CHAPTER II

LITERATURE SURVEY AND SCOPE OF THE WORK

2.1 COPPER ELECTRODEPOSITION

Copper deposits find extensive applications in nickel [1] and chromium plating as an undercoat, in printing and electronics industries [2,3]. Of the plating systems that have been studied only a few have proved to be commercially viable. These are acid based fluoborate and sulphate solutions, alkaline cyanide and pyrophosphate complex ion systems. While the acid baths offer 100% cathode efficiency, the alkaline baths excel in producing fine-grained, smooth deposits without the problem of displacement reaction along with good throwing power.

2.1.1 Baths used for copper electrodeposition

2.1.1.1 Acid copper bath

Acid copper deposition has been referred since 1810. In 1831, Bessemer [4] copper plated steel castings by immersion in copper sulphate solution. In 1836 the Daniel cell was first used for electrodepositing copper and a technical report was published [5]. Most of the efforts dealt with copper sulphate-sulphuric acid solutions but nitrate [6], acetate [6] and copper chloride [7] solutions were also investigated. In recent times, the following solutions have been evaluated; sulphate-oxalate [8] copper chloride [9], copper chloride-sodium thiosulphate [10], iodide and chloride [11], fluoborate [12] alkane sulfonic acid [13], sulphamic acid [14], copper$^{2+}$-formate with ammonium salts [15], phosphate-sulfate [16] fluosilicate [17], fluosilicate-silicic acid [18], copper$^{2+}$ glycolate, lactate, malate or tartrate [19] etc.
Copper sulphate and sulphuric acid are the primary constituents of the sulphate solutions. The concentration of copper sulphate is not particularly critical although the resistivity of the solution is greater, when the concentration is increased [20]. G.M.Kimber et al. Suggested that cathode polarization increases slightly at copper sulphate concentrations above 1M [21]. Changes in the concentration of copper sulphate have little effect on grain size. Chloride ion, in bright and high-throw acid sulfate solutions, reduces anode polarization [22].

An extensive list of additives used in acid copper plating, have been reported in technical literature publication include benzothiazole [23-26], cadmium [27], casein [28], cobalt dextrin [29], dimethyl amino derivatives [29], disulphide [30,31] 1-8-disulphonic acid [25] disodic-3, 3-dithiobispropane sulphonate [31], 4,5,dithiooctane-1-8-disulphonic acid [25], dithioetheritol [32], ethylene oxide [31], gelatin [33], glue [28,34], lactose benzoyl hydrazone [35], 2-mercapetoethanol [36], molasses [28] sulphonated petroleum [34], 0-phenanthroline [27,37], poly ethoxy ether [38], poly ethylene glycol, [39-41],poly ethylene imine [40], polyN,N-diethyl saphranin [31], polypropylene ether [42], propylene oxide [31], sugar [28] thiocarbamoyl-thioalkane sulphonates [43] and thio urea [44-47]. Chloride ion can also be considered as an additive. An increase in bath temperature results in higher conductivity and reduces anode and cathode polarization. Clear evidence has been reported of grain refinement produced by increasing the current density [48, 49].

The concentration of addition agent is controlled by many techniques such as cyclic voltammetry stripping [50-52] cyclic pulse voltammetric stripping [53] chromatography [33], high-performance liquid chromatography [54-56] differential pulse polarography [57] and spectrophotometry [58-60]. Mechanical properties of copper
electrodeposits [61, 62] such as hardness [63, 64], tensile strength [65, 66], and stress [67] have also been reported.

2.1.1.2 Cyanide copper bath

The first commercially successful high-efficiency solutions were introduced in 1938. It was extensively used throughout the automotive industry in subsequent years for plating die-castings as well as steel parts. Copper cyanide solutions may be classified in three categories, viz., strike, Rochelle and high-efficiency baths. Strike solutions are used extensively to apply relatively thin coatings of copper as an undercoating [68].

The Taguchi method was used to evaluate a number of parameters in copper cyanide solutions. An increase in copper concentrations and decrease in potassium cyanide resulted in good current efficiency over a wide current density range. Hydroxide and carbonate concentration were of secondary importance [69]. Additional information on kinetics is also dealt with [70]. The concentration of the free cyanide increases at high temperatures, since lower complexes are formed and free cyanide is there by liberated. Alkali is essential for anode corrosion [71].

Additives for cyanide copper system include compounds having active sulphur group and/or containing metalloids such as selenium or tellurium. Other reported addition agents include organic amines or their reaction products with active sulphur containing compounds. An extensive listing of additive used in acid and cyanide copper prior to 1959 are available in patents [72-85]. Polarisation phenomena in copper cyanide solution have been extensively investigated [86]. Copper plated from cyanide solution in highly embritiling to high strength steel substrates because of the low current efficiency of the solution and the easy entry of hydrogen into steel in cyanide solutions. Cyanide
solutions are finding least importance nowadays because of their toxicity, waste disposal and effluent treatment problems. They are being replaced by non-cyanide solutions.

2.1.1.3 Copper pyrophosphate bath

A number of desirable features have been observed with copper pyrophosphate bath. It is non-corrosive, non-toxic, with good throwing power and produces smooth to bright copper deposits with 100 % cathode efficiency. It is commonly used in the electronic industry for plating of PCB, due to its good throwing power. Though the cyanide baths are having very good throwing power they cannot be used in the electronic industry because cyanide is harmful to the plastic laminated boards.

Organic and inorganic additives such as mercaptothiadiazoles [87-94] pyrimidnes [95, 96] glycerol, triethanol amine, sodium sulfite [97], naphthalene disulphonic acid [98], gelatin, bakers yeast, casein, glycol [99] sodium selelnite [96] have been used as brighteners. The influence of pH, temperature, agitation, and current density on throwing power and efficiency has been dealt with by B.F.Rothschild [100]. Tam and coworkers [101,102] used cyclic voltammetry stripping technique to study the effects of all constituents of cathodic and anodic reactions. Structure of deposit [103], porosity, adhesion [104], physico-mechanical properties of coatings and their application [105] has also been reported for pyrophosphate bath. Pyrophosphate solutions are considerably more expensive to make up than high-throw acid copper formulations. Waste pyrophosphate solutions are difficult to treat because of ammonia in the solutions and also the complexes that are formed [106]. Hence, these solutions have been almost entirely replaced by acid copper, except for some military and special applications.
2.1.1.4 Copper-EDTA bath

In the case of electrodeposition of copper from EDTA bath, complexation of copper and effect of ultrasonic agitation on initial process of copper deposition was studied [107-110]. The properties of copper deposit obtained from EDTA bath was reported [111]. The influence of dipyridal ion on kinetics of cathodic reaction of copper from EDTA solution has been studied [112].

2.1.1.5 Alkaline non-cyanide copper bath

Alkaline non-cyanide plating solutions have found increasing popularity since the mid 1980s because of environmental issue. It is having very good throwing power than the high-throw acid formulations used in PCB boards. Alkaline copper plating baths based on tripolyphosphate [113], phosphate [114], ethylenediamine [115-117], polyethylene polyamine [118], triethanolamine [119], glycerolate [120] alkaline glycerol [121] have been reported. Disadvantages of alkaline non-cyanide bath (i) include higher operating costs, (ii) difficulty during plating of Zinc die-castings, (iii) greater sensitivity to impurities and (iv) more difficult chemistry for controlling purposes [122].

2.1.1.6 Copper methane sulphonate bath

Deposits from sulphonate bath are similar to those from sulphate bath but are useful for high current density operations. The copper methane sulphonate was obtained by dissolving copper carbonate in pure methane sulphonic acid. However, the literature available on this bath is scarce, not much work has been carried out on this bath.

2.1.2 Application of Copper electrodeposits from various bath

Electrodeposition of copper from acid solution is extensively used for electroforming, electrorefining and electroplating. Acid copper sulphate solutions are
widely used for plating of printed wiring boards and for semiconductor interconnect technology. Electroformed copper articles include band instruments, heat exchangers, reflectors and a variety of articles for military and aerospace applications [123]. Zinc die-castings are plated with approximately 15 micron of leveling acid copper [124] before nickel and chromium plating, to eliminate buffing before plating. Metal powders produced by deposition in acid solutions are used for making sintered compacts and pigments [125]. IBM researchers have successfully implemented copper electroplating technology for the fabrication of chip interconnecting structures [126,127].

Electroforming with acid copper is used as one of the primary methods of fabricating the outer shells of regenerative cooled thrust chambers for advanced design rockets and other applications. High-speed copper plating has been used for commercial applications such as electroforming of flexible printed circuits [128], in mold plating of polymeric materials [129].

Deposits obtained from cyanide baths are used as undercoats for other deposits (i) to protect basis metal or promote adhesion, (ii) for surface improvement in buffing, (iii) to improve soldering operations (iv) to improve lubricity and (v) on printing rolls. A high-speed cyanide copper-plating process is used to produce heavy coatings of copper on steel wire for electrical application [130].

The production of electroformed objects such as wave-guides, paint spray masks, helical antennae [131], high strength deposits are produced from pyrophosphate bath. Other applications include, plating on zinc die castings before nickel and chromium plating on steel for selective hardening operations such as nitriding and carburizing [132], and in roll plating [133]. Pyrophosphate solutions are also used for plating through holes
on PCB, although in most cases this application has been replaced by high throw-acid copper sulfate formulations.

2.2 LEAD ELECTRODEPOSITION

Lead has high hydrogen over potential. The values for the hydrogen over potential are dependant on the structure and surface of the electrode, as varying between 0.84 V for 99.8 % pure lead [134] to about 1.2 V for electrolytically deposited coatings [135]. Electrodeposited lead has good ductility and higher hardness then metallurgical lead. In addition, lead plating is superior to lead dipping since objects can be stamped and machined without distortion and there is a minimum amount of stress present in electrodeposited lead coating. The principle uses of electrodeposited lead are for the protection of accumulator clips, and terminals horticultural spraying equipment, fire extinguisher bodies, and small items of chemical plant that are subjected to corrosion by sulfuric acid. Electrolytic deposition of lead has been investigated using acid alkaline and neutral solutions. An important perquisite for such a process is a high solubility of the lead salts to be used and stability of the anion against hydrolysis in the electrolyte.

2.2.1 Electrolytes used for lead electrodeposition

2.2.1.1 Per chlorate Electrolyte

Per chloric acid electrolytes are very suitable for electrodeposition of lead because of the high solubility of lead is such electrolyte and the high electrical conductivity of the solution. However such electrolytes are not widely used in practice, partly because of the high price of the acid and its hazardous nature which can lead to the high risk of explosion, if wood or paper becomes saturated with it [136,137].
2.2.1.2 Amido sulphonate Electrolyte

Electrodeposition of lead from amido sulphonic acid, based electrolytes is also reported in literature [138,139]. It is used for electrolytic refining of raw lead. One problem with the use of this electrolyte is the tendency for sulphamate anion to get hydrolyzed to ammonia and sulfate [140], which cause the precipitation of lead sulfate forming huge amount of sludge.

2.2.1.3 Fluorosilicate Electrolyte

It was developed for electrolytic refining of lead by a process known as the Betts process. It is suitable for production of raw lead. It is more stable and economical than sulphate electrolyte. The kinetics of lead deposition in fluorosilicate electrolyte has been widely studied [141-143], although the fluorosilicate solution is difficult to prepare and is somewhat unstable.

2.2.1.4 Fluoborate Electrolyte

The fluoborate electrolyte is the most common process for the electrodeposition of lead [144]. It is stable lead salt, which is very soluble in water. Concentrated solutions are used for barrel plating and the continuous plating of mild steel sheet. A number of addition agents, mostly organic compounds, have been used to prevent treeing in the deposit, arrest crystal growth and improve appearance. Extensive experimentation was carried out by Graham and Pinketron [145,146] to select suitable additive for the lead deposition. The kinetics of lead deposition was studied by Thomas.M.Tam [147].

In the fluoborate electrolytes temperature will increase the limiting current density and lead to coarser grain structure to a greater or less extent, depending on the grain refiner used in the electrolyte [148,149]. Graham and Pinketron [150] investigated the
influence of cathode rotation on the limiting current density. The properties of electrodeposited lead from fluoborate electrolytes such as hardness, elongation, and tensile strength are given in the literature [151]. The density and electrical resistivity have been measured [152]. The corrosion resistance of the electrodeposited lead coatings has been investigated by Graham et al [153] in atmospheric exposure tests in several industrial, rural and marine climates.

2.2.1.5 Sulphamate and Acetate Electrolytes

Alternatives to electrodepositing lead from non-fluoborate systems are sulphamate and acetate. Certain basic parameters for lead sulphamate have been established [171]. Sulphamate electrolytes are used to obtain a compact lead deposit of required thickness [154]. The properties of the solution and the conditions for electrodeposition of lead from sulphamate solutions were studied using polarization behaviour of the system [155]. The main disadvantage of sulphamate bath, the hydrolysis of sulphamate resulting in an insoluble lead sulfate made it unsuitable for continuous process.

Electrodeposition of lead from acetate electrolyte in the absence and in the presence of chloride ions was investigated [156]. A highly adherent and smooth deposit of lead has been obtained on steel substrate from acetate electrolytes containing hexadecyl pyridinium bromide and sodium dodecyl sulphate [157].

2.2.1.6 Alkaline Electrolytes

The two most usual alkaline electrolytes used for the deposition of lead are the pyrophosphate and plum bite process [158]. In the alkaline solution the lead ion is present in a complexed form. The electrodepositon has therefore a higher over potential
compared to acidic solution. Hence it can be operated without inhibitors and show a high-throwing power. It is less corrosive against the plants and equipment. The main disadvantages are process-engineering problems. Hence no commercial use has been made of this bath.

2.2.2 Application of lead electrodeposits

Lead is commonly used in the chemical industry, lead battery technology, piping, roofing solders etc. mainly because it undergoes limited corrosion in many media [159] such as sulphuric acid, chromic acid, and phosphoric acid. The surface of lead coating is covered by a tightly adhering layer of lead sulphate, which protects the underlying metal against any further attack by the sulphuric acid. Lead plating on aluminium and its alloys may find considerable importance in the lead acid battery industry where plated aluminium sheet can be used in place of conventional copper sheet. This results in a considerable economic savings [160].

Some new application for lead deposition has been developed in the field of electronics and component manufacture in recent years. In PCB manufacture a layer of lead is deposited to act as etch resist. Bright tin or matt tin-lead coatings are reflowed and used as metal resists [161]. In comparison to tin or tin-lead alloys, lead has the advantage that no intermetallic layers can be formed. Deposition of thin undercoating of pure lead under a tin-lead layer on reflowed PCB’s improves their solderability. The use of electrodeposited lead layers for application in the field of fabrication of electrochromic devices and semiconductor devices is described in the literature [162,163].
2.3 TIN ELECTRODEPOSITION

Tin is useful for its resistance to corrosion and tarnish, for its nontoxic nature, and for its solderability, softness and ductility; it owes most of its acts as a coating to one or more of these characteristics. Tin is employed as a coating on refrigerator evaporators, dairy, and other food-handling equipment, washing machine parts, hardware, radio and electronic components, electrical lugs and connectors, copper wire for telecommunications and piston rings. There are four basic choice of electrolytic plating processes that can be used to deposit tin viz., acid fluoborate, acid sulfate, acid sulphonate, neutral gluconate and alkaline stannate.

2.3.1 Electrolyte used for tin electrodeposition

2.3.1.1 Fluoborate electrolyte

It is one of the acid-electroplating baths usually used in high-speed plating [164-166]. Tin fluoborate is highly soluble; therefore it permits the use of high current densities. Deposition in the absence of organic addition agents gives mostly porous, coarse and poorly adherent coatings. Formation of needle, whiskers and dendrites cause short circuit in electronic and related industries [167,168]. Organic additives most commonly used are peptone [169], gelatin [170], beta naphthol [171], catechol and hydroquinone [172], the last two are generally used as anti oxidants. The mechanisms of inhibition for Sn (IV) formation by antioxidants and mechanism of additives has been summarized in the literature [173-175]. With the above-mentioned additives smooth-fine grained deposits obtained [176]. Rob schetty studied the influence of several variables of the electroplating chemistry on tin whiskers growth [177]. The major disadvantages of
fluoborate system are the environmental concerns for the fluoride and the high host of waste treatment. It is also the most corrosive of all acidic tin electroplating solutions.

**2.3.1.2 Sulphate/sulphuric acid electrolyte**

Sn (II) sulphate electrolytes are gradually replacing the fluoborate electrolyte. The characteristics of this chemistry are its high cathode and anode current efficiency under normal operating conditions. It is important to avoid adding too much sulphuric acid since concentration exceeding 400 g/l decreases the conductivity of the solution [178]. Deposits ranging from matt, semi-bright to bright can be obtained from sulphate bath using addition agents [179]. The effect of non-ionic addition agents on electrodeposition of tin from sulphate has been studied [180]. Solderability of bright tin deposit has been studied [181,182]. Various organic additives such as surface-active agents [183-186], aromatic carbonyl compounds [187,188] and amine- aldehyde reaction products [189] are used in the plating solution to modify the deposit properties and the kinetics of tin deposition. Tin electrodeposition process has been studied from sulphate bath using electrochemical and morphological (nano-micrometric) techniques [190]. In bright tin-plating, chloride concentration is kept as low as possible. Higher chloride concentration causes a decrease in brightness of the deposit [191].

**2.3.1.3 Phenol sulphonic acid (PSA) electrolyte/Halogen electrolyte**

These two baths are mostly used to plate tin in the continuous steel strip plating industry. An attractive feature of these two processes is their ability to operate at very high current densities, which is very important in the steel industry. The PSA process used with either soluble or insoluble anode, whereas the halogen process utilizes with soluble anode only. S.Hirano et.al [192] studied the effect of current density, Sn (II)
concentration and flow rate on tin plate characteristics. Yung-Herng Yari et al. [193] compared the electrodeposition of tin between halogen and sulphonate bath. Sludge formation in a major problem in halogen bath where typically more than 20% of tin goes to sludge. Another problem is related to the waste treatment of the sludge because of ferro-ferric cyanide hazardous waste. Compared with halogen process PSA process produces much less sludge, due to its anti-oxidizing power. A drawback of PSA process is the toxicity of the phenolic group, which is released during electrodeposition.

### 2.3.1.4 Alkaline tin plating electrolyte

Alkaline stannate process is based on either sodium or potassium stannate. For high speed plating applications the potassium stannate is used because of its very high solubility. Anode efficiencies in the range of 75 to 95% and cathode efficiencies in the range of 80 to 90% are typical for the alkaline process [194,195]. It has superior throwing power. It does not require the use of organic addition agent but must operate at elevated temperature. In this bath the critical need is the proper control of the anode. If the tin anodes are not controlled during deposition rough, porous deposits will result. Figure 2.1 shows the characteristics of tin as anode in an alkaline solution. Starting at A and increasing the anode current density along the line AB and voltage increases slowly: The anode is dissolving as stannite and is grey in appearance. It may be covered with a gray-black smut, which rubs off easily. Plating in this range is entirely unsatisfactory.

When the current density reaches the point C, the voltage rises suddenly along the line CD and anode acquires a yellow-green film and begins to dissolve as stannate. If, the current density is maintained at C or increased further along the curve DE, the film turns black and the anode become passive, oxygen is evolved and behaves as insoluble anode.
Having reached point D on the curve, if the current density is decreased, the current-voltage curve will be found not to retrace itself; instead it follows the dashed line DF. The yellow-green film on the anode persists, and dissolves in the desirable stannate form. The portion DF is therefore the proper operating range, which can be reached only by first impressing on the anodes the critical current density C and then decreasing the current density to desired value. If the current density is further decreased, the curve follows the line FG, and the anode film becomes lighter at about G the film is lost entirely, and the tin is dissolving as stannite.

2.3.2 Application of tin electrodeposits from various bath

Tin deposits are widely used in the production of food processing and shipping equipment and containers pump parts and automotive pistons, copper and steel wire for telecommunication and in plating electrical components and printed wiring boards. Tin is appealing to the food processing industry because tin is a non-toxic, ductile and rather than corrosion resistant metal. Thicker deposits up to 30 micron are generally required in food processing equipment and shipping containers.

Although tin is used primarily for corrosion resistance to sulfur containing atmosphere it is often used where a solderable ductile finish is required on small chassis parts, brackets and on contact areas subjected to hydrogen sulfide contamination and to a minor extent for decorative purposes. Tin has excellent anti-scuffing properties, and is widely used in engineering to reduce fretting corrosion and to combat the effects of abrasion. Lubricants adhere well to tin and tin coatings can thus help in reducing friction between sliding components. Thick deposits [50 to 250 micron] are electroplated on pump parts and piston rings.
Tin is widely used in electronic industry because of its ability to protect the base metal from oxidation. Tin thus preserves solderability of the base material, a critical requirement when plating for electronic applications. Electrodeposited tin needle like structure have applications as novel cathodes in the field of vacuum microelectronics.

Figure 2.1 Anodic behaviour of tin in alkaline solution
2.4. Electrodeposition of lead and tin from Methane Sulphonic Acid bath (MSA)

In the 1940s Proell [196] recognized the utility of alkane sulphonic acids for electroplating applications. Alkane sulphonic acids, having between one and five carbon atoms in the alkyl group form water soluble salt of various metals (mesylates) [197]. Proell indicated that it is possible to plate many metals from alkane sulphonate baths including cadmium, lead nickel, silver, zinc and tin.

Although the usefulness of methane sulphonic acid systems was known for several decades, it only gained importance during the early 1980’s and became a desirable electrolyte for tin and lead plating [198]. MSA chemistry shows clear advantages over fluoborate, sulphate, halogen and phenol sulphonic acid chemistry. It is less corrosive than fluoborate and sulphate chemistries and it is less costly than fluoborate, phenol sulphonic acid and halogen chemistries for effluent treatment and disposal. It is environmentally more friendly [199]. The ‘green character of MSA especially as compared to fluoboric acid and fluorosilicic acid is derived from several factors. In general MSA is less toxic than fluoboric and fluorosilicic acid. Fluoboric acid and fluorosilicic acids have lachrymatory properties and both acids evolve HF. MSA solutions do not, under normal conditions, evolve any dangerous volatile chemicals. In general, the low toxicity of MSA, especially when compared to HF complex acids, makes it a safe electrolyte to handle. MSA is considered readily biodegradable ultimately forming sulfate and carbon dioxide. In fact, MSA is considered to be a natural product and MSA is part of natural sulfur cycle [200,201].
An additional attractive feature of MSA chemistry is its ability to access very high current densities [202]. The throwing and covering power of this chemistry are adequate to applications such as PWB and connectors with restricted areas [203]. Insoluble anodes can be used in MSA based plating baths.

The use of MSA for deposition of lead was first mentioned in a patent by Proell in 1950 [204]. Nobel Fred [205] described tin and lead plating baths that remained stable over a broad pH range. The design of acid electrolytes for the electroplating of lead and tin is dominated by solubility, performance and environmental considerations. Two important modern technologies depend integrally on the aqueous electrochemistry of lead: these are the electrodeposition of tin-lead solder in the electronic industry and the electrodeposition of lead on aluminium, which has been developed for bus bars of accumulator lead acid batteries. Only certain acid electrolytes will allow a high aqueous solubility of lead (II) ions. These electrolytes include Methane sulfonic acid, fluoboric acid, fluorosilicic acid, nitric acid, perchloric acid, acetic acid and dithionic acid. The aqueous saturation solubilities of the relevant lead salts are shown in the Table 2.1

The methane sulphonate ions form less stable complexes than fluoborate, fluorosilicate and associated fluoride ions [206]. The complexing nature of the fluoborate, fluorosilicate and fluoride anions make it difficult to efficiently remove metal ions (e.g. Pb\(^{2+}\)) from effluent streams. Basically, the residual level of lead left in an effluent after a caustic precipitation operation is directly related to the complexing ability of the anions present in the effluent. The residual level of Pb(II) left in solution after optimized caustic precipitation of lead from MSA(aq) based Sn/Pb plating solution is less than 1 ppm. While the residual level of soluble Pb (II) left in solution after caustic
Table 2.1 Saturation solubility of some lead salts

<table>
<thead>
<tr>
<th>Lead salts</th>
<th>Aqueous saturation solubility</th>
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<tbody>
<tr>
<td>Methane sulphonate</td>
<td>143 g /100 g water (25°C)</td>
</tr>
<tr>
<td>Fluoborate</td>
<td>50 wt % (20 °C)</td>
</tr>
<tr>
<td>Fluorosilicate</td>
<td>69 wt % (20°C)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>37 wt % (25°C)</td>
</tr>
<tr>
<td>Per chlorate</td>
<td>226 g / 100 g water (25°C)</td>
</tr>
<tr>
<td>Chlorate</td>
<td>225 g /100g water (25°C)</td>
</tr>
<tr>
<td>Acetate</td>
<td>55 g/100 g water (25°C)</td>
</tr>
<tr>
<td>Dithionate</td>
<td>115 g/100 g water (25°C)</td>
</tr>
</tbody>
</table>
precipitation of lead from HBF₄ (aq) based solutions is typically more than 10 times higher than the former [207]. In total, the lower toxicity and greater ease of waste treatment of MSA based solutions makes MSA the ‘green’ choice for commercial electrolytes, especially those containing lead. The suppression of lead electrodepositon by organic compounds in MSA bath has been studied [170].

In tin electrodeposition the oxidation of stannous to stannic is very less in MSA based plating formulation due to its less oxidizing power compared to sulphuric acid [208]. The effect of process variables like agitation, current density and temperature on plating efficiency and coating morphology were examined in high-speed tin electrodepositing process based on MSA electrolyte [209]. The electrochemical dissolution behavior of tin in MSA solution was also studied [210]. The kinetics of tin electrodeposition in presence of organic surfactants [211] and the role of glycol type additives in electrochemical and morphological changes [212] were studied from MSA based plating formulations. C.Lizzul Rinne et.al reported that electrodeposition of tin needle like structure can be produced from MSA bath using ethoxylated surfactant and Pb (II) salts [213]. The uses of gallic acid with the multiple rolls of antioxidant, grain refiner, selective precipitation and selective chelator in MSA based tin-plating bath have been patented by Genon Michael.D et.al. The initiation growths of tin immersion coating on copper substrate from MSA bath proceed by the formation of tin nano-crystals [214]. Effects of sulphate [215] and chloride [216,217] ions are studied in acid methane sulphonate electrolytes.
MSA has largely replaced fluoboric acid as the electrolyte of choice for the electrodeposition of tin, lead on electronic devices. These changes have been driven by the superior functional properties and environmental advantages of MSA [218].

2.5 Application of Methane sulphonie acid (MSA) in various processes

MSA offers all the qualities sought by today’s increasingly demanding chemical industry and finds application in several areas.

Metallurgy

MSA has been described for a variety of metal stripping processes. It has been used to design selective electrochemical stripping procedures that only dissolve one metal while they leave the other unaffected [219, 220]. MSA can be used to regenerate cation exchange resins. The acid can be recovered by electro winning to remove the dissolved metal.

The feasibility of MSA for metal stripping, ion exchanger regeneration and electro winning processes makes it a powerful tool for metal recycling. MSA triggers innovation in aluminium surface treatment. It has been used in a two-step process for anodizing and colouring of aluminium [221]. Moreover, it can be used for electro polishing of aluminium.

Batteries

Based on the table of electrode potentials, the cerium ion is expected to be a good candidate for a high-energy electrolyte in a battery. Still, the low solubility of the cerium sulfate has limited its use in this application. MSA is used advantageously. The construction of a high-energy density zinc/cerium battery has been made possible through the identification of MSA as an electrolyte for this system.
The familiar lead-acid battery operates with sulfuric acid and the source of lead (II) is insoluble lead sulfate. The electrode reactions involve the conversion of one solid phase to another, thus reducing the performance of the battery. Using MSA allows the concept of a battery with a lead (II) soluble in the electrolyte, using carbon electrodes and no cell separator [222,223]. The soluble-lead (II) battery has the potential to serve as a large storage battery in electricity networks.

**Advanced materials**

MSA is particularly attractive for surface modification reactions and solid-state reactions because it is at the same time a nonoxidizing and a strong acid. Moreover, it forms highly soluble salts. It is the combination of these properties that allows the use of MSA in innovative processes leading to high-performance materials.

Alumina-based, sprayable cement can be partly neutralized with MSA [224]. Organophilic clays have been made by partly neutralizing clay with MSA [225]. Crystalline aluminosilicates such as zeolites may be readily dealuminated-using MSA to provide catalysts or catalyst precursors. A high degree of aluminum removal with minimal loss of crystallinity is possible even when an organic template is not present in the aluminosilicate [226].

MSA offers great potential for new polymer-based materials. Methane sulfonic acid has been shown to improve the strength of reinforcement fibers for composites [227]. For this purpose, both carbon fibers and polyaramide fibers can be treated with methane sulfonic acid. Polyaramide fibers may also be directly spun from methane sulfonic acid. Aromatic high-performance Polymers such as polyether ketones are soluble in methane sulphonic acid [228] and may be processed from such solutions. This opens a
pathway to the use of these polymers in applications requiring thin cast layers. MSA allows post-cross linking of vinyl polymers in macro porous polymeric adsorbents [229].

MSA is a technical standard as catalyst in the synthesis of formaldehyde resins and other condensation resins. MSA has been discussed as a catalyst for the synthesis of silicones [230]. Cataphoretic dip coats based on epoxyamine-isocyanate resins may be neutralized with methane sulphonic acid. MSA is useful in lead-free cataphoretic dip coats where it serves as a counterion for cations such as vanadium, manganese, iron, zinc, zirconium, silver, tin, lanthanum, cerium or bismuth without impairing their solubility, like other acids would do [231].

Methane sulphonic acid has been used to modify electrically conductive polymers and to prepare composites [232] or to cast films or fibers of them [233]. Optical light-emitting devices (OLED’s) are based on thin luminescent polymer films. Such films have been spin-coated from MSA solution [234].

Ionic liquids based on quaternary ammonium salts and methane sulphonate are discussed as non-toxic solvents for chemical synthesis [235] and as lithium-conducting electrolytes [236] for lithium batteries. The removal of MSA from a reaction mixture as a liquid salt allows easy working-up of the reaction mixture by phase separation [237].
2.6 SCOPE OF THE PRESENT WORK

Methane sulphonic acid (MSA) based electrolytes are being actively investigated as environmentally superior alternatives to the currently used system such as fluoborate and sulphate. The primary advantages for MSA based plating process are (i) less toxicity and biodegradability (ii) higher metal ion solubility (iii) Wider operating window (iv) the ease of treating MSA effluents (v) higher conductivity and (vi) possible to use insoluble anode. These salient features of MSA electrolytes makes it as a green choice for electrodeposition of silver, nickel, chromium, cadmium, zinc, copper, lead, and tin metals. Among these metals copper, lead and tin has numerous application in electronics and engineering fields. Hence the objective of this study is adopting MSA electrolyte for copper, lead and tin electro depositon process.

Copper is commonly electroplated from acid sulphate and cyanide baths. The cyanide baths is commonly used in the commercial plating, but it has its drawbacks, viz., (i) its poisonous nature,(ii) costly effluent treatment method . Normally the acid sulphate bath has 100 % cathode efficiency. Deposition of copper from methane sulphonate bath is similar to those from sulphate bath, but it is useful for high current density plating operation. The methane sulphonic acid baths have high conductivity, and are less corrosive than sulphate bath. It can be operated at room temperature. However, literature survey shows that, not much work has been carried out on this bath. Hence attempt has been made to carry out copper deposition using MSA bath and the results are compared with sulphate system.

Since a long time fluoborate electroplating baths have been used to commercially
plate tin and lead. Alternatives to electroplating from non-fluoborate systems have been sought such as fluorosilicate, gluconate, sulphamate and sulfate. Sulphamate lead bath, due to its hydrolysis resulted in the formation of sulfate ions which precipated and made the bath commercially unsuitable. The less conventional fluorosilicate, gluconate and pyrophosphate baths are employed mainly for lead, tin, plating. They are however, more expensive than the fluoborate based electrolytes. Fluoborate baths, though most widely used, have disadvantages such as high corrosivity owing to oxidation of Sn$^{2+}$ to Sn$^{4+}$ in tin baths and environmental contamination due to fluoride ion. Nowadays the methane sulphonic acid bath is quickly replacing the fluoborate bath mainly because of environmental concern. The deposits obtained from MSA baths are highly adherent, and less porous, which are important factors in the tin plate and electronic industries. However, literature survey shows that less work has been done on the electrodeposition of lead, and tin using MSA bath. Hence attempt has also been made to carry out lead, tin electrodeposition using MSA baths and all the results are compared with fluoborate bath.

To start with, Hull-cell studies have been carried out to fix the maximum operating current density for the deposition of copper on brass from the MSA and sulphate bath. The effect of various additives such as Gelatin (GE), Poly ethylene glycol (PEG), Octyl phenoxy poly ethoxy ethanol (Triton-X-100), peptone on the process of lead and tin electrodeposition on steel from MSA bath has also been studied.

The current efficiency and throwing power of MSA bath have been measured for copper, lead, and tin deposition, which is compared with sulphate and fluoborate system respectively. The polarizations behavior of copper, lead and tin electrodeposition from MSA bath has also been studied.
Cyclic voltammetry has been used to study the reaction mechanism of copper, tin, lead deposition from MSA bath, sulphate (for copper) and fluoborate (for lead, tin) bath. The corrosion resistance of the deposits obtained from MSA bath has been studied by potentiodynamic polarization method, and electrochemical impedance method, and compared with deposits obtained from sulphate and fluoborate bath. The corrosion behaviour of copper, tin and lead, in MSA was studied by self-corrosion method. The samples were subjected to various tests to assess properties of deposits such as, adhesion, porosity, hardness and solderability (for tin deposition). The surface morphology of the deposits has been obtained from SEM photomicrograph. The phase orientation of the deposits has been ascertained using XRD.

Based on the results of all these studies, a comparative study has been made on the electrodeposition of copper, tin and lead from MSA electrolytes with other commercially adopted electrolytes. The study indicated the superiority of MSA bath compared to sulphate bath for copper deposition and fluoborate bath for lead and tin deposition.
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