

Methane Sulfonic Acid as an Electrolyte for Tin, Lead and Tin-Lead Plating for Electronics

by Charles Rosenstein
CP Chemicals, Inc., Sewaren, NJ

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The growing requirements of the electronics industry have prompted an increased interest in tin, lead and tin-lead electroplating solutions. These solutions are used to plate components used in numerous engineering, communications, military and consumer product applications, such as printed circuit boards, connectors, valves, bearings, semiconductors, transistors, wire and strip. Tin and tin-lead alloys are solderable and, therefore, are used extensively in the electronics industry to bond electronic components. This precludes the need for strong fluxes to wet the deposit.

For many years, fluoborate based solutions were the universally used solutions to commercially plate tin, lead and tin-lead alloys. Fluoborates possess several inherent advantages over other solutions, including high deposition rate, stability, high anode and cathode efficiencies and fine grained deposits.

ALTERNATIVES TO THE FLUOBORATE SYSTEM

Various nonfluoborate systems have been investigated for the deposition of tin, lead and tin-lead alloys. Lead may be plated from sulfamate,¹ gluconate,² pyrophosphate³ and fluosilicate⁴ electrolytes. Recently, a lead bath was proposed⁵ utilizing lead sulfate in an acidic ammonium acetate solution.

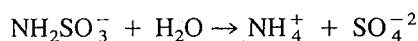
Tin is plated from alkaline stannate baths or from acidic baths based on stannous sulfate, stannous chloride ("Halogen")⁶ or phenolsulfonate ("Fer-rostan").⁴ While acidic baths deposit tin from the divalent (+2) state, stannates deposit tin from the quadrivalent (+4) state. Advantages of acidic tin baths are:

1. Electrochemical equivalent of tin is double that of stannate baths.
2. Higher cathode efficiencies.
3. Operation close to room temperature.

Bright tin was recently electroplated

from a stannous sulfate-pyrophosphate system⁷ operated at pH 7-9. Only the acidic stannous sulfate bath and the alkaline stannate bath are still commercially popular. The acidic stannous chloride bath is used occasionally.

Fluosilicates were used in plating⁸ and in the electrolytic recovery⁹ of tin-lead alloys. Sulfamate baths^{10,11} were investigated, but were not practical because of the ease of hydrolysis of sulfamate, resulting in insoluble lead sulfate:



Pyrophosphate based baths^{12,13} were investigated for usage in tin-lead plating. Nevertheless, the fluoborate system remained the system of choice for tin, lead and tin-lead plating.

HISTORY OF ALKANE SULFONIC ACID BASED SYSTEMS

In the 1940s, Wayne Proell^{14,15} was one of the first to recognize the utility of alkane sulfonic acids for electroplating applications. He found that alkane sulfonic acids, having between one and five carbon atoms in the alkyl group, formed water soluble salts of various metals (mesylates). The alkane sulfonates did not undergo any appreciable hydrolysis, regardless of the temperatures used. Additionally, the alkane sulfonates were stable in acidic, neutral or alkaline solutions. Proell indicated that it was possible to plate many metals from alkane sulfonate baths, including cadmium, lead, nickel, silver and zinc.

Although the usefulness of the alkane sulfonic acid system was known for several decades, the system only gained some commercial acceptability during the early 1980s. Methane sulfonic acid (MSA) became a potential electrolyte for usage in tin, lead and tin-lead plating. One attractive feature of the MSA based plating systems was the ease of treating MSA effluents.

Various plating baths and additives

have been formulated for MSA based electroplating systems and many patents have been granted.¹⁶⁻¹⁸ Obata¹⁹ described tin, lead and tin-lead plating baths that remained stable over a broad pH range (2.0-9.0) and were used over a wide current density range.

ESSENTIAL FEATURES OF TIN AND TIN-LEAD ALLOY DEPOSITS

Quality control testing helps to confirm the reliability of a deposit. Many of these tests are incorporated in the American Society for Testing and Materials (ASTM) methods and US Military Standards. These rigorous tests are necessary to ensure that a plated component will function reliably. Tin and tin-lead deposits must possess all of the following characteristics:

1. Good solderability and reflowability.
2. Low porosity.
3. Good corrosion resistance.
4. Uniformity of alloy composition, thickness, smoothness and appearance over a wide current density range.

Organic additives are required in tin and tin-lead electroplating solutions to produce smooth and uniform deposits and to impart good throwing power. During plating, electrolysis causes some decomposition of the organics, resulting in occlusion of some of the organics in the deposit. If present in sufficiently large amounts in the deposit, organics can cause solderability and reflow problems. Accelerated aging tests are performed on tin and tin-lead deposits to help predict their shelf life, as components are sometimes used long after they are plated.

The mat deposit from a tin or solder bath can be rendered bright by a technique known as reflowing or fusing. The reflow process involves heating the deposit 10°F above its melting point to produce a bright deposit. The reflowed deposit has greater corrosion resistance

and improved solderability. The eutectic alloy of 63Sn/37Pb melts at 362°F. The fused deposit reflects the cleanliness of the plated surface, as improper cleaning and activation of the substrate results in dewetting after reflowing.

Porous deposits will allow corrosion of the substrate, thereby resulting in poor solderability. Significant amounts

of occluded organics and rough deposits lead to surface corrosion and solderability problems.

Tin-lead deposits should have a uniform alloy composition and appearance to prevent reflow problems. A nonuniform surface appearance denotes areas of varying alloy compositions. Reflow problems will then occur, as varying

temperatures are needed to melt varying alloy compositions.

MSA BASED ELECTROPLATING BATHS

Electroplating baths are carefully selected to meet specific engineering requirements. The plating equipment and bath composition must be maintained in order to obtain acceptable deposits. The formulation and operating conditions of a particular MSA bath depend on the specific application that is required.

As with fluoborates, metal salts of MSA are very soluble and various concentrations of MSA and its metal salts

Table I. Concentrations of MSA and MSA Salts Used in Tin, Lead and Tin/Lead Alloy Plating

Product	Concentration, g/L	Specific Gravity (20°C)
50% MSA	MSA 100% = 613	1.225
70% MSA	MSA 100% = 945	1.350
Stannous methane sulfonate	Sn = 120	1.230
	Sn = 150	1.285
	Sn = 200	1.390
	Sn = 240	1.450
	Sn = 300	1.560
Lead methane sulfonate	Pb = 450	1.630
	Pb = 500	1.700
Copper methane sulfonate	Cu = 100	1.260

Table II. Bath Compositions for a 90Sn/10Pb Plated Alloy Deposit

	Bath A	Bath B	Bath C
Tin, g/L	21	30	20
Lead, g/L	3	4	1
MSA, g/L	225	120	140

Table III. Methane Sulfonic Acid Bath Compositions and Operating Parameters

	MSA g/L	Tin g/L	Lead g/L	Copper g/L	Temp. °F(°C)	Current Density A/ft ²	Anodes
Tin Bath:							
Range	200-250	35-55	—	—	70-130	1-250	Pure tin
Optimum	225	45			(21-54)		
Lead Bath:							
Range	30-50	—	56-72	—	70-100	1-40	Pure lead
Optimum	40		64		(21-38)		
60 Tin/40 Lead Solder Bath:							
Barrel and Still:							
Range	200-250	12-20	6-10	—	70-85	1-250	60 tin/40 lead
Optimum	225	16	8		(21-29)		
High Speed:							
Range	200-250	12-20	8-12				
Optimum	225	16	10				
90 Tin/10 Lead Bath:							
Range	200-250	17-25	2-4	—	70-130	1-250	90 tin/10 lead
Optimum	225	21	3		(21-54)		
93 Lead/7 Tin Bath:							
Range	30-50	4-5	56-72	—	70-85	1-40	93 lead/7 tin
Optimum	40	4.5	64		(21-29)		
10 Tin/88 Lead/2 Copper Bath:							
Range	30-50	4-5	65-75	0.8-1.2	70-100	1-40	10 tin/88 lead/ 2 copper or 90 lead/10 tin or pure lead
Optimum	40	4.5	70	1.0	(21-38)		

- Notes: 1. Agitation required, mechanical or barrel; vigorous for high speed plating.
 2. Platinized titanium anodes can be substituted for the soluble anodes.
 3. Periodic filtration through 1-micron Dynel or polypropylene cartridges.
 4. Anode to cathode ratio for all baths is 1 to 1.
 5. Additive concentration as required.

are available (see Table I). Additives are necessary in plating baths to produce deposits that are smooth, uniform and have good reflowability. They also improve the throwing power of the solution. Additives for tin, lead and tin-lead methane sulfonate baths are usually composed of organics and/or surfactants.

Oxidation of stannous tin is a problem in MSA systems, as well as in other electrolytes. Loss of stannous tin, due to its oxidation to stannic tin, will decrease deposition rates and change the composition of the tin-lead alloy. Sludges build up when stannic tin accumulates and rough deposits may result. Anti-oxidants are usually included in tin and tin alloy based baths to inhibit the formation of stannic tin.

Mat, bright and semibright deposits are possible. Additives are developed for a particular type of deposit and a unique bath composition. For example, different manufacturers may recommend different bath compositions for the same type of bath. Recommendations for the bath composition of a 90Sn/10Pb methane sulfonate still and barrel bath by three manufacturers are given in Table II.

Each of the baths in Table II utilizes a custom made additive for that specific

content of tin, lead and MSA. The ideal additive will not decompose to any great extent, under normal usage, in order to minimize occlusion of organics in the deposit and to prevent potential solderability and reflow problems.

TESTING AND CONTROL OF MSA PLATING BATHS

Tin, lead and MSA levels in MSA baths are monitored by standard wet analyses. Hull cell plating tests determine the quality of the deposit obtained from a particular plating bath. Incremental additions of additives are made to the Hull cell to obtain optimum deposits and these additions are then prorated to the actual plating tank. Metallic impurities are determined by atomic absorption spectroscopy and are reduced in the bath by dummy plating. Organic contamination develops in the bath from resist breakdown, oils and organic decomposition products. Unlike fluoroborates, MSA baths cannot be easily carbon treated for organic contaminants. A practical method to effectively remove organics from an MSA bath has yet to be developed.

Alloy compositions are determined by beta backscatter methods or by X-ray diffraction. A reliable method of testing the alloy composition is by heat-

ing a suitable reflow oil 10°F above the melting point of the alloy being tested, e.g. 372°F for 60Sn/40Pb. The plated panel is then immersed in the heated oil. If the tin-lead alloy has the proper composition, the deposit will reflow. If reflow does not occur, the alloy composition is incorrect.

EQUIPMENT USED FOR MSA PLATING SYSTEMS

Tanks, pumps and filters should be constructed of polyethylene, polypropylene or Koroseal. Glass may also be used for tanks. Heating and cooling equipment should be constructed of Karbate or Teflon. Anodes should be of pure tin, pure lead or of the alloy composition required by the specific bath. Inert platinized titanium anodes are also suitable.

ADDITIONAL USES OF MSA IN METAL FINISHING

MSA, like its fluoboric acid counterpart, is used as a predip (10% solution) prior to plating to remove oxides from parts to be plated. It is also used to strip metals such as nickel, tin, lead, tin-lead and cadmium from copper and its alloys or from zinc and its alloys.²⁰

TIN, LEAD AND TIN-LEAD MSA BATHS

Table III gives bath compositions and operating conditions for various tin, lead and tin-lead alloy MSA baths.

TIN METHANE SULFONATE BARREL, STILL AND HIGH SPEED BATHS:

Uniform, smooth, satin tin deposits are obtained from this bath. The bath is well suited for electrolytic tin plate and is used to plate transistors, semiconductors, various electronic parts, refrigerator parts and kitchenware. The versatility of this bath enables using the same bath composition and additive for barrel/still plating and for high speed (reel to reel) plating. Higher temperatures permit higher current densities and wire speeds. Troubleshooting guidelines for this bath are given in Table IV.

LEAD METHANE SULFONATE BARREL AND STILL BATH:

Lead methane sulfonate baths are used in the plating of bearings, connectors, internal and conforming anodes for chromium plating, valves, seals and

Table IV. Troubleshooting Tin Based Baths

<i>Problem</i>	<i>Possible Causes</i>	<i>Corrective Actions</i>
Treeing	Low additive Low MSA	Add additive Increase MSA
Roughness	Metallic contamination Stannic tin Solids in bath Organic contamination	Dummy bath Filter bath and exclude air from bath Filter bath Carbon treat the bath
Lack of adhesion	Poor cleaning	Correct the cleaning cycle
Burning	Low metal Low MSA Low additive	Increase metal Increase MSA Add additive
Whiskers	Low metal Low additive Too high a current density Low temperature	Increase metal Add additive Decrease current density Increase temperature
Graininess	Low tin Low additive	Increase tin Add additive
Poor throw	Low MSA Low additive	Increase MSA Add additive
Gassing	Organic contamination Too high a current density Low metal Low additive Low temperature	Carbon treat the bath Decrease current density Increase metal Add additive Increase temperature

Table V. Troubleshooting Lead Based Baths

<i>Problem</i>	<i>Possible Causes</i>	<i>Corrective Actions</i>
Treeing	Low metal	Add metal
	Low additive	Add additive
Poor throw	Low metal	Add metal
	Low additive	Add additive
Roughness	Metallic contamination	Dummy bath
	Solids in bath	Filter bath
	Current density too high	Lower current density
	Low agitation	Increase agitation
	Low additive	Add additive
	Low MSA	Add MSA
	Chloride/sulfate contamination	Filter bath and check cycle
Lack of adhesion	Poor cleaning	Correct cleaning cycle
Dark deposit	Organic contamination	Carbon treat
Thin deposit	Low lead	Increase lead
	Current density too low	Increase current density
Mossy deposit (ternary alloy only)	Excess copper in bath	Analyze and adjust copper

Table VI. Troubleshooting 60/40 Solder Baths

<i>Problem</i>	<i>Possible Causes</i>	<i>Corrective Actions</i>
Poor throw	Low tin and lead	Increase tin and lead
	Low acid	Increase acid
	Low additive	Add additive
	High anode:cathode ratio	Remove several anodes
	Organic contamination	Carbon treat the bath
Gassing	Too high current density	Decrease current density
	Organic contamination	Carbon treat the bath
Treeing	Low additive	Add additive
	Low MSA	Increase MSA
Lack of adhesion	Poor cleaning	Check the cleaning cycle
Burning	Low tin and lead	Increase tin and lead
	Low MSA	Increase MSA
	Too high current density	Decrease current density
Graininess	Organic contamination	Carbon treat the bath
Rough deposit	Organic contamination	Carbon treat the bath
	Stannic tin	Filter the bath and exclude air from the bath
	Solids in bath	Filter the bath
	Chloride/sulfate contamination	Filter the bath and check the cleaning cycle
Incorrect alloy	Metallic contamination	Dummy the bath
	Low MSA	Increase MSA
	Wrong current density	Use correct current density
	Improper agitation	Use proper agitation
	Imbalance in tin and lead ratio of bath	Analyze bath and correct ratio
	Incorrect anodes	Use anodes with correct composition
Unsatisfactory reflow	Incorrect thickness	Use correct plating time
	Dewetting caused by: Improper cleaning	Check the cleaning cycle
	Organic contamination	Carbon treat the bath
	High reflow temperature	Use proper reflow temperature
	Incorrect alloy	See above

parts for storage batteries. Since lead deposits are soft, slow barrel speeds are recommended in order to prevent heavy parts from bonding to one another. See Table V for troubleshooting guidelines.

60Sn/40Pb SOLDER METHANE SULFONATE BARREL, STILL AND HIGH SPEED BATH:

This solder bath deposits a uniform, smooth, mat 60Sn/40Pb alloy over a wide current density range. The high throw of the bath and the excellent solderability and shelf life of the deposit make this bath suitable for use on printed circuit boards, connectors and other specialized electrical devices. The high speed bath is used for reel to reel applications, such as wire and strip plating. The still/barrel bath and the high speed bath have distinct additives. The Sn/Pb deposit is reflowed by standard methods. Troubleshooting guidelines are given in Table VI.

90Sn/10Pb METHANE SULFONATE BARREL, STILL AND HIGH SPEED BATH:

This bath provides a uniform, smooth, mat deposit which is used for various engineering applications. The flexibility of this bath makes it also suitable for rapid deposition of the 90Sn/10Pb alloy and it may be used for reel to reel operations, such as wire and strip plating. Higher temperatures permit higher current densities and wire speeds. The barrel/still bath and the high speed bath have distinct additives. See Table IV for troubleshooting.

93Pb/7Sn METHANE SULFONATE BARREL AND STILL BATH:

Deposits plated from the 93Pb/7Sn bath are harder than those obtained from a lead methane sulfonate bath. The 93Pb/7Sn bath is used to plate bearings and seals. Since 93Pb/7Sn alloys are soft, slow barrel speeds are recommended in order to prevent heavy parts from bonding to one another. See Table V for troubleshooting.

10Sn/88Pb/2Cu METHANE SULFONATE TERNARY ALLOY BARREL AND STILL BATH:

The operation of the ternary alloy bath is similar to that of the 93Pb/7Sn methane sulfonate bath. The ternary alloy deposit results in bearing metals that exhibit a greater resistance to fatigue than the 93Pb/7Sn alloys. The

alloy is used to plate linings in sleeve bearings. Use Table V for troubleshooting.

CONCLUSION

MSA based electroplating systems appear promising for plating tin, lead and tin-lead alloys on electronic components. Current technology requires electronic component miniaturization, high plating speed, improved reliability of performance and reduced cost of operation. Additionally, simplified wastewater treatment is a major consideration in all plating operations. These stringent requirements will only be satisfied through continued research and development of existing and evolving plating technologies. MF

References

1. F. Mathers et al, Trans. Electrochem. Soc., 76, 371 (1939).
2. A.T. Kuhn, "The Electrochemistry of Lead", Academic Press, London, 1979.
3. J. Vaid et al, J. Electrochem. Soc., 104,

460 (1957).

4. D.R. Gabe, Proc. Electrochem. Soc., 87-17, 13-41 (1987).
5. R.G. Baradas et al, J. Electroanal. Chem. Interfacial Electrochem., 243 (2), 435-444 (1988).
6. E.W. Schweiker, US Patent 2,407,579 (1946).
7. T. Sonoda et al, Hyomen Gijutsu, 40 (2), 306-310 (1989).
8. C.H. Chandler, US Patent 1,373,488 (1921).
9. L.S. Dietz, US Patent 2,393,239 (1946).
10. R. Piontelli et al, Proc. 3rd Intern. Conf. on Electrodep., 121-125 (1947).
11. F.L. Clifton, US Patent 2,489,523 (1949).
12. T.L. Rama Char, Electroplating and Metal Finishing, 10, 391 (1957).
13. A.N. Gongliashvili et al, USSR Patent SI 1,407,998 (1988).
14. W.A. Proell et al, Ind. Eng. Chem., 40, 1129 (1948).
15. W.A. Proell, US Patent 2,525,942 (1950).
16. K. Obata et al, US Patent 4,555,314 (1985).
17. F.I. Nobel et al, US Patent 4,617,097 (1986).
18. V. Opaskar et al, US Patent 4,582,576 (1986).
19. K. Obata et al, European Patent Application EP 192,273 (1986).
20. J.C. Chen, US Patent 4,678, 552 (1987).

Biography

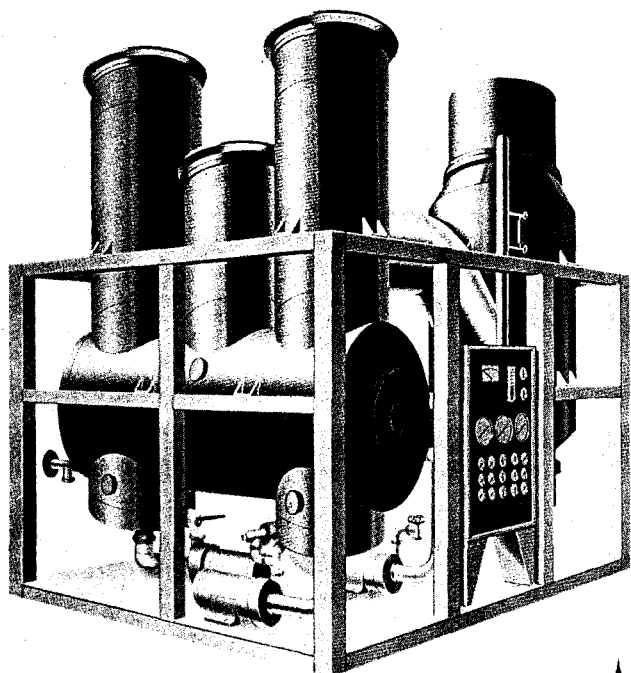
Charles Rosenstein is a senior chemist for CP Chemicals. He has been engaged in the metal finishing field for 10 years. He received his BS degree in chemistry from the Polytechnic Institute of Brooklyn, where he has continued his chemistry education. For more information on this article Rosenstein can be contacted at: CP Chemicals, Arbor St., Sewaren, NJ 07077. Tel: 201/636-4300.

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