

# REVIEW ON RECENT ADVANCES IN ELECTROFORMING DURING THE LAST DECADE

SM SILAIMANI AND S JOHN

*Central Electrochemical Research Institute, Karaikudi 630 006. Tamil Nadu. INDIA*

*Electroforming technique has been employed to produce components, structures and articles that would be difficult or impossible to produce by other methods of fabrication with a high degree of surface finish and dimensional accuracy. Electroforming differs from electroplating in that the electrodeposit is not a surface coating but actually forms the component. Electroforming is an expanding technology and hence used for a variety of applications. This paper reviews the status of electroforming technology particularly during the last decade preceding the new millennium. Recent developments in the applications of electroforming are discussed which includes moulds, electronic components, jewellery, aerospace applications and other industrial applications. Developments with respect to the alloy electroforming process, anode, electrolyte, pulse electroforming and new processes are also highlighted.*

*Keywords: Electroforming, electroplating.*

## INTRODUCTION

Electroforming is one of the secondary manufacturing processes of forming metals, in which parts are produced by electrolytic deposition of metal upon a conductive removable mold or matrix. The mold establishes the size and surface smoothness of the finished product. Metal is supplied to the conductive mold which is the cathode from an electrolytic solution in the form of suitable anode material. The process differs from plating in that a solid shell is produced which is later separated from the mandrel upon which it was deposited. Electroforming is particularly valuable for fabricating thin walled parts requiring a high order of accuracy, internal surface finish and complicated internal forms which are difficult to core or machine. It may also be used to advantage in producing a small number of parts which would otherwise require expensive tooling. Recent developments in the electrodeposition of metals have brought this somewhat obscure art into the category of precision manufacturing methods. This interesting technique makes available to the design engineer the means for solving many complicated fabrication problems encountered in the design of present day machines and instruments.

Watson reviewed and summarized the applications of electroforming [1-2]. John reviewed the

applications of electroforming [3-5]. The familiar gramophone record is a moulding the sound pattern which is formed upon its surface by pressing a reversed image of the sound track known as a matrix into a mass of heated thermoplastic material. An impression of the sound track is formed in the pressing and the sound track is of very small dimensions in the microgroove record being only 62  $\mu\text{m}$  width and 25  $\mu\text{m}$  deep and having a length of upto 630 m. In the case Compact Diskette (CD) and Digital Video Diskette (DVD) bears a helical track of shallow pits 0.1  $\mu\text{m}$  deep, 0.4 to 0.6  $\mu\text{m}$  wide and the distance between the tracks varies from 0.5 to 2  $\mu\text{m}$ . The length of the track runs to 30 Km and contains  $30 \times 10^9$  pits and allows 30 minutes playing time. Electroforming process has been universally adopted by the optical disc industry to produce stampers from glass masters. To date, electroforming is the only practical and proven method of producing stampers suitable for CD manufacturing [6-8]. Legierse described high speed electroforming process for CDROM storage disk manufacture [9].

## Mould

The moulds for electroforming of microstructured bodies are made by electrodepositing on thermoplastic materials with a film of conductive materials by Kernforschungszentrum [10]. Ulmer



*et al.* described the manufacture of the electroformed nickel-X-ray mirrors with finish of  $< 10\text{-}20$  Å rms from mandrels with thin layer of acrylic lacquer [11]. Metal is electrodeposited on mould by applying elastic moulding material to the surface of original object to be duplicated by Czar [12]. Very small high precision wave guide for operation in mm wavelength band can be made by copper electroforming on aluminium mandrel which is then dissolved out using sodium hydroxide etch solution was described by Bogenschiit *et al.* [13-14]. Toagosei Chemical Industries Co Ltd., produced copper clad laminate by contacting surface of conductive surface with catalyst liquid comprising platinum group metals, gold and or silver and forming copper foil by electrodeposition [15].

United Technologies Corp. electroformed nickel sheath for propellant blade comprising electrical conductive die whose exterior surface has shape conforming to interior portion of nickel sheath for electroforming [16-17]. Stark and Bacher described LIGA process involving lithography, electroforming and plastic moulding is used for fabrication of X ray mask nickel plastic moulding tools [18]. Mandrel for manufacturing inkjet orifice plate is formed by providing electroconductive layer on substrate having reusable pattern through electroforming and surface treating to reduce adhesion between subsequently applied electroplated film for separation of the film from the mandrel surface by Hewlett Packard Co. [19-20].

Tools for moulding plastic parts for anatomical applications are electroformed using epoxy or epoxy diamide resin mandrels [21]. United Technologies Corp used stereo lithographic techniques for making mandrels out of polymeric materials [22]. Xerox Corp separated the mandrel from the article by providing opening in tapered end portion of the mandrel [23-24]. Heuberger studied the possibilities for rendering wax mandrel conductive with conductive paints or use of high conductive  $\text{TiO}_2$  in automatic plants [25]. Michelsen-Mohammadein discussed the use of nickel electroforming for injection moulds with micro structure [26]. Bade described miniature moulds for microengineering which was manufactured using deep X ray lithography

followed by nickel electroforming [27]. Saumer and his team described the use of polymeric materials as mould in WGD micro nickel electroforming process [28]. Gultman *et al.* produced metallic micro components and structures using disposable plastic moulds by electroforming [29]. Electroforming of optical wave guides and transmission system using nickel mandrel to form the injection moulding tools is described by Sommer [30].

### Press tools

Orifice plate for ink jet printer is electroformed by Eastman Kodak Co [31] by forming an anodisable metal panel having photo resist pattern with smooth surfaced cylindrical cavity. Hewlett Packard Co [32] produced thermal inkjet print head orifice plate by electroforming method using mandrel having metallic and non metallic regions. GAO used substrates with defined surface structure for the production of reflection holograms on bank notes etc. from masters in dissolvable form and transferred directly to corresponding substrate [33]. Sharp made stampers from nickel electroformed master coated with tantalum or chromium layer having photo sensitive material pattern [34]. Jinting and Jinzhou described the electroforming process for the reproduction of holographic images and trouble shooting [35]. Xerox Corp encapsulating electroformed nickel with other material to prevent wear of nickel [36]. Scitex Digital Printing Inc [37] fabricated orifice plate for ink jet printer by aligning holder to mandrel and plating is applied to cause mandrel and holder to form single orifice plate directly bonded to holder. Pioneer Video Corp and Pioneer Electronic Corp manufacturing master disk for double sided optical disk from electroformed stamper having imaged photo resist layer [38]. Eastman Kodak Company using substrate having relief pattern as film as a mandrel for electroforming preciously defined aperture [39].

Bacher discusses variant of the LIGA system using UV lithography in place of X-ray and negative working epoxy resin photo resist [40]. Process comprising forming electroformed closed line graphic pattern and surrounding line on conductive substrate and then transfer them on to pressure sensitive adhesive layer on to surface of



adherent was patented by Tefco International Co [41].

### Electronic components

Micro parts Gesellschaft [42] produced stepped mould inserts having lateral and vertical precision used in the manufacture of stepped microbodies. Bergum discussed about the electroformed copper foil with improved adhesion by special treatment for multiplayer printed circuit boards [43]. Onfory and Saida developed new electroformed copper foil having smaller grain size which result in faster etch rate [44]. Romankiw described the evolution in lithography through mask plating technology in electronics [45]. Kukla *et al.* discussed the production of miniature plastic injection moulding by electroforming with LIGA process [46].

Detter [47], Reinecke [48], Weber and Chrfeld [49] reviewed the micro electroforming in the production of various microengineering components used for electronic applications by using various new plastic materials. Michaeli and Rogalia produced micro engineered components by LIGA electroforming process while somewhat larger components by micro injection moulding [50]. In High Aspect Ratio Micro Structure Technology (HARMST) Conf in Japan discuss the efforts to reduce the cost of LIGA manufacturing technology including electroforming and rapid phototyping using reusable electroformed mask [51].

### Jewellery and ornaments

Simon described different karat gold-silver alloy electroforming process at 313 K [52]. Ultralite Technology Inc produced gold jewellery articles by electroforming gold alloy jewellery from the first bath giving Vickers hardness 100-175 to predetermined thickness and then in second bath giving Vickers hardness 200-275 [53]. Electroforming thin walled precious metal or precious metal alloy hollow jewellery articles are produced by Josef Eberle GmbH & Co [54]. Simon reported gold and silver electroforming of hollow jewellery using wax core mandrel and also described the properties of the electroformed 18 and 24 K Au-Ag alloy [55]. Arnet described the new electroforming process in which deposition Au-Ag alloy directly on waxcore from cyanide bath at 313 K. Alloy composition may be selected from 8 K (white) to 18 K (yellow) [56].

Simon recalled the recent developments in Electroforming of Au, Ag and Pt and their alloys for jewellery [57]. Yasui & Co patented methods for hollow metal electroformed jewellery using low melting point material or chemically soluble material as mandrel [58-59]. Avon Products patented fusible alloy as mandrel for the production of hollow jewellery [60]. Electroplating Engineers of Japan Ltd prepared hollow platinum products by electroforming of platinum onto mandrel in a bath comprising chloroplatinic acid, alkali metal chloroplatinates and soluble carboxylate [61]. Ruprechi and Bacher describes the manufacture of IR band filters using LIGA process in which thin copper membranes with accurately located slit apertures are electroformed in copper fluoborate bath [62]. DiBari and Dini discussed the use of electroformed nickel foil to replace asbestos gaskets and forming of large thin walled parts copper targets for neutron source [63].

### Electroforming for aerospace applications

Thangavelu *et al.* reported copper electroforming of cryogenic upper stage main rocket engine using aluminium mandrel [64]. Abrasion shield with top and bottom legs and bonded leading portion for blade of low pressure fan of turbofan jet engine is produced by electroforming from Optical Radiation Corp. [65]. John *et al.* reported the nickel electroforming process for fabricating the high pressure extension nozzle based on stainless steel [66]. Electroforming of copper-zirconium alloy for cryogenic engineering applications is reported by Veeramani *et al.* [67]. John and co-authors reviewed the major steps involved in electroforming of cryogenic rocket engine thrust chamber for space applications [68-69]. Thangavelu *et al.* reported on copper electroforming of cryogenic upper stage main engine [70]. John and co-authors reported on the electroforming process for the manufacture of complex structures [71]. Electroforming of oxygen free high conductivity copper for cryogenic applications is reported by John and co-authors [72].

### Other industrial electroforming applications

Kato and Miyagi fabricated small core wave guide for medical application by the electroforming process [73]. Electrochemical codeposition of metal



and diamond powder directly on special matrix thereby producing diamond tools with metal base is described by Sadakov and Dyubankov [74]. The above authors described the electrodeposition of self lubricating composite coatings (nickel matrix containing fluoro hydrocarbons) on moving parts of the watches and manufactured watch cases with different colours by electrodeposition of Ni based composite coatings containing  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  particles [75]. John *et al.* reviewed the methods and materials employed for the electrofabrication process [76]. Electroforming of thin channel heat exchangers for nuclear applications reported by Srinivasan and coauthors [77].

### Alloy electroforming

Newer developments are reported in the field of alloy electroforming. Shen *et al.* [78] investigated the parameters influencing the properties of iron and iron alloy electroforming from solution containing  $\text{FeCl}_2$  300-400,  $\text{CaCl}_2$  100-150  $\text{g.l}^{-1}$  and additive. Balathandan and Seshadri discussed electroforming of nickel-cerium dioxide composites by both conventional and sedimentation deposition method [79]. Li Qing *et al.* studied the Nickel-Cobalt alloy electroforming regarding the effect of solution composition and operating conditions on internal stress, hardness, tensile strength and elongation [80]. Hyang, Chein-ho studied the effect of organic additives on Nickel-Cobalt alloy with low internal stress and high tensile strength from sulphamate bath [81]. Ratzker produced electroformed metallic glass alloy of Cobalt and phosphorous for dental applications [82]. Huang reported the effect of diammonium citrate on electroformed nickel-tungsten alloy [83]. Golodnisky *et al.* discussed the cathode process in nickel-cobalt alloy electroforming from sulphamate bath [84]. Some attempts was made by Thangavelu *et al.* in electroforming of nickel-tin-zinc alloy [85]. Huang *et al.* discussed the effect of stress reducers in nickel-tungsten alloy electroforming bath [86]. Silaimani *et al.* reported the nickel-copper alloy electroforming from citrate-sulphamate mixed electrolyte [87] as well as from the gluconate-sulphamate bath [88]. Fath *et al.* [89] studied the properties of nickel-iron electroform as a mould for moulding microstructures in high performance plastics. Silaimani *et al.* studied the characteristics

of zinc-manganese alloy electroforming using a mixed sulphate-gluconate bath [90]. Veeramani *et al.* studied the characteristics of electroformed copper-zirconium alloy for aerospace applications [91].

### Anode

The insoluble anode electrode with electroactive coating of composite oxides of iridium and tantalum on oxygen impermeable coating was produced as thin film on metal substrate for use as anode is reported by Permelec Electrode Ltd [92]. The same organization used platinum group metal oxides coated material as anode for electroforming applications [93,94]. Subramanian and Co-authors studied the recovery of activated nickel from the residues for electroforming applications [95].

### Cathode

Nippon Stainless Steel Kozai Co Ltd [96] patented drum for electroforming of metal foil which comprises an inner drum body and an outer cylindrical skin having insulating layer around the outer surface of the inner drum body. Metal foil is produced by Yates Industries [97] by electrodeposition on drum cathode comprising cylindrical titanium top cylinder on outer surface of base cylinder. Electrolytic copper foil is produced by Nikko Gould Foil Co Ltd., by passing stream of electrolyte between rotating cathode drum and anode electrode depositing copper on drum to form copper foil [98]. The same organization [99] used unifying sub anodes for electrode depositing metal on rotating cathode drum faced by anode shells. Continuous electrodeposition of metal foil comprising cylindrical drum and means for rotating semi cylindrical anode is reported by United Foil Inc. [100]. Gould Electronic Inc [101-102] made titanium cathode used for production of metal foil by welding together the ends of strip of titanium.

### Electrolyte

Dini and Gourdin observed the behaviour of conical shaped charge liners electroformed in proprietary acid copper sulphate solution [103]. Furukawa Circuit Foil Co Ltd., produced copper foil from solution containing water soluble cellulose ester as addition agent [104]. Gould Inc produced copper foil from a solution containing



chloride ion [105]. Sadakov and Burygina discussed about the effect of budin diol and propargyl alcohol in nickel electroforming from a bath containing nickel sulphamate, sodium chloride, boric acid pH 3.5-4.0 at 313 K [106]. High quality nickel sieves used in filtration of juices and in centrifuges can be obtained from periodically cleaned nickel plating electrolyte of composition nickel sulphate  $-600 \text{ g.l}^{-1}$ ,  $\text{H}_3\text{BO}_3$ -40  $\text{g.l}^{-1}$ , nickel chloride 7-12  $\text{g.l}^{-1}$  using chromoscane and sulphaethoxylate at 25  $\text{A.dm}^{-2}$  at 333 K was reported by Davydova and co-workers [107]. Stark *et al.* [108] discussed about contact angle measurements and the factors affecting the selection of surfactant for the nickel sulphamate electroforming bath.

Porous electroformed sheet from a solution containing surfactant which restrain pin hole formations on first layer and then second electroforming in a solution containing less surfactant to form larger pores was manufactured by KTX Co Ltd [109]. Copper foil used in secondary battery cells are electroformed by Circuit Foil Japan Co Ltd from the electrolyte containing 3 mercapto 1-propan sulphamate 0.5-5, polysaccharide 0.1-15, glue 0.3-35 and chloride ion 10-60 ppm [110]. The temperature of the electrolyte in electroforming of stampers for production of compact disc/laser data carriers was controlled by circulating the electrolyte from the storage tank to electroforming tank by Technostains GmbH [111]. Use of low concentrated copper electroforming bath for the production of linear electron accelerator structure investigated by Shanmugam *et al.* [112].

Thangavelu *et al.* produced hard nickel electroformed stampers from sulphamate bath containing 5 sulpho salicylic acid as an additive for increasing the hardness [113]. Malone described the fabrication of 500 MHz buncher cavity by copper electroforming using acid copper bath [114]. A low concentrated nickel sulphamate based activation bath for nickel electroforming of stainless steel extension nozzle reported by John *et al.* [115]. Veeramani *et al.* studied the induced codeposition of zirconium in acid copper electroforming solution [116]. The role of zirconium on electroforming of copper is studied by Silaimani *et al.* [117].

### Pulse electroforming

Pulse deposition has been employed as a technique since the 1950's but in the last ten years, it has been recognised as being useful in certain specific applications [118]. In recent years, electroplating of precious metals by pulse electrolysis have attracted considerable attention in electronic industries. The properties of electrodeposited metals are affected by electroplating conditions as well as number of physicochemical parameters. Among them form of the current used in electrolysis is particularly important. In the pulse electrolysis one has to consider the influence of three pulse parameters namely pulse current density ( $I_p$ ), pulse length ( $T_p$ ) and off time ( $T_0$ ) or pulse period ( $T = T_p + T_0$ ), whereas only one parameter in direct current electrolysis. Because these three quantities can be varied independently, various conditions would be used for metal deposition. These parameters however, make it intricate to determine the optimum conditions for electroforming of metals.

In conventional nickel electroforming using direct current, lot of metal is deposited as nodules which cause considerable wastage of high priced nickel anode. In addition, metal distribution is badly affected due to the over growth of nodules. John *et al.* reported the utilization of pulse current for the prevention of nodular growth during nickel electroforming [119]. Qu and his coworkers [120-121] investigated the effect of pulse current and pulse reverse current on electroforming of nickel micro components and also study the effect of pulse current on crystallographic texture. Wong used Taguchi analysis to identify the key factors in optimizing surface roughness in nickel electroforming [122].

### Process

Deposition of copper from acid copper sulphate electrolyte using the high speed selective jet electrodeposition technique was examined by Bocking [123]. Think Laboratory Co patented nickel electroformed rotary screen [124] from roll coated with high sensitivity photo resist film rotating at a predetermined speed in nickel electroforming bath and the laser beams are exposed on desired points. Koelzer discussed the texture and orientation of pulse electroforming and



their link with magnetic properties [125]. Quality of electroforms in terms of surface roughness improvement by types of waveforms was studied by Wang *et al.* [126]. Veeramani *et al.* employed high speed flow technique for electroforming of copper [127]. John and co-authors discussed the quality control aspects during the electrofabrication of complex structures [128]. The problem of achieving uniform thickness distribution on complicated shapes is reported by John *et al.* [129]. John reported on metal distribution contour map during nickel electroforming [130].

### Future of electroforming

Electroforming has interesting future in store for practitioners. Electroformed alloys have special properties of interest to engineers and scientists. Laminated metals with layers of different metals are electrodeposited to produce new and interesting structures. One of the promising system is copper layered with hardened or alloyed nickel, which would give the electrical properties of copper but the strength of nickel. Pulse electroforming also offers unique properties for specialized application. Electroforming is truly a choice for the future. The potential for new and cost effective product is abundant. The science and technology of electroforming has come of age and will continue to progress.

### CONCLUSION

Electroforming is a versatile, powerful and creative technique where the possibilities for the future are immense. The most important lines of development are likely to be in the materials field where unusual alloys or composites will be tailor made to particular end products with higher specifications from micro devices at one end of the scale to large components for the aerospace industry at the other. New electroforming developments can also be expected in the fascinating field of art form and or jewellery, where precision is less important than certain metallurgical requirements such as a good finish and a low cost mass production capability. All these developments will be aided by the availability of modern techniques for microprocess control and the electronic capabilities afforded by pulse plating in its various forms. Ancillary

technologies such as laser irradiation may well be applied to electroforming to achieve particular goals. In certain cases, electroforming time will be reduced by the use of forced high speed jet electrolyte flow technique around the cathode.

### REFERENCES

1. S A Watson, *Electroplating and Metal Finish*, **28**(7) (1975) 6
2. S A Watson, *Proc Intl Conf on Electrodeposition and Electroforming*, (1986) Bangalore, India, (Eds) E S Dwarakadoss, R P Dambal and J Balachandra, *Electrochem Soc of India*, Tata McGraw Hill Pub Co Ltd, New Delhi
3. S John, *Trans Met Fin Assoc India*, **7**(2) (1998) 131
4. S John, *Nat Conf on Emerging Trends in Electrometallurgy*, organized by SAEST, Karaikudi, (1998)
5. S John, *Trans Met Fin Assoc India*, **6**(4) (1997) 285
6. Karen Faux, *One to One*, **47** (2001) 135
7. Tim Frost, *One to One*, **32** (2001) 127
8. Roberto Kmbbs, *One to One*, **49** (2001) 134
9. P E J Legierse and R V Dam, *Galvanotechnik*, **84**(3) (1993) 787
10. Kernforschungszentrum Karlsruhe GmbH, Karlsruhe Germany, *US Pat 5073237* (1991)
11. M P Ulmer, R Haidle and R Altkorn, *Plating and Surface Finish*, **77**(10) (1990) 23
12. D Czar, 10008 Caddie N W, Albuquerque, MN 87114, *US Pat 5 013 409* (1991)
13. A F Bogenschütz, A Knoll and W Mussinger, *Galvanotechnik*, **82**(4) (1991) 1192
14. A F Bogenschütz, A Knoll and W Mussinger, *Galvanotechnik*, **82**(5) (1991) 1544
15. Toagosei Chemical Industrial Co Ltd, 14-1 Nishi shinbashi 1-chome, Ayase-shi, Kanagawa 252, Japan, *Europ Pat Appl 405369* (1991)
16. United Technologies Corp, United Technologies Bldg, 1 Financial Plaza, Hartford, CT 06101, USA, *Europ Pat Appl 399 943* (1991)
17. United Technologies Corp, United Technologies Bldg, 1 Financial Plaza, Hartford, CT 06101, USA, *US 4950375* (1991)
18. W Stark and W Bacher, *Galvanotechnik*, **83**(9) (1992) 2646
19. Hewlett-Packard Co, 3000 Hanover, St Palo Alto, CA 94304 USA *Europ Pat Appl 489246* (1992)
20. Hewlett-Packard Co, 3000 Hanover, St Palo Alto, CA 94304 USA *Europ Pat Appl 490061* (1992)
21. E Brandt, *Kunststoffe*, **83**(7) (1993) 531
22. United Technologies Corp, United Technologies Bldg, 1 Financial Plaza, Hartford, CT 06101, USA, *Europ Pat Appl 508 935* (1994)
23. Xerox Corp, Stanford, CT, *US Pat 5 385660* (1995)
24. Xerox Corp, Stanford, CT, *US Pat 5 389227* (1995)
25. U Heuberger, *Galvanotechnik*, **86**(11) (1995) 3557



26. Michelsen-Mohammadein, *Metalloberflaeche*, **52(11)** (1998) 856
27. K Bade, *Galvanotechnik*, **90(3)** (1999) 8018
28. M Saumer, K Teit, O Roetting and W Bacher, *Galvanotechnik*, **90(11)** (1999) 1100
29. M Gultman and E Watch *et al*, *Metalloberflaeche*, **54(11)** (2000) 16
30. V Sommer, *Galvanotechnik*, **91(3)** (2000) 791
31. Eastman Kodak Co, 2260 Lake Ave, Rocheder, New York 16550, USA, *US Pat* 4971665 (1990)
32. Hewlett Packard Co, 3000 Hanover St, Palo Alto, CA 94304, USA, *Europ Pat Appl* 509669 (1992)
33. GAO Gesettschaft fur Automation und Organisation MbH Portfach 70 07 03 D - 81307 Munich, Germany, *Europ Pat Appl* 6563 992 (1995)
34. K K Sharp, Osaka Japan, *US Pat* 5 385 638 (1995)
35. C Jinting and C Jinzhou, *Electroplat and Finish*, **15(1)** (1996) 13
36. Xerox Corp, Stamford, CT, *US Pat* 5681440 (1997)
37. Scitex Digital Printing Inc, Dayton, OH 45420-4099, USA, *Europ Pat Appl* 784105 (1997)
38. Pioneer Video Corp, Pioneer Electronic Corporation, Japan, *US Pat* 5843626 (1998)
39. Eastman Kodak Co, *EP* 1 002 647 A2 (2000)
40. W Bacher, *Galvanotechnik*, **91(8)** (2000) 2265
41. Tefco International Co Ltd, Japan, *US Pat* 5891 317 (1999)
42. Microparts Gesellschaft fur Mikrostrukturtechnik mbH, Dostmunal Germany, *US Pat* 5529 681 (1996)
43. E J Bergum, *Circuit Work*, **22(1)** (1995) 10
44. G Onfory and M Saida, *Trans Inst Met Fin*, **74(4)** (1996) 133
45. L T Romankiw, *Plating and Surface Fin*, **84(1)** (1997) 10
46. C Kukla, H Lobi and H Detter *et al*, *Kunststoffe*, **88(9)** (1998) 1333
47. H Detter, *Kunststoffe*, **88(10)** (1998) 1888
48. H Reinecke, *Galvanotechnik*, **90(1)** (1999) 191
49. L Weber and W Chrfeld, *Kunststoffe*, **89(10)** (1999) 192
50. W Michaeli and A Rogalia *et al*, *Kunststoffe*, **89(9)** (1999) 80
51. HARMST'99-LIGA Acquires A Competitor, *Galvanotechnik*, **90(9)** (1999) 2547
52. F Simon, *Surface*, **226** (1991) 37
53. Ultralite Technology Inc, Attleboro, MA *US Pat* 5393405 (1995)
54. Josef Eberle GmbH and Co, KG, D-75233, Tiefenbornn, Germany, *Europ Pat Appl* 702910 (1996)
55. F Simon, *JOT*, **36(4)** (1996) 98
56. E Arnet, *Galvanotechnik*, **86(11)** (1995) 35795
57. F Simon, *Trans Inst Metal Fin*, **75(3)** (1997) B56
58. M Yasui and Co Ltd, Tokyo, Japan, *Europ Pat Appl* 727 511 (1996)
59. M Yasui and Co Ltd, Tokyo, Japan, *Europ Pat Appl* 5837118 (1998)
60. Avon Products Inc, New York, *US Pat* 5891 317 (1999)
61. Electroplating Engineering of Japan Ltd, *US Pat* 5 529 680 (1996)
62. R Ruprechi and W Bacher, *Metalloberflaeche*, **12** (1991) 531
63. G DiBari and J Dini, *Plating and Surface Finishing*, **84(12)** (1997) 20
64. PR Thangavelu, S John *et al*, *Bull Electrochem*, **16(11)** (2000) 493
65. Optical Radiation Corp, Azusa, CA, *US Pat* 5674370 (1997)
66. S John, K N Srinivasan, P Veeramani, N V Shanmugam, PR Thangavelu, SM Silaimani and M Raghavan, *Tenth National Convention of Electrochemists, April (2001) organized by SAEST, karaikudi, India*
67. P Veeramani, RM Krishnan, S John and T Vasudevan, *18th national Symposiumon Cryogenics, New Delhi, Nov (2001)*
68. S John, *Electrochem Soc of India*, **48(3)** (1999) 177
69. S John, P Veeramani, K N Srinivasan, PR Thangavelu, N V Shanmugam and M Raghavan, *Proc XVIII Intl Cryogenic Engine Conf, IIT Bombay, Feb (2000)* 675
70. PR Thangavelu, P Veeramani, K N Srinivasan, N V Shanmugam, M Raghavan and S John, *Natl Seminar on Recent Trends in Mat Sci, Alagappa University, Karaikudi*, (1999)
71. S John, PR Thangavelu, N V Shanmugam, P Veeramani, K N Srinivasan and M Raghavan, *Trans Indian Inst Metals*, **51(5)** (1998) 449
72. S John, PR Thangavelu, K N Srinivasan, N V Shanmugam, P Veeramani, Malathy Pushpavanam and M Raghavan, *Proc Nat Seminar on Emerging Trends in Electrochem Ind, Alagappa University, Karaikudi* (1996) 52
73. Y Kato and M Miyagi, *J Surf Finish Soc Japan*, **43(8)** (1992) 750
74. G A Sadakov and EN Dyubankov, *Electroplat and Surf Treat*, **3(1)** (1994) 29
75. G A Sadakov and EN Dyubankova, *Electroplat and Surf Treat*, **3(3)** (1994) 38
76. S John, P Veeramani, K N Srinivasan, N V Shanmugam and PR Thangavelu, *Seminar on Met Finish for Millenium 2000, Electrochem Soc of India, Bangalore, July (1999)*
77. K N Srinivasan, P Veeramani, PR Thangavelu, N V Shanmugam, M Raghavan and S John, *Trans Met Fin Assoc India*, **7(2)** (1998) 119
78. S Shen *et al*, *Materials Protection*, **23(7)** (1990) 138
79. S Balathandan and S K Seshadri, *Metal Finishing*, **90(4)** (1992) 51
80. Li Quing, Wu Yao, Wu Jiang and You Wei-Qing, *Electroplating and Finishing*, **11(1)** (1992) 46
81. Hyang, Chein-ho, *Met Finish*, **91(6)** (1993) 197
82. Ratzker, *US Pat* 5316650 (1994)
83. C H Huang, *Plat and Surf Finish*, **84(4)** (1997) 62



84. D Golodniský, N V Gudín and G A Volyanuk, *Plat and Surf Finish*, **85**(2) (1998) 65
85. PR Thangavelu, SM Silaimani and S John, *Bull Electrochem*, **15**(5-6) (1999) 186
86. C H Huang, W Y She and H M Wu, *Plat and Surf Finish*, **86**(12) (1999) 79
87. SM Silaimani, PR Thangavelu and S John, *Bull Electrochem*, **16**(7) (2000) 326
88. SM Silaimani, PR Thangavelu and S John, *Natl Sem on Recent Trends in Met Sci, Alagappa University, Karaikudi*, May (1999)
89. A Fath, W Leskopf *et al*, *Galvanotechnik*, **91**(6) (2000) 1690
90. SM Silaimani, K N Srinivasan and S John, *Annual Technical Meeting of the Electrochem Soc of India, Bangalore*, July (2001)
91. P Veeramani, RM Krishnan, S John and M Raghavan, *Proc of the Fourth Indian Chemical Emerging Congress-2000, Chemcon, NMFP17*
92. Permelec Electrode Ltd, No 1159 Ishikawa Fujisawa-Sh Kanagawa, Japan, *Europ Pat Appl* 598 517 (1994)
93. Permelec Electrode Ltd, No. 1159 Ishikawa Fujisawa - Sh Kanagawa, Japan, *Europ Pat Appl* 598 519 (1994)
94. Permelec Electrode Ltd, No 1159 Ishikawa Fujisawa - Sh Kanagawa, Japan, *Europ Pat Appl* 540 7556 (1995)
95. A Subramanian, K N Srinivasan, S John and T Vasudevan, *J Applied Electrochemistry*, **31** (2001) 35
96. Nippon Stainless Steel Kozai Co Ltd, Nilgala, Japan, *US Pat* 4975169 (1990)
97. Yates Industries Bordetown, New Jersey, *US Pat* 5 019 221 (1991)
98. Nikko Gould Foil Co Ltd, Tokyo, Japan, *Europ Pat Appl* 491 163 (1992)
99. Nikko Gould Foil Co Ltd, Tokyo, Japan, *Europ Pat* 5 326 455 (1994)
100. United Foils Inc, San Marcos, CA *US Pat* 5360525 (1994)
101. Gould Electronic Inc, 35129 Curtis Blud, Eastlake OH 44095 - 4001, USA, *Europe Pat Appl* 632146 (1995)
102. Gould Inc Eastlake, OH, *US Pat* 403 465 (1995)
103. J W Dini and W H Gourdin, *Plat and Surf Finish*, **77**(8) 1990 54
104. Furukawa Circuit Foil Co Ltd, Tokyo, Japan, *US Pat* 4 976 826 (1990)
105. Gould Electronic Inc., 35129 Curtis Blud, Eastlake OH 44095 - 4001, US A, *Europe Pat Appl* 485 558 (1992)
106. G A Sadakov and E Kh Burygina, *R Zn Korr Zashch Ot Korr*, (1990) 11K467
107. I M Davydova, L V Egorova, V M Mikhailin, S V Kolsol, I B Malanina and O N Krytova, *R Zh Korr C Zashch Ot Korr*, (1990) 2K439
108. W Stark, B Mattnis and M Saumer, *Galvanotechnik*, **87**(4) (1996) H07
109. KTX Co Ltd, Aichi-Ken Japan, *US Pat* 5728284 (1998)
110. Circuit Foil Japan Co Ltd., Tokyo, Japan, *US Pat* 5834140 (1998)
111. Technostains GmbH, Sassenberg, Germany, *US Pat* 5833 828 (1998)
112. N V Shanmugam, PR Thangavelu, P Veeramani and S John, *Natl Symp on Electrochem in Nucl Tech organized by SAEST, IGCAR, Kalpakkam* (1998)
113. PR Thangavelu, SM Silaimani, N V Shanmugam and S John, *Bull Electrochem*, **13**(3) (1998) 115-B
114. G Malone, *Plating and Surface Finishing*, **86**(3) (1999) 36
115. S John, K N Srinivasan, P Veeramani and M Raghavan, *Natl Symp on Electrochem Sci and Tech, Electrochem Soc of India, Bangalore*, July (2000)
116. P Veeramani, RM Krishnan and S John, *9th Natl Conv of Electrochem*, Nov (1999) organized by SAEST, Karaikudi, India
117. SM Silaimani, S John and V S Muralidharan, *Bull Electrochem*, **17** (2001) 10
118. S John, *Natl Symp on Electrochem Sci and Tech, July (1999) organized by Electrochem Soc of India, Bangalore*
119. S John, K N Srinivasan, P Veeramani, S Vincent and PR Thangavelu, *Annual Technical Meeting of the Electrochem Soc of India, Bangalore*, July (1994)
120. N S Qu, K C Chan and D Zhu, *Surf and Coat Tech (Swit)*, **98**(3) (1997) 220
121. K C Chan, S Qu and D Zhu, *Surf and Coat Tech*, **99**(1-2) (1998) 69
122. R P Wong, K C Chan and T M Yue, *Plat and Surf Finish*, **86**(5) (1999) 125
123. C Bocking, *Trans Inst of Met Finish*, **69**(4) (1991) 119
124. Think Laboratory Co Ltd, Chiba Japan, *US Pat* 5 338 627 (1994)
125. S Koelzer, *Plat and Surf Finish*, **86**(5) (1999) 110
126. K P Wong, KC Chan and T M Yue, *Surf and Coat Tech*, **115**(2-3) (1999) 132
127. P Veeramani, RM Krishnan, S John and M Raghavan, *10th Natl Conv of Electrochemists, April (2001), organized by SAEST, Karaikudi, India*
128. S John, V Ananth and T Vasudevan, *Bull Electrochem*, **15**(5-6) (1999) 202
129. S John, P Veeramani, K N Srinivasan and PR Thangavelu, *Proc of Natl Conf on Quality Control in Metallurgical Industries, organized by P S G College, Coimbatore* (1999) 531
130. S John, *Natl Symp on Electrochem Sci and Tech, organized by Electrochem Soc of India, July (1997)*