CHAPTER-II

2. SCOPE OF THE ELECTROLESS COPPER PLATING PROCESS

2.1 LITERATURE SURVEY

EDTA has been one of the most widely used chelating agents in electroless copper plating (Mallory G.O., *et al*., 1990; Salkauskas M., *et al*., 1985; Vaskelis A. *et al*., 1966; Vaskelis A *et al*., 1986; Vaskelis A., *et al*., 1991), but its poor degradability causes serious environmental problems (Norkus E., 2006.a). Polyhydroxylic compounds have therefore gained importance as chelants in electroless plating because they are easily bio-degradable (Norkus E., *et al*., 2005).

The interactions of saccharose and xylitol with Cu(II) ions in alkaline medium were studied in the late 20th century. It was found that the chelating abilities of saccharose and xylitol depend on pH solution and the concentrations of Cu(II). The formation of soluble Cu(II)-saccharose and xylitol compounds was observed at pH values >10. Saccharose was able to adequately chelate Cu(II) ions under conditions of excess saccharose, to prevent $Cu(OH)_2$ precipitation at pH values > 12. Thus calculated pCu values were higher than those necessary to prevent formation and precipitation of copper (II) hydroxide. Experiments indeed confirmed that $Cu(OH)_{2(s)}$ precipitates were not formed at pH values > 12 and solutions became dark blue, whereas at lower pH values formation of $Cu(OH)_{2(s)}$ was clearly seen. No predominate species was observed in pH region from 12.25 to 13, whereas at pH 13, 50 % of Cu(II) was in the form of the $CuSa_2(OH)_2^{4-}$ complexes that clearly predominate at higher pH values.

Xylitol was found to be a better chelating agent than saccharose because it greatly changed all the physical and electrochemical properties of the bath. Xylitol had optimum performance at pH 13.25. Saccharose and xylitol have been proposed

as ecofriendly chelating agents to be used in MSA baths because they form sufficiently stable complexes with Cu(II) ions in alkaline solutions.

A survey of literature shows that, the studies on biodegradable 'green' methanesulphonic acid (MSA) with environmentally safe polyhydroxlic compounds such as saccharose and xylitol are limited. It has been shown that replacing copper sulphate by methanesulphonate produces a stable ligand in alkaline solution. Using formaldehyde as reducing agent is not new, but its combined with methanesulphonic acid and natural polyhydroxylic compounds is new and promising.

The current work studied the following:

(i)   Development of a novel copper methanesulphonate bath by the addition of stoichiometric quantity of methanesulphonic acid to copper carbonate.

(ii)   Establishment of the utility of environmentally safe natural polyhydroxylic compounds such as sacchaorse and xylitol as complexing agent.

(iii)   Study of the suitability of formaldehyde as a reducing agent in the above bath. Formaldehyde was chosen because it is suitable for all conditions and works well with most electroless baths.

(iv)   The suitability of using KOH as the pH adjuster for this electroless plating work. KOH is the better pH adjuster than NaOH, because it can alter film properties and increase the solubility of byproducts formed.

(v)   Twelve stabilizers are selected for investigating viz., pyridine, glycine, 2-mercaptobenzothiazole, thiourea, imidazole, N-methylthiourea, 2,2-dipyridyl, benzotriazole, benzimidazole, 1,10-phenanthroline, phenylthiourea and diphenylthiourea. These specific stabilizers are chosen because of their excellent physical and electrochemical properties in electroless plating baths.

In order to optimize the electroless plating bath, the influences of the following factors on the efficiency of electroless plating were investigated further.

(i)   Concentration of copper methanesulphonate ions

(ii)   Concentration of reducing agent

(iii)   Bath temperature

(iv) pH

This work also studied the morphology of electroless coated copper through SEM and AFM analysis and crystallite sizes were measured using XRD techniques

The quality and quantity of electroless copper deposition from the methanesulphonate bath were investigated through cyclic voltammetry and corrosion kinetics parameter was investigated by Tafel polarization technique. Charge transfer resistance and double layer capacitance were also measured by electrochemical impedance technique.

2.2 PARTICULATE MATTER

Particles present in electroless copper solution act as nuclei for seeding. Rochelle's salt is commonly produced as a byproduct during electroless copper plating. This is colloidal in nature and can cause seeding out of the bath. Cu_2O is also a common precipitate in such processes and can act as a local point for seeding. The Cu_2O however tends to disproportionate readily and the copper particles formed are randomly dispersed throughout the solution (Saubestre E.B., *et al*., 1965) and contribute to the instability of the bath. Several workers such as Bockris (1949) have improved bath stability and minimized the formation of Cu_2O by

(i)   Mechanical agitation.

(ii)   Maintaining all the constituents at a very low concentration.

2.3 EFFECT OF CHELATING AGENTS

In general, complexing agents are extensively used in many fields of industry. They are used to provide effective control of trace metal ions in cleaning industries, textile, pulp and paper production, water treatment, agriculture, food industries,etc. Recently, the poor biodegradability of compounds used as complexing agents and their accumulation in the environment has become a cause for concern.

The commercial electroless copper deposition baths are strongly alkaline solutions of complexes of cupric salt, complexing agent, reducing agent and functional additives of different organic and inorganic compounds. Various complexing agents such as EDTA, triethanolamine, tartarate, quadral, trisodium citrate, malic acid and lactic acid (Norkus E., *et al*., 2000; Pauliukait E.R., 2006; Regina Fuchs-Godec., 2013) have been used in electrolysis bath. Ethylenediaminetetraacetic acid (EDTA) is one of the most widely used chelating agents for electroless copper plating, because it is not only very weakly adsorbed on copper (Balakrishma P., *et al*., 1973; Dumesic J., 1974; Satas D., 1991) surface, but also has excellent chelating properties over a wide *p*H range. EDTA bath shows dual chelating property and is employed to avoid cupric hydroxide precipitation and to prevent the bath from becoming unstable as electroless plating proceeds. The EDTA bath is stable up to 70 ºC and the optimum operating temperature and *p*H for the bath are 45-60 ºC and 13.0 respectively. The use of EDTA, however, raises environmental pollution issues (Norkus E., 2007) because of the following reasons:

      (i)   EDTA forms stable heavy metal complexes.

      (ii)   EDTA increases the total nitrogen content of waste water.

      (iii)   It is very weakly bio-degradable.

      (iv)   Treatment of waste water containing EDTA is difficult.

The use of triethanolamine (TEA) as a chelating agent has been reported to result in plating rate about 20 times higher than when using EDTA (Kondo K., *et al*., 1991; Kondo K., 1992). The SEM analysis of copper deposition with TEA as chelant showed shrinkage in the grain while grain size was more uniform with EDTA.

Polyhydroxylic compounds have been gaining importance as chelating agents in electroless plating because they are bio-degradable. Many natural polyhydroxylic compounds like xylitol, alditol, erythritol, adonitol, D-mannitol, D-sorbitol, maltitol, lacticol and dulicitol have been proposed as environmentally friendly chelating agents for alkaline electroless plating. These natural polyhydroxylic chelators are stable and possess good chelating properties for Cu (II) ion in alkaline medium (Balaramesh P., *et al*., 2014.b). Xylitol forms three mononuclear copper (II) hydroxyl complexes at high ligand-to-metal ratios and under optimal operating conditions a plating rate of 2.5-3 µm/h has been observed. The plating solutions are stable and no signs of Cu (II) reduction in the bulk solution are observed. The copper surface obtained at *p*H 13.5 is catalytically less active due to the formation of Cu (I) oxy and hydroxyl species. These species are also found in studies of electroless copper plating that use ligands such as glycerol and L (+) tartarate. The Cu(I) species retard the auto catalytic reduction of Cu(II) by retarding the oxidation of formaldehyde (Norkus E., 2006.b ; Vaškelis A., 2004). When hexilitol is used as complexing agent, only Cu(II) reduction is observed.

Saccharose is another ecofriendly chelating agent that has been studied by Norcus *et al*., (1995). Saccharose forms sufficiently stable complexes with Cu(II) ion in alkaline solution (Norcus E., *et al*., (2004). The plating starts at *p*H value above 12, and maximum plating rate is observed at *p*H of 12.75, the plating rate is

reduced at higher pH values. A plating rate of 3 µm/h has been observed under optimal condition.

Glycerine (Koyano H., *et al.*, 1992) and Triethanolamine have also been reported as complexing agents and accelerators have been found to increase the deposition rate. Ethylenediamine exhibits strong adsorption on copper surface and enhances Cu (II) reduction over EDTA and TEA. It would serve as an outstanding grain refining agent. Changes in the concentration of copper sulphate have little effect on grain size.
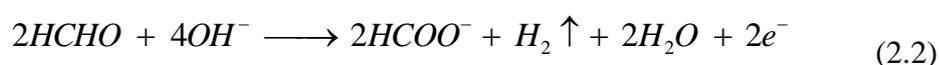
2.4 EFFECT OF REDUCING AGENTS

Traditionally, the electroless copper bath has used formaldehyde as the reducing agent along with various complexing agents (Mishra K.G., *et al.*, 1999). Wein (1959) and Saubestore (1959) have reviewed reducing agents used in electroless copper solution. A good reducing agent for electroless copper baths should be capable of completely reducing divalent copper to metallic copper and not to intermediate cuprous oxide. Some common reducing agents that have been used in electrolysis baths are formaldehyde (Gottesfeld S., *et al.*, 1986), ascorbic acid, dimethylamine borane, borohydride, hypophosphite and hydrazine (Deckert C.A., 1994; Deckert C.A., 1995.a) ; Deckert C.A., 1995.b). When formaldehyde is used as the reducing agent in the plating bath, the electroless copper deposition can be considered to consist of the following "two half-reactions".
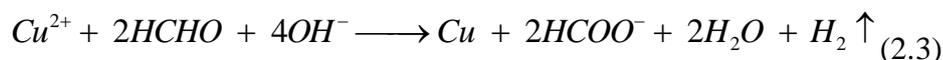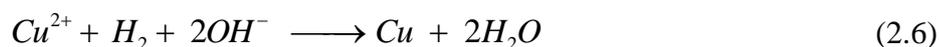
Cathodic reaction,

$$Cu^{2+} + 2e^- \longrightarrow Cu \tag{2.1}$$

Anodic reaction,

$$2HCHO + 4OH^- \longrightarrow 2HCOO^- + H_2\uparrow + 2H_2O + 2e^- \tag{2.2}$$

Over all reaction,

$$Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu + 2HCOO^- + 2H_2O + H_2\uparrow \quad (2.3)$$

The complete set of reactions is given below,

$$Sn^{2+} + Pd^{2+} \longrightarrow Sn^{4+} + Pd \qquad (2.4)$$

$$HCHO + OH^- \xrightarrow{Pd} H_2 + HCOO^- \qquad (2.5)$$

$$Cu^{2+} + H_2 + 2OH^- \longrightarrow Cu + 2H_2O \qquad (2.6)$$

$$HCHO + OH^- \xrightarrow{Cu} H_2 + HCOO^- \qquad (2.7)$$

Equations (2.5) and (2.7) resemble each other except in the fact that the catalyst Pd is replaced by Cu, hence the reactions proceeds auto catalytically as in (2.7). Equation (2.4) shows the role of stannous ions in the reaction. The reaction can proceed in their absence in metallic substrates, the formaldehyde in the alkaline electroless copper bath acts as the reducing agent according to the equation

$$Pd^{2+} + HCHO + 3OH^- \longrightarrow Pd + HCOOH + H_2O \qquad (2.8)$$
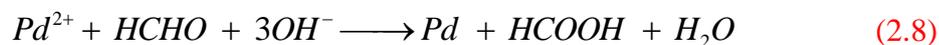
Equation (2.8) may replace equation (2.4) when the specimen is first immersed in $PdCl_2$ and then transferred to the alkaline electroless bath. A black film is formed on the surface which is presumably Pd present in the active state. Presence of cupric ion is essential to evolve hydrogen gas. From quantitative experiments involving OH^- and Cu^{2+} consumption as a function of H_2 evolution, the following data were proposed

(i) For each mole of copper deposited, at least two moles of formaldehyde and four moles of OH^- are consumed.

(ii) For each mole of copper deposited, one mole of hydrogen gas is evolved.

Paunovic M (1968) supported and made a noteworthy contribution by elucidating the electrochemical nature of the electroless processes.

Generally, autocatalytic reduction of Cu(II) by formaldehyde from solution containing the ligands begins at pH above 12, is maximum between 13.2 and 13.7, and becomes slow at higher pH values.

Formaldehyde is conventionally used as a reducing agent in electroless copper plating (Meerakker J., *et al*., 1981.a ; Mishra K.G., *et al*., 2010), but it presents problems such as those listed below (Honma H., 1994).

(i) The high vapour pressure involved makes the working conditions tough.

(ii) Formaldehyde corrodes the tracheal tissues and is also a carcinogen.

Brookshire (1962) and Cheng DH., *et al.,* (1997) have studied hypophosphite as a reducing agent and have compared the rates of deposition as a function of hypophosphite concentration and temperature with formaldehyde based solutions. The use of non-formaldehyde (Li J., *et al*., 2003) reducing agents such as hypophosphite is attractive because of lower pH of operation, low cost and relative safety, but the process is complicated because copper is not a good catalyst for the oxidation of hypophosphite resulting in little or no plating on a pure copper surface. Hence traces of Ni are added as catalyst (Hung A., *et al*., 1989; Li J., *et al*., 2002).

The main overall reaction for electroless copper using hypophosphite as reducing agent is,

$$Cu^{2+} + 2H_2PO_2^{2-} + 2OH^- \longrightarrow Cu + 2H_2PO_3^- + H_2 \uparrow \qquad (2.9)$$
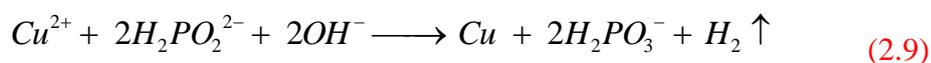
Additionally, there is a side reaction that consumes hypophosphite and evolving hydrogen gas (Hung A., *et al*., 1985.a).

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + H_2 \uparrow \qquad (2.10)$$
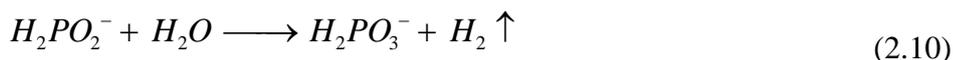
Glyoxylic acid was the next choice as reducing agent for electroless copper plating. The overall reaction is,

$$Cu^{2+} + 2CHOCOOH + 4OH^- \longrightarrow Cu + 2HC_2O_4^- + 2H_2O + H_2 \uparrow \qquad (2.11)$$
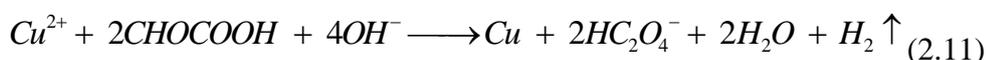
Standard redox potential

$$CHOCOOH + 3OH^- \longrightarrow HC_2O_4^- + 2H_2O + 2e^- \quad = +1.01V / SHE$$

$$(2.12)$$
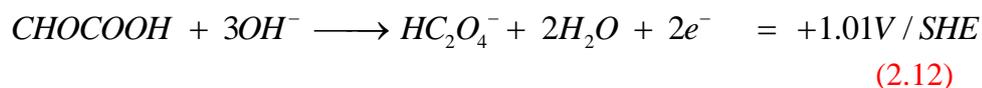
This reaction is commonly accompanied by the Cannizzaro reaction,

$$2CHOCOOH + 2OH^- \longrightarrow C_2O_4^{2-} + HOCH_2COOH + H_2O \quad (2.13)$$
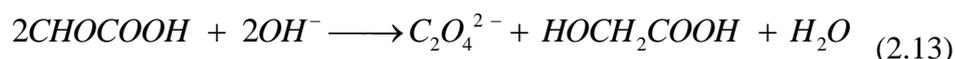
The Cannizzaro reaction results in the accumulation of glyoxyalate and oxalate ions in the bath, resulting in the precipitation of sodium oxalate when NaOH is used as the pH adjusting agent and potassium oxalate when KOH is used. This has been confirmed by I.R spectrophotometry. The plating rate, uniformity, ductility and stability in glyoxylic acid bath (Lu Yu., 2013) were superior to those obtained using formaldehyde bath under standard condition The bath had no vapour pressure and showed good reducing power in electroless copper plating (Wu X., *et al*., 2008). Hence, glyoxylic acid can replace formaldehyde and eliminate health and environmental problems (Karthikeyan S.*, et al*., 2002; Wu X., *et al*., 2009). Other reducing agents have been investigated such as phosphinate, hydrazine (Ohno I., 1985), aminoborane and phenylhydrazine, but their applications are limited, because bath stability and deposited film properties are not optimal (Meerakker J., 1981.b; Van den Meerakker J. E. A. M., 1989).

2.5 EFFECT OF ADDITIVES

Schoenberg (1971&1972), Paunovic and Arndt (1983) have shown that additives may have two opposing effects, acceleration and inhibition (Balaramesh P., *et al*., 2014.c). Trace quantities of additives present in an electroless plating solution can act as stabilizers, accelerators, modifiers of deposit properties or inhibitors (Lin Y.M., *et al*., 2001; Nuzzi F.J., 1983; Paunovic M., 1980; Paunovic M., *et al*., 1981) and can influence the following:

(i)   Kinetics (Donahue F.M., 1980; El-Raghy S.M., *et al*., 1979)   and mechanism of the crystal growth process (Donahue F.M., *etal*., 1973); Molenaar A., *et al*., 1974) Schumacher R., *et al*., 1985; Shippey FL., 1973).

(ii)   Bath passivation process.

(iii)   Structure and morphology of the deposit (Balaramesh P., *et al*., 2014.d).

(iv)   Physical properties of metal deposit.

(v)   Purity of deposit (Hirohata H.*, et al*., 1970).

The stability of the solution can be improved by the addition of a stabilizer (Saubestre E.B.,(1972). This stabilizer can affect the deposition process and properties of the electroless copper coatings and can be selected from a long list of inorganic compounds. The list includes carbonates and phosphates, and salts of magnesium, lanthanum, gallium, thallium (Bhattacharya RN *et al*., 1999) and ammonia; other compounds include borates, silicates and arsenates.

The use of inorganic additives as stabilizer has been reviewed by Bielinski and Kaminski (1987), over two hundred papers and patents had been published on the effects of large number of these stabilizers on the plating solution. Compounds having planar and other structures with lone pairs of electrons such as sulphur and nitrogen containing organic compounds have been proposed to serve as stabilizers (Ramasubramanian M., *etal* ., 1999) : pyridine, cytosine, thiourea, guanidinehydrochloride, 2-mercaptobenzothiozole (2MBT), KCN, potassium ethylxanthogenate, benzotriazole, polyethyleneglycol (PEG), dithiocarbamate (Balaramesh P., *et al*., 2014.e; Balaramesh P., *et al*., 2014.f) and 2,2'-dipyridyl (Hung A., 1985; Duda L.L., (1998) etc.

Hetereo-organics that contain heteroatoms such as nitrogen and sulphur, affect the plating rate through the following effects (Saito M., 1966),

(i)   Absorption of the additives on copper surface decreases the plating rate.

(ii)   Delocalized π-electron enhances the plating rate.

(iii)   Stronger the complexing ability of additives with Cu(I) than with Cu(II) stabilizer will be solution.

The effect of these heteroatom-containing organic compounds on elecroless copper deposition from EDTA solution was studied by weight gain method and microdensitometry by Platti R.C.V., *et al*., (1989).   It was found that small concentration of these hetero-organics improves bath stability and result in bright copper deposit at 75°C.   The presence of delocalized π electron in their structure enhances the plating rate as a function of *p*H as explained by Nuzzi F.J., (1983).

Glycine and cytosine act as corrosion inhibitors.   In reversible equilibrium, glycine reacts with formaldehyde to form a condensation product.

$$NH_2CH_2COOH \ + \ HCHO \ \longleftrightarrow \ CH_2NCH_2COOH \ + H_2O \qquad \text{(2.14)}$$

Increasing the glycine concentration tends to lower the free formaldehyde concentration, which in turns decreases the plating rate and increases ductility and tensile strength of the copper deposits.

Adenine and guanine act as accelerators in electroless copper deposition, and also suppress oxidation and passivation of metallic copper in alkaline solution.

The accelerating property is due to the N atom, π electron density and π electron adsorbed molecules.   Sulphur compounds have also been used in conjugation with nitrogen compounds like nitrile (Schneble F.W., 1968). The sulphur compounds such as thiourea, generally act as stabilizers (Schneble F.W., 1966; Torigai E., 1968.a; Torigai E., 1968.b).

Hung A., (1985.b) found that guanidinehydrochloride enhances the plating process thermodynamically and kinetically. It was also observed that the composition of the deposited copper changes, which influences the follow-up deposition. Ammonia acts as an effective accelerating agent in electroless copper plating. The electroless deposition rate has been found to decrease with the addition of 2,2'-dipyridyl to the plating solution and the colour of the deposit changes from dark brown to semi-bright. The deposit was also found to have smaller crystals and higher (111) plane orientation. 2,2'-dipyridyl has been reported to improve the micro structure and properties in hypophosphite bath (Oita M., *et al*., 1997; Li.J., *et al*., 2004a). The deposits became uniform and compact because 2,2'-dipyridyl inhibited catalytic oxidation, thus reducing the deposition rate and making the deposit fine in structure (Fumihiro Inoue., *et al*., 2014; Kondo K., *et al*., 1993; Li.J., *et al*., 2004b). Sodium dodecylsulfate (SDS) is a good anodic inhibitor very close to the rest potential. The inhibition efficiency copper corrosion increases with an increase in concentration (Chadwick D., *et al*., 1978).

Benzotriazole (BTA) is a well-known organic inhibitor in acidic medium. It contains a nitrogen-based polar group. These nitrogen atoms act as electron donors and enhance chemisorptions on the surface of the metal (Fox P.G., *et al*.,1979; Kahled K.F, 2009; Vaskelis A., *et al*., 2007;) the vacant 'd' orbitals in copper atom form coordinate bonds with electron donating atoms such as nitrogen. Additionally, there is also interaction with rings containing conjugation, and these result in corrosion inhibition (Antonijevic M.M., 2008). BTA shows two polymeric structures, depending on the nature of the copper oxide present. Cuprous oxides yield Cu(I) BTA, which consists of linear polymeric chains. Cuprous oxide yields Cu(II) BTA, which has a network structure.

2.6 EXAMPLES OF ELECTROLESS COPPER BATHS

Table 2.1 Examples of various electroless copper baths

	Cu $^{2+}$ ion	Complexing agent	Reducing agent	Stabilizer/ surface activator	pH	Tempe- ratue
Bath-1	$CuSO_4.5H_2O$ (0.05 M)	Xylitol/ D-Mannitol/ D-Sorbitol (0.10 M)	HCHO (0.15 M)	-	13.5	20-30ºC
Bath-2	$CuSO_4.5H_2O$ (0.05 M)	Saccharose (0.1M)	HCHO (0.15 M)	-	12.2	20ºC
Bath-3	$CuSO_4.5H_2O$ (6.0 g/L)	Triethanol- amine (0.6 g/L)	HCHO (10 ml)	-	13.5	45±0.1ºC
Bath-4	$CuSO_4. 5H_2O$ (0.04 M)	Sodium citrate (0.051M)	Sodium hyphophos- phite(0.28 M)	Formadine disulfide (250 ppm)	9.5	70±5ºC
Bath-5	$CuSO_4.5H_2O$ (0.04 M)	Sodium citrate (0.051M)	Sodium hyphophos- phite(0.28 M)	2,2'-dipyridyl (20 ppm)	9.5	70±5ºC
Bath-6	$CuSO_4.5H_2O$ (0.05 M)	L-tartrate (0.15 M)	HCHO (0.15 M)	-	12.5	20ºC
Bath-7	$CuSO_4.5H_2O$ (0.06 M)	EDTA (0.08 M)	HCHO (0.18 M)	NH_3 (50 mg/L)	12.7	30ºC
Bath-8	$CuSO_4.5H_2O$ (0.04 mol/L)	EDTA (0.1 mol/L)	Glyoxylic acid (0.03 mol/L)	2,2,dipyridyl (0.005 M/L)	12.6	70ºC
Bath-9	$CuSO_4.5H_2O$ (6.0 g/L)	EDTA (70 g/L)	Glyoxylic acid (18 g/L)	2,2,dipyridyl (0.04 g/L)	12.5	70ºC
Bath-10	$CuSO_4.5H_2O$ (13.3 g/L)	Quadrol (16.8 g/L)	HCHO (16 ml/L)	2-MBT (2.0 mg/L)	12.7	30 ºC
Bath-11	$CuSO_4.5H_2O$ (18 g/L)	EDTA (48 g/L)	HCHO (22.5 ml/L)	$K_4Fe(CN)_6$ (57.3mg/L)	12.8	30ºC
Bath-12	$CuSO_4.5H_2O$ (5.0 g/L)	EDTA (21 g/L)	HCHO (16 ml/L)	PEG 1000 (1 g/L)	12.7	50 ºC

There are three primary uses for benzotriazole:

(i)   Corrosion inhibitor.

(ii)   U.V light stabilizer for plastics.

(iii)   Antifoggand in photography (Wu X., *et al*., 1998).

BTA derivatives have been found to be good inhibitors in stimulated carbonation attack on concrete and afford protection to steel in SCP solution, indicating their applicability in reinforced concrete construction (Ababneh A., *et al*., 2009). BTA is the only inhibitor that provides effective protection to copper archeological artifacts during preservation process (Guilminot E., *et al*., 2000).

Tolytriazole is superior to benzotriazole and it is used as anti corrosive additive in cooling and hydraulic fluids, antifreeze formulation, aircraft deicer and anti-icer fluid (ADAF) and dishwasher detergents for silver protection (Alkharafi F.M., *et al*., 2009; Giger W., *et al*., 2006).