

# Methanesulphonic acid in electroplating related metal finishing industries

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**SUMMARY** – During the past ten years, methanesulphonic acid has largely replaced fluoroboric acid as the electrolyte of choice for the electrodeposition of tin and tin-lead solder on electronic devices. Certain other electrochemical processes involving lead, most notably the electrorefining of lead by the Bett's process, are currently carried out in fluorosilicic acid based electrolytes but those based on methanesulphonic acid (MSA) are being actively investigated as environmentally superior alternatives to the currently used systems. Also, a number of commercial strip steel tin-plating operations have recently converted to methanesulphonic acid based tin-plating electrolytes. There are also developing markets for methanesulphonic acid in silver, nickel, copper, cadmium and zinc electroplating. This paper reviews the chemical and physical properties of methanesulphonic acid and its current applications in the field of metal finishing and also its superiority over other electrolytes especially with respect to environmental pollution.

**Keywords:** Methanesulphonic acid, metal plating, waste disposal, environmental benefits, electronics.

## INTRODUCTION

Electroplating processes typically involve electrolytic deposition of a thin coating of a metal onto a conductive substrate. In this, acid based electrolytes are desirable in that they allow for very high solution conductivity and metal ion solubility. Though metal salts are generally soluble in acid electrolytes, some metal salts *i.e.* silver and lead are soluble only to a limited extent and solubility considerations are paramount in the design aspects of acid electrolytes of such metals.

Methanesulphonic acid (MSA) based plating formulations have gained wider popularity over the past decade especially in the electroplating related to the electronic industry<sup>1,2,3</sup>. They are replacing the conventional fluoroborate baths, are relatively less harmful and their waste can be easily treated. In addition, they are stable in acidic, neutral and alkaline solutions and do not undergo any appreciable hydrolysis, regardless of the temperatures used. Since, MSA is less aggressive to the shop environment and equipment, no special requirements are necessary. The baths produce less wastage and sludge formation and cause less oxidation of the metallic species present in the solution. It is possible to use inert anodes and thus the initial investment or capital can be minimised. The baths are not aggressive to ceramic and glasses and produce nodular free deposits, which are the main requirement for plating related to electronics.

Comparison of some of the properties of methanesulphonic acid<sup>4</sup> with sulphuric acid, as given in Table I, indicates that methanesulphonic acid is less oxidising in nature.

This property is very much desired in the case of plating of those metals which exist in multivalent states *e.g.* tin, iron *etc.*, and those operating with additives. Hence, these baths

offer the advantage of using insoluble anodes.

Methanesulphonic acid is a strong acid ( $pK_a = -2$ ), which is completely ionised at concentrations of  $0.1 \text{ mol dm}^{-3}$  in aqueous solutions. MSA baths have a lower equivalent conductance than hydrochloric acid and sulphuric acid, for the same hydrogen ion concentrations, which is compensated by the higher solubility of its salts. (Table II) This enables the bath to be operated at very high current density as in high-speed plating and continuous plating and also increases productivity. MSA also offers higher solubility for surfactants and other organic additives.

Methanesulphonic acid baths are less toxic than counterparts such as fluoroboric acid and fluorosilicic acid. While the lethal oral dosage for the fluoro-acids is  $464\text{--}495 \text{ mg kg}^{-1}$ , that of the former is around  $1158 \text{ mg kg}^{-1}$ . In addition, fluoroboric and fluorosilicic acid have lachrymatory properties and both acids evolve HF. As a result of this, they have established OSHA PEL (Permissible Exposure Limit) levels of  $2.5 \text{ mg HF per cubic metre}$ . Hence, plants using fluoroboric acid and fluorosilicic acid need first-rate ventilation. Unless disposed of properly, the fluoride ions cause water pollution. In potable water fluoride in ppm levels causes dental and skeletal fluorosis<sup>5</sup>. Worldwide, fluoride removal from water resources is receiving prime attention and in the near future, it is quite likely that fluoride/fluoroborate-based formulations will be subject to legislation similar to that for cyanide formulations. In general, the low toxicity of methanesulphonic acid, when compared to HF complex acids like fluoroboric and fluorosilicic acids, makes it a safe electrolyte to handle.

Above all, it is biodegradable ultimately forming sulphate and carbon dioxide and it is recyclable up to 80%. In general, the environmentally benign nature of methanesulphonic acid, especially when compared to the HF complex acids, makes it an environmentally advantageous electrolyte<sup>6</sup>.

Table I Physical Properties of Methanesulphonic Acid.

Properties	Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> )	Methanesulphonic acid (CH <sub>3</sub> SO <sub>3</sub> H)
Colour	Colourless	Colourless
Molecular weight (g mol <sup>-1</sup> )	98	96
Density (g cm <sup>-3</sup> )	1.82	1.48
Boiling point (°C)	279.6	122
Freezing point (°C)	10.4	19
Thermal stability (°C)	340	180
Acid diss. constant (pK <sub>a</sub> )	-3	-2
Corrosive nature	More	Less
Oxidising power	Active oxid. power	Non-oxidising agent
Equivalent conductance (S cm <sup>2</sup> mol <sup>-1</sup> )		
1N	413.84	232.97
1N	444.88	299.60
0.5N	464.12	336.47
Solubility of metal salts	Less	More

Table II Solubilities of Metal Sulphonates<sup>a</sup>

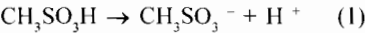
Metals	Methanesulphonates lg dm <sup>3</sup>	Sulphates lg dm <sup>3</sup>
Lithium *	771.79	555.56
Sodium*	666.64	197.35
Potassium*	601.80	108.86
Magnesium*	300.00	316.34
Calcium@	671.80	3.39
Strontium@	707.80	—
Barium@	520.44	—
Manganese@	710.33	531.30
Cobalt@	630.00	334.8
Nickel@	529.70	377.44
Copper@	507.10	336.90
Lead@	1032.72	—
Silver#	754.67	8.67
Zinc#	551.64	535.81
Cadmium#	967.71	646.07
Tin#	1151.59	303.88

\* Metal sulphonates are prepared from their corresponding metal hydroxides.  
@ Metal sulphonates are prepared from their corresponding metal carbonates.  
# Metal sulphonates are prepared from their corresponding metal oxides.

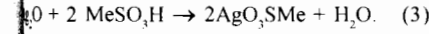
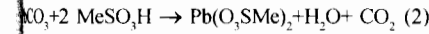
Preparation of sulphonates

Metal sulphonates are produced by chemical and electrochemical methods.

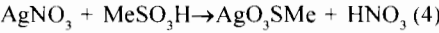
On dissolving methanesulphonic acid in water, it dissociates into methanesulphonate anion and a proton as is represented in equation (1).



The most straightforward method for producing the simple metal salt involves the reaction of stoichiometric amounts of a base metal salt with the acid form of the anion of interest. Typical base metal salts include carbonates, hydroxides, and oxides. The reactions for the preparation of lead and silver methanesulphonic acid are shown in equations (2) and (3),



A less common method of salt manufacture involves ligand metathesis between an acid and acid salt. This method is used in the preparation of the silver salt,

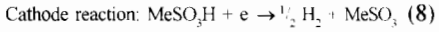
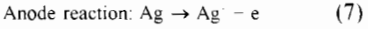
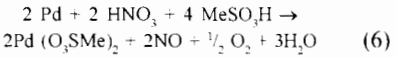
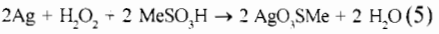


where HNO<sub>3</sub> produced is removed by distillation.

Another common method for preparation of salts involves chemical or anodic oxidation of the metal of interest in an electrolyte containing the acid form of the desired anion. Methods of this type generally avoid the problems associated with the sluggish reaction of the passive metal oxides. Many metal oxides (e.g., precious metal oxides) dehydrate and become passive on standing; it is sometimes more convenient to react such oxides immediately, as they are formed.

For anodic oxidation of a metal in an acid medium, the process can be viewed most simply as the introduction of the metal cation into solution. Anodic oxidation requires a method for preventing the metal cation of the salt from re-depositing on the cathode. In general, divided electrochemical cells are employed for this purpose. The cells can be divided by simple micropore frits or more desirably, by anion exchange membranes. Silver<sup>4</sup> and palladium<sup>7</sup> methanesulphonates are

produced using chemical methods equations (5) and (6) whereas tin and silver methanesulphonates are produced electrochemically, equations (7) and (8).



It should be noted that silver methanesulphonate is a useful intermediate for the preparation of other metal methanesulphonic acid salts via silver chloride precipitation driven reactions with appropriate metal chlorides. Preparation of tin methanesulphonate for laboratory scale preparations is done in this way<sup>8</sup>.

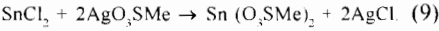


Table II summarises the chemical method of preparation of various sulphonates.

Recovery of methanesulphonic acid

An electrowinning acid recovery method which allows for the recovery of pure methanesulphonic acid from corresponding metal sulphonate salts has been developed<sup>9</sup>.

The process is based on electrowinning from an anion exchange membrane-divided cell. The anode process is O<sub>2</sub>/H<sup>+</sup> generation and the cathode process is metal deposition. While similar processes are available for fluoroborate and fluorosilicate based electrolytes, these have a number of practical problems. HBF<sub>4</sub> and H<sub>2</sub>SiF<sub>6</sub> tend to dissociate into BF<sub>3</sub>/HF and SiF<sub>4</sub>/HF respectively during transport through anion-exchange membranes. Such dissociation results in the formation of more mobile fluoride anions as compared to the bulkier fluoroborate and fluorosilicate anions. In addition, fluoroborate and fluorosilicate undergo hydrolysis reactions in alkaline solutions, and acid recovery catholyte solutions often become alkaline during the recovery process. All things considered, the recovery of methanesulphonic acid from metal alkane sulphonates-based waste, is easier than the recovery of fluoroboric acid or fluorosilicic acid from metal fluoroborate and metal fluorosilicate wastes, respectively.

Application area

Methanesulphonic acid is an excellent catalyst for esterification<sup>10</sup>, condensation reactions, for alkylation, olefinic polymerisations and for curing of conversion coatings. Methanesulphonic acid is used in petroleum refining, textile treatment and as a solubilising agent or as a combination catalyst for reaction mediums.

A total of 70 % of methanesulphonic acid produced is used for electrochemical applications and those related to the metal finishing industry are given below:

- (i) replacement of fluoroboric acid and fluoroborates in tin/lead and tin/lead alloy plating.
- (ii) wire and steel strip tin plating.

**Table III Saturation Solubility of Some Lead Salts<sup>9</sup>**

Lead Salts	Aqueous saturation solubility
Lead methane sulphonate $\text{Pb}(\text{O}_3\text{SMe})$	143 g per 100 g $\text{H}_2\text{O}$ (25°C)
Lead fluoroborate, $\text{Pb}(\text{BF}_4)_2$	50 wt. % (20°C)
Lead fluorosilicate, $\text{PbSiF}_6 \cdot 4\text{H}_2\text{O}$	69 wt. % (20°C)
Lead nitrate, $\text{Pb}(\text{NO}_3)_2$	37 wt. % (25°C)
Lead perchlorate, $\text{Pb}(\text{ClO}_4)_2$	226 g per 100 g $\text{H}_2\text{O}$ , (25°C)
Lead chlorate, $\text{Pb}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	225 g per 100 g $\text{H}_2\text{O}$ , (25°C)
Lead acetate, $\text{Pb}(\text{O}_2\text{CMe})_2$	55 g per 100 g $\text{H}_2\text{O}$ , (25°C)
Lead dithionate, $\text{PbS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$	115 g per 100 g $\text{H}_2\text{O}$ , (20°C)

**Table IV MSA Based Bath Compositions and Operating Conditions<sup>21</sup>**

	MSA / g dm <sup>-3</sup>	Tin / g dm <sup>-3</sup>	Lead / g dm <sup>-3</sup>	Silver / g dm <sup>-3</sup>	Bismuth / g dm <sup>-3</sup>	Temp / g dm <sup>-3</sup> °C	Current density / A dm <sup>-2</sup>
Tin	200-250	35-55	—	—	—	21-54	0.1-28
Tin-lead (60/40)	200-250	12-20	6-10	—	—	21-29	0.1-28
Tin-lead (90/100)	200-250	17-25	2-4	—	—	21-54	0.1-28
Tin-Bismuth	130	4	—	—	1-1.5	25	0.5-2
Tin-Silver	pH adjusted to 5	20-24	—	0.5-1	—	25	0.5-3
Lead	30-50	—	56-72	—	—	21-38	0.1-4
Silver	pH adjusted to 5	—	—	25-29	—	50	0.5-3

- (iii) metal finishing of silver, copper, nickel and palladium,
- (iv) immersion and spray stripping of metals such as nickel, tin, lead, tin-lead and cadmium from copper and its alloys or from zinc and its alloys<sup>11</sup>,
- (v) lead recovery from scrap batteries,
- (vi) electropolishing,
- (vii) immersion plating, and
- (viii) regeneration of ion exchange resins.

### Tin Plating

The growing requirements of the electronic industry have prompted an increased interest in tin and tin-alloy plating. Tin plating is used in engineering, communications, military and consumer product applications such as in printed circuit boards, connectors, valves, bearings, semiconductors, transistors, wire and strips.

Two types of electrolytes have commonly been used. One is the phenolsulfonic acid based electrolyte<sup>12</sup> popular in Japan, the other, the halide-based electrolyte<sup>13</sup> popular in the USA. The former generates no chloride or fluoride sludge but has the drawback of poor conductivity. The latter achieves high productivity due to excellent electrolysis properties, but requires the disposal of voluminous amounts of sludge accumulated in the bath. The new methanesulphonic acid bath with special additives enables uniform plating over a wide range of current densities, and achieves productivity equal or superior to that of the halide bath and generates virtually no fluoride sludge. In terms of the chemical oxygen demand (COD) the methanesulphonic acid electrolyte reduced COD to one third that required by the phenolsulphonic acid electrolyte. The versatility of this bath allows the same bath composition and additives for

barrel/still plating and high speed reel-to-reel plating.

In the halide-tin process, the steel substrate corrosion by the bath and the resulting oxidation of  $\text{Sn}^{2+}$  is intrinsic. The bath contains excess amounts of non-reactive ions in  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{F}^-$  that carry the majority of the current in the bulk electrolyte. The two reactive species  $\text{Sn}^{2+}$  and  $\text{H}_2$  account for only 1.76 and 0.05 % of the total current respectively. Thus, the majority of currents are carried by diffusion of  $\text{Sn}^{2+}$  through the concentration gradient across the boundary layer. Since, the migration current carries the negatively charged  $\text{SnF}_3^-$  complex away from the cathode, diffusion would be more critical in the halide process. In the methanesulphonic acid bath, there are only three ionic species, unlike the halide process; 71.3 % of the current in the bulk electrolyte is carried by hydrogen ions migrating to the cathode while only 3.5 % is carried by  $\text{Sn}^{2+}$  ions. The remaining 25.2 % of the current is carried by methanesulphonic acid ions migrating to the anode. The conductivity is 176 mS cm<sup>-1</sup> for the methanesulphonic acid bath and 129 mS cm<sup>-1</sup> for halide bath. Smirnov and Tyutina<sup>14</sup> found that tin reduction without any additive is mass transport controlled and the reaction becomes both mass transport and kinetically controlled when using additives.

The  $\text{Sn}^{2+}$  oxidation rate of the halide bath containing ferrocyanide is 0.45 g dm<sup>-3</sup> h<sup>-1</sup> and the corrosion of steel panels is 3.0 g m<sup>-2</sup> h<sup>-1</sup>. In the absence of ferrocyanide the oxidation rate of steel increases to 4.4 g dm<sup>-3</sup> h<sup>-1</sup> whereas that of  $\text{Sn}^{2+}$  increases drastically to 3.3 g dm<sup>-3</sup> h<sup>-1</sup>. This demonstrates the deleterious effect of iron on the stability of the halide bath, and the importance of ferrocyanide, which removes all ferrous and ferric ions by forming

precipitates of sodium ferrous ferrocyanide and sodium ferric ferrocyanide. These ferrocyanide precipitates and the precipitate of sodium fluorostannate, generated by the oxidation reaction of stannous ion, form heavy sludge at the bottom of the plating cells and recirculation tank. Consequently, a halide line must be shut down approximately every eight weeks to remove the accumulated sludge. For the methanesulphonic acid bath, the oxidation rate of the stannous ions is extremely low, about 0.07 g dm<sup>-3</sup> h<sup>-1</sup>. This low oxidation rate allows the use of filtration to continuously remove the precipitate of stannic oxide, thus eliminating the sludge removal operation. This low oxidation rate in the methanesulphonic acid bath, however, requires the use of several insoluble anodes instead of the soluble tin anodes normally used in a halide line to maintain the stannous ion concentration. The high corrosiveness of halide baths to the steel substrate requires constant removal of dissolved iron from the bath and protection of the structure and equipment in the production line.

The MSA baths offer a higher plating efficiency at current densities above 30 A dm<sup>-2</sup>, but a lower efficiency at lower current densities. The morphology and preferred crystal orientation from the two baths are different, which could cause a difference in reflectance and reflow characteristics. The coating morphology in the MSA baths also exhibits a greater variation with the operating conditions especially below 6 A dm<sup>-2</sup>. Because of the above factors, the current density for the methanesulphonate bath should be above 10 A dm<sup>-2</sup><sup>15</sup>.

In electronic applications, bright tin plating is not generally preferred since commercial processes produce high internal stress in the deposits along with high organic inclusions, which affect the solderability. Hence, smooth satin deposits with good solderability and low resistivity and long life are mostly preferred. So, research on additives for methanesulphonic acid baths is continuing. Some work by producing large, well polygonised grains with minimum organic inclusions, which are believed to be instrumental in reducing the internal stress, the root cause of whisker formation. Additives like catechol suppress the electrochemical oxidation of  $\text{Sn}^{2+}$  ions and the precipitation of tin sludge consisting mostly of stannic compounds<sup>16</sup>; others help in reducing excessive foam formation in the bath<sup>13, 17, 18</sup>.

It is known that additives can also be used to produce needle-like structures used as novel cathodes in the field of vacuum microelectronics<sup>19</sup>.

### Lead plating

The design of acid electrolytes for the electroplating of lead and lead alloys, most importantly tin/lead, 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 electronics industry and the production of lead acid batteries for the automotive industry. In

addition, the refining of crude lead obtained from mining and/or recycling operations is sometimes carried out electrolytically. As of today only fluoroboric acid, fluorosilicic acid and methanesulphonic acid based electrolytes are used with commercial success<sup>20</sup>.

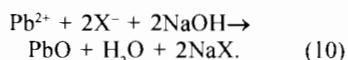
Methanesulphonic acid is functionally and environmentally superior to fluoroboric acid, fluorosilicic acid and other HF complex acids (e.g.  $\text{HPF}_6$ ,  $\text{HSbF}_6$ ) as an electrolyte for electrochemical processing. In the electrochemical cell, metals are electrolytically dissolved and simultaneously cathodically deposited, in a purer form from fluorosilicic acid based electrolytes. The substitution of methanesulphonic acid for fluorosilicic acid in the electrorefining of lead offers a number of functional and environmental advantages. In both tin/lead solder electroplating and lead electrorefining, acidic aqueous solutions with a high concentration of  $\text{Pb}(\text{II})$  ions are used.

However, only certain acid electrolytes will allow for a high aqueous solubility of  $\text{Pb}(\text{II})$  ions. These electrolytes include methanesulphonic acid, fluoroboric acid, fluorosilicic acid, nitric acid, perchloric acid, chloric acid, acetic acid and dithionic acid.

The aqueous saturation solubilities of the relevant lead salts are shown in Table III.

Various factors make the use of many of these solubility permissible lead electrolytes untenable. For instance the dithionate anion in lead dithionate is unstable at low pH decomposing into sulphate and sulphite. Aqueous solutions of lead acetate in combination with acetic acid have insufficient conductivity to allow for high-speed electroplating operations. Lead chlorate, lead perchlorate and lead nitrate all tend to decompose cathodically and the corresponding acids are very corrosive.

The methanesulphonate ion forms less stable lead complexes than do the fluoroborate, fluorosilicate and associated fluoride ions. The complexing nature of the aforementioned anions make it difficult to efficiently remove lead ions from effluent streams. By far the most common method of dealing with metal containing aqueous effluent solutions is by caustic precipitation of the metal oxide followed by filtration. The caustic precipitation of lead, for instance, is shown in equation (10),



The insoluble lead oxide formed is removed from the aqueous effluent by filtration. 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 soluble  $\text{Pb}(\text{II})$  in solution after optimised caustic precipitation of lead from methanesulphonic acid (aqueous) based lead or tin/lead plating solutions is less than 1 ppm, while the residual level of soluble  $\text{Pb}(\text{II})$  left in solution after caustic precipitation of lead from fluoroboric acid (aqueous) based solutions is typically more than ten times as much.

Capelato *et al.*<sup>21</sup>, from their study on the anodic dissolution of lead in MSA concluded

that the latter has a tendency to form stepwise complexes with lead (II) ions in moderately acid solutions. Three lead (II) methanesulphonate complexes have been characterised as predominant species in the ligand concentration of range 0.2-2.0 M. In electroplating baths where the concentration levels are high, various soluble species are in equilibrium. Hsuen and Wan<sup>22</sup> studied the anodic dissolution of lead in MSA and found that the reduction of lead is diffusion controlled and there is no sulphonate ion involved in the charge transfer reaction, with the lead ion existing in the completely dissociated state.

Lead methanesulphonate baths are used in the plating of bearings, connectors, and as internal and conforming anodes for chromium plating valves, and for parts of storage batteries<sup>20</sup>.

### Lead/tin Plating

The advantages of methanesulphonic acid are evidenced by its recent substitution for fluoroboric acid in the commercially important electroplating of tin/lead solder. In this process, acidic aqueous solutions of  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ , free acid and surface-active additives are employed. From these carefully formulated methanesulphonic acid based electroplating solutions it is possible to produce solderable tin/lead coatings with specific properties (appearance, alloy content, thickness, ductility, etc.). Such engineered tin/lead coatings are for example, deposited on the connecting pins of electrical devices, where they function, among other things, to protect the connecting pins from oxidation and the associated loss of solderability.

Solderable tin/lead coatings are also sometimes electroplated onto printed circuit boards as part of the fabrication process, and tin or tin/lead is electroplated onto wire as a solderable and corrosion inhibiting coating. A number of industrial electrochemical processes still employ fluoroboric and/or fluorosilicic acid based electrolytes. For many of these applications, active research programs aimed at replacing the fluoric acid complex acid with methanesulphonic acid are in place.

The main drawback of pure tin deposits is the formation of whisker growth that is normally controlled by alloying it with a small amount of lead. Alloys of lead with tin ranging in composition from 10-93 % lead, used for various purposes are produced from MSA baths; 60% tin and 40% lead alloys are used as solder on PCBs, connectors and other specialised devices. Deposits are either dull or bright coatings according to the additive nature and concentration. The baths operate at lower additive concentration than fluoroboric acid baths. Methanesulphonic acid solutions are similar to  $\text{HBF}_4$  in that on PCBs lowering the metal content of the solution and increasing the acid content can augment throwing power.

The latest flip chip technology relies on solder bumps produced on silicon chips for interconnection. Though solder bumps can be produced by vapour deposition and screen printing as well as by electroplating, only electroplating allows the manufacturing of fine-pitch small volume solder bumps. Solder

plating needs to be controlled to produce uniform solder bumps. A chip may contain hundreds of bump pads. Because a wafer contains hundreds of chips, it can be assumed that thousands of solder bumps will be plated simultaneously during the plating process. It is reported that solder bumps produced from MSA baths have uniform bump height and are smooth<sup>23</sup>. It is also reported that laser enhanced electrodeposition of lead-tin solder from MSA baths yield deposits with good surface morphology at a reduced overpotential<sup>24</sup>. Use of pulse current yields more uniform and smooth deposits compared to the direct current process<sup>25, 26</sup>.

### Copper-lead-tin alloys

These alloys, produced from MSA-based electrolytes are presently used as lubricating coatings in bearings but may find application in electronics in future.

Some of the bath compositions used for depositing alloys are given in Table IV.

### Lead-free depository Tin Alloys

The use of tin-lead solders for the formation of solder joints in the production of electronic equipment is a known technology, but the environmental risk resulting from the use of lead forces a substitution. There is a potential risk of environmental contamination when discarded electronic equipment with tin-lead solder joints is deposited in landfills. For this reason consideration is being given to substituting lead in this field.

Any alternative for lead has to match the profile of requirements of the existing tin-lead solders and the technological properties of the interconnections must not be negatively influenced. It is also important that the alternative solders can be used with the existing assembly technologies. One important requirement in this connection is the melting point of the solder. Any alternative to lead should give a melting point or melting-range, which is similar to the existing tin-lead solders. High soldering temperatures are unsuitable, because they can cause an intolerable high thermal stress on the component. Furthermore the search for lead-free solders has also to consider the availability and the costs of the possible alternatives.

Possible candidates for soft-solders using a tin-base are those where tin is alloyed with the metals like bismuth, indium, silver, zinc and antimony. Tin-bismuth<sup>27, 28</sup> and tin-silver<sup>29</sup> are the most preferred as copper-tin suffers from the problem that measuring the alloy composition on the actual parts by XRF is not possible for copper substrates because of the interference from the base metal. Both preferred alloys are being produced adopting MSA formulation<sup>30</sup>.

### Immersion tin coatings

Recently the immersion tinning of copper tubes for drinking water purposes, has been given special consideration because of copper contamination in water above the permissible limits. While the formation of immersion coating by conventional hydrochloric acid takes place semi-coherently, those formed

from MSA baths are formed as nanocrystals showing preferred orientation, and have compact and regular surface morphology<sup>31, 32</sup>. The maximum thickness that can be obtained is around 1.5  $\mu\text{m}$  which also might have applications in electronics.

### Silver plating

Silver plating is widely used in interconnectors because it provides high electrical conductivity, good corrosion resistance and good soldering properties. To dispense with the conventional cyanide baths, MSA base formulations are emerging.

With the help of additives, white silver deposits, comparable with those produced from cyanide bath *in all respects* has become possible<sup>33</sup>.

### CONCLUSIONS

Methanesulphonic acid based formulations are finding increasing interest in plating especially in the area of electronics. Though the main emphasis is on its less polluting nature and the possibility of recycling, unlike the conventional fluoroboric or fluorosilicic acid baths, it has many other exceptional qualities and it enables the co-deposition of many alloys.

### ACKNOWLEDGEMENTS

The authors wish to place on record their sincere thanks to The Director, Central Electrochemical Research Institute, Karaikudi, for permission to publish this paper.

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