negative IE) takes place in the presence of TSPC alone. This suggest a synergistic effect between the binary inhibitor MBT and TSPC enhances the IE.

**Table.1. Inhibition efficiency of MBT on brass in 3% nacl by weight loss method**

| S.No | Conc.of MBT ppm | CR (mpy) | IE % |
|------|-----------------|----------|------|
| 1.   | 0               | 0.395    | -    |
| 2.   | 50              | 0.225    | 43   |
| 3.   | 100             | 0.169    | 57   |
| 4.   | 150             | 0.113    | 71   |
| 5.   | 200             | 0.169    | 57   |
| 6.   | 250             | 0.282    | 29   |

**Table 2 Inhibition efficiency of TSPC on brass in 3% nacl by weight loss method**

| S. No | Conc. of TSPC, ppm | CR, mpy | IE% |
|-------|--------------------|---------|-----|
| 1.    | 0                  | 0.395   | -   |
| 2.    | 350                | 0.495   | -25 |
| 3.    | 400                | 0.470   | -18 |
| 4.    | 450                | 0.454   | -15 |
| 5.    | 500                | 0.417   | -6  |
| 6.    | 550                | 0.405   | -3  |

**Table 3. Inhibition efficiency of mixture of 150 ppm of mbt with different concentration of TSPC on brass in 3% nacl by weight loss method**

| S.No | Conc.of MBT, ppm | Conc.of TSPC,ppm | CR, mpy | IE% |
|------|------------------|------------------|---------|-----|
| 1.   | 0                | 0                | 0.395   | -   |
| 2.   | 150              | 350              | 0.056   | 86  |
| 3.   | 150              | 400              | 0.038   | 90  |
| 4.   | 150              | 450              | 0.058   | 85  |
| 5.   | 150              | 500              | 0.077   | 81  |
| 6.   | 150              | 550              | 0.106   | 73  |

### 3.2.Synergism Parameters ( $S_i$ )

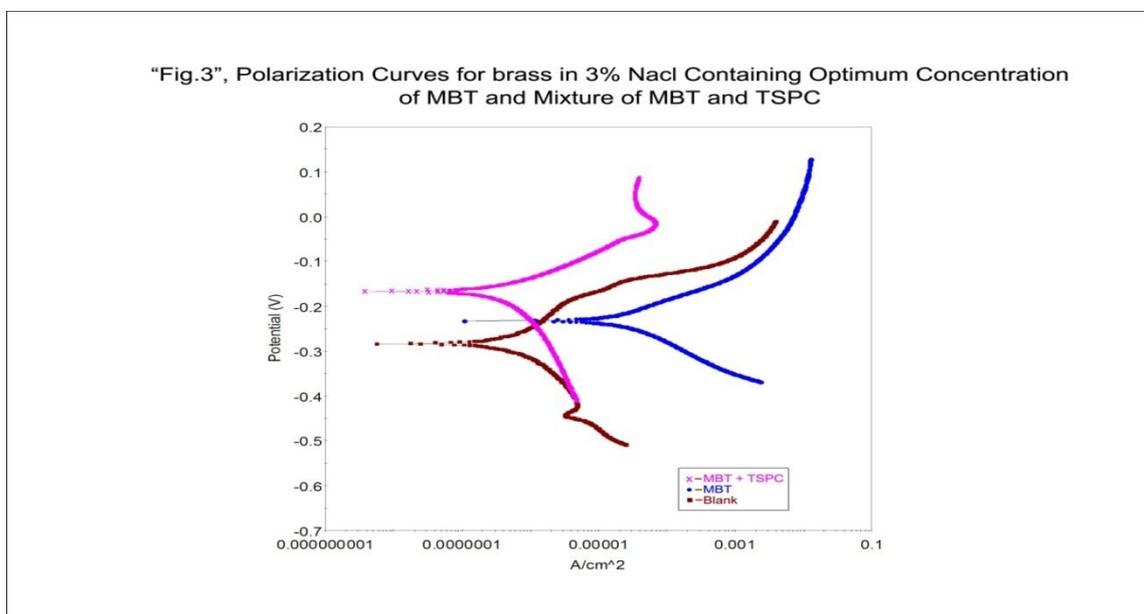
The values of synergism parameters ( $S_i$ ) are shown in Table 4. The values of  $S_i$  are greater than one, suggesting a synergistic effect<sup>[7]</sup>.  $S_i$  approaches 1 when no interaction exists between the inhibitor compounds. When  $S_i > 1$ , this points to the synergistic effect. In the case as  $S_i < 1$ , the negative interaction of inhibitors prevails (i.e., corrosion rate increases).

**Table 4 Synergism parameters  $s_i$  for different concentration of TSPC and with addition of 150 ppm Of MBT on brass in 3% nacl by weight loss method**

| S.No | $I_1$ (IE of MBT) | $I_2$ (IE of TSPC) | $I'_{1+2}$ (IE of MBT+TSPC) | $I_{1+2}$ | $S_i$   |
|------|-------------------|--------------------|-----------------------------|-----------|---------|
| 1.   | 71                | -25                | 86                          | 1821      | 21.4118 |
| 2.   | 71                | -18                | 90                          | 1331      | 14.9438 |
| 3.   | 71                | -15                | 85                          | 1121      | 13.3333 |
| 4.   | 71                | -6                 | 81                          | 491       | 6.125   |
| 5.   | 71                | -3                 | 73                          | 281       | 3.8889  |

### 3.3. Potentiodynamic polarization studies

The potentiostatic polarization curves recorded for brass immersed in various environments are given in “Fig.3”. The respective corrosion parameters are given in Table 5. This shows that the formulation consisting of mixture of MBT(150) and TSPC(400), shifts the corrosion potential to anodic site. This suggests that this formulation effectively controls the anodic reaction. The corroding piece of metal is described as a mixed electrode since simultaneous anodic and cathodic reactions are proceeding on its surface. Anodic inhibitors reduce the anode area by acting on the anodic sites and polarize the anodic reaction. They displace the corrosion potential in the positive direction and reduce the corrosion current, i.e.  $I_{corr}$  value for this formulation is reduced from 23.33 to 7.42 for MBT and 1.45 for the mixture 150 ppm of MBT and 400 ppm of TSPC thereby retard anodic reaction and suppress corrosion rate.



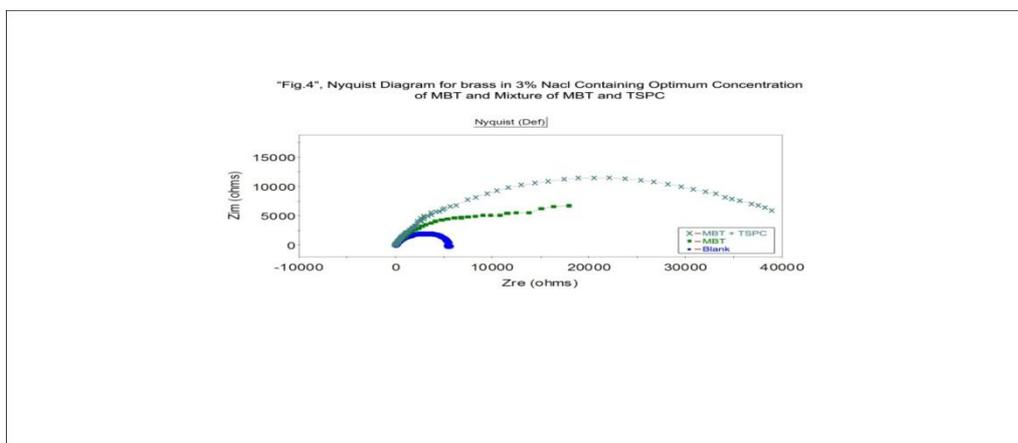
**Table 5. Electrochemical parameters and  $i_e$  for brass in 3% NaCl Containing Optimum Concentration of Inhibitors.**

| S.No | Inhibitor Conc, ppm | $I_{corr}$ $\mu A/cm^2$ | CR,mpy | IE%   |
|------|---------------------|-------------------------|--------|-------|
| 1.   | Blank               | 23.33                   | 6.98   | -     |
| 2.   | MBT (150 ppm)       | 7.42                    | 2.44   | 68.17 |
| 3.   | MBT+TSPC            | 1.45                    | 1.14   | 93.5  |

### 3.4. Analysis of Ac Impedance Spectra

The AC impedance parameters calculated for brass immersed in various test solutions are given in Table 6. The corresponding spectra are shown in “Fig.4”. When brass is immersed in 3% NaCl, the charge transfer resistance ( $R_{ct}$ ) is found to be 4977  $\Omega$ . But for the inhibitor solution, namely 150 ppm of MBT, 150ppm of MBT+ 400 ppm of TSPC ppm, the  $R_{ct}$  value

increases from 4977  $\Omega$  to 15040  $\Omega$ , 30740  $\Omega$  respectively. These results suggest that a protective film is formed on the metal surface.



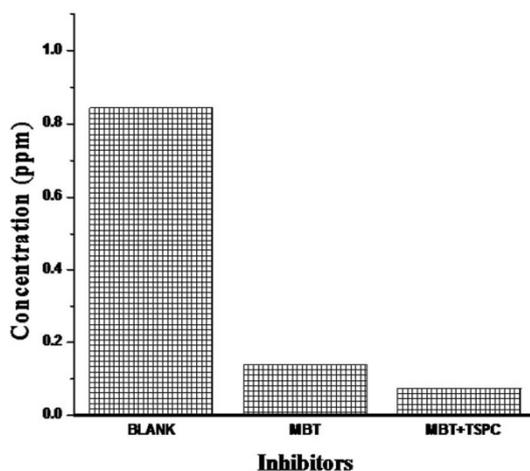
**Table 6. AC Impedance Parameters and IE For Brass in 3% NaCl Solution Containing Optimum Concentration of Inhibitors.**

| Inhibitors | $R_t$ | IE%   |
|------------|-------|-------|
| Blank      | 4977  | -     |
| MBT        | 13040 | 61.80 |
| MBT+TSPC   | 30740 | 83.8  |

### 3.5. Solution Analysis

The results of solution analysis and the corresponding dezincification factor ( $Z$ ) for brass in 3%NaCl, 150 ppm MBT and for the mixture of 150ppm MBT and 400 ppm of TSPC are presented in Table 4. The dezincification factor ( $Z$ ) was calculated using the relation. The results revealed that both copper and zinc are present in the solution. The copper/zinc ratio in solutions were found to be smaller than that of the bulk alloy shown in “Fig.5” and “Fig.6”. This indicates that the growth of surface film and the dissolution of alloy are controlled by diffusion, which is related to the difference between the ionic radii of  $Zn^{2+}$  and  $Cu^{2+}$  ions, 0.074 and 0.096 nm, respectively. The results indicated that the inhibitors are able to minimize the dissolution of both copper and zinc. The %IE against the dissolution of zinc was higher as compared to the dissolution of copper. The dezincification factor obtained in the presence of optimum concentration of MBT and the mixture of (MBT+ TSPC) are 19.16 and 14.85, respectively. This observation suggests that the mixture of MBT and TSPC effectively inhibit the dezincification of brass in 3% NaCl.

"Fig.5". Concentration of copper leached out from brass at optimum concentration of MBT and the optimum concentration of the mixture of MBT and TSPC



"Fig.6". Concentration of zinc leached out from brass at optimum concentration of MBT and the optimum concentration of the mixture of MBT and TSPC

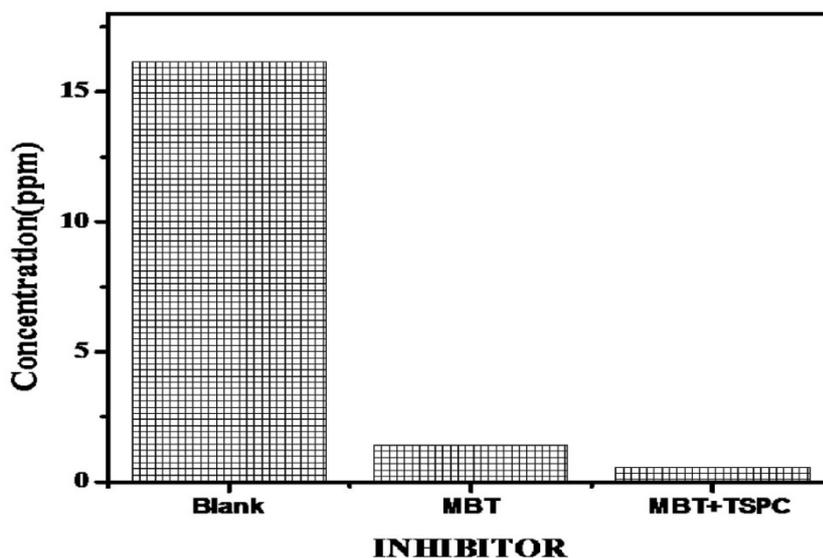


Table.7. Effect of Optimum Concentrations of Inhibitors on The Dezincification of Brass in 3% Nacl Solution

| Inhibitors | Solution Analysis |        | Dezincification factor (z) | % IE  |       |
|------------|-------------------|--------|----------------------------|-------|-------|
|            | Cu                | Zn     |                            | Cu    | Zn    |
| Blank      | 0.844             | 16.157 | 36.34                      |       |       |
| MBT        | 0.140             | 1.413  | 19.16                      | 83.4  | 91.25 |
| MBT+TSPC   | 0.074             | 0.579  | 14.85                      | 91.23 | 96.42 |

### 3.6. Surface Composition Analysis

The surface composition (wt.%) of the alloy in the presence and absence of inhibitors are given in Table 7. In the absence of inhibitors, the wt.% of Cu and Zn are present in the surface were reduced due to the leaching of metal ions in 3% NaCl solution. Moreover, the higher concentration of chloride ions on the surface shows the penetration of Cl<sup>-</sup> ions into the alloy<sup>(18)</sup>. However, in the presence of MBT and in the mixture of MBT+TSPC, the wt.% of Cu and Zn is closer to that of the bulk composition of the alloy. Based on the surface analysis, these inhibitors exhibited excellent inhibition efficiency in sodium chloride solution.

**Table 8. Surface Composition (wt%) of Brass in 3% NaCl after Polarization with Optimum Concentration of inhibitors.**

| Inhibitor | Cu (wt%) | Zn (wt %) | Cl (wt %) |
|-----------|----------|-----------|-----------|
| Alloy     | 65.3     | 34.4      |           |
| Blank     | 57.86    | 24.82     | 17.32     |
| MBT       | 63.58    | 33.35     | 3.07      |
| MBT+TSPC  | 65.10    | 33.89     | 1.01      |

## 4. CONCLUSIONS

1.The corrosion of brass in 3% NaCl has been inhibited by the addition of MBT and the mixture of MBT+TSPC. The IE of MBT+TSPC is higher than that of MBT. 2. The mixture of MBT and TSPC acts as a mixed type inhibitor for brass in 3% NaCl. Significant improvement in inhibiting efficiency was observed in th presence of the mixture of MBT and TSPC. The IE was enhanced to 90% and showed a synergism of inhibition. 3.Electrochemical impedance spectroscopy shows that  $R_t$  values increases in the presence of inhibitors. 4.Solution analysis reveals that the inhibitors excellently prevent the dezincification of brass.

## REFERENCES

1. Mohammed Emad.(Effect of some organic compounds as corrosion inhibitors for brass in cooling water systems). J.American Sci. 2012;8(12): 266-269.
2. Ranjana M, Nandi M M., (Corrosion inhibition of brass in presence of sulphonamidoimidazoline and hydroprimidine in chloride solution).Indian J. Chem.Techn. 2009;16: 221-227.
3. Abdallah M, Al-Agez M, Fouda A.S.( Phenylhydrazone derivatives as corrosion inhibitors for  $\alpha$ -brass in hydrochloric acid solutions). Int.J.Electrochem.Sci, 2009;4:336-352.

4. Karpagavalli Ramji, Darran R, Cairns, Rajeswari S.(Synergistic inhibition effect of 2-mercaptobenzothiazole and tween-80 on the corrosion of brass in NaCl solution). *Appl.Surf.Sci*, 2008; 254: 4483-4493.
5. Jayasree A.C, Ravichandran R.( Corrosion inhibition of new class of substituted benzotriazoles on the brass-mm55 in artificial sea water).*Asian J. Sci and Technology*, 2013; 4(11): 212-219.
6. Ravichandran R, Rajendran N.( Electrochemical behavior of brass in artificial seawater: effect of organic inhibitors).*Appl. Surf.sci*. 2005; 241: 449-458.
7. Fouda A.S, Mahfouz H.( Inhibition of corrosion of  $\alpha$ -brass (Cu-Zn, 65/33) in HNO<sub>3</sub> solutions by some arylazo indole derivatives).*J.Chil.Chem.Soc.*, 2009; 54(3): 302-308.
8. Ravichandran R, Rajenderan N, (Influence of benzotriazole derivatives on the dezincification of 65-35 brass in sodium chloride).*Appl Surface Sci.*, 2005; 239:182-192.