**IONMET - New Ionic Liquid Solvent Technology to Transform Metal Finishing**

In his *EIPC Perspective* column in April's CircuiTree, European Institute of Printed Circuits managing director Frank Smulders referred to EIPC's involvement as a partner in IONMET, an integrated project within the European Community's 6th Framework programme whose stated objectives are to promote innovation, to strengthen the scientific and technological bases of European industry and to encourage its international competitiveness.

IONMET is a four-year funded project which began in 2005, aimed at the development of new techniques of metal deposition and dissolution using ionic liquids, which has brought together 33 partners from 11 EU countries, the majority being industrial SME'S (small to medium enterprises - less than 250 employees, less than 50M Euro turnover), with the support of universities, research organisations and trade associations.

All partners of the IONMET project Düsseldorf 2006

Traditional techniques for electroplating and metal finishing have been based on aqueous chemistry, which effectively limits the range of possible finishes and related processes. And typical process solutions contain toxic and corrosive chemicals.

IONMET set out to establish radically new technology with the potential to transform the scope and competitiveness of industrial metal finishing processes. This new technology would introduce a generic group of ionic liquid solvents to provide tools to significantly transform the innovative capability of SME'S involved in surface finishing and printed circuit board manufacturing.

What are ionic liquids? (I confess I had no idea until I tried Google and got over a million results! - PS) In principle they are non-molecular ionic solvents melting at less than 100 deg C, often at room temperature or below Whereas high temperature melts are commonly referred to as "molten salts" or "fused salts", salts in the liquid phase at low temperature are described by the terms "room-temperature ionic liquids", "non-aqueous ionic liquids" or "liquid organic salts". Ionic liquids in their molten form are composed wholly of ions. General characteristics are that at least one of the ions is large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower its melting point. There are two main categories: simple salts made of a single cation and anion, and binary ionic liquids. Invariably, these ionic liquids are either organic salts or mixtures consisting of at least one organic component. The composition and properties of ionic liquids are determined by the combination of cation and anion, and the differences in their structures and inter-ionic interactions. Until recently, room-temperature ionic liquids were considered to be rare, but it is now known that many salts form liquids at or close to room temperature. To make an ionic liquid, researchers can select from dozens of small anions and thousands of large cations to produce “designer solvents” which can be customised to suit a particular need such as dissolving certain chemicals in a reaction or extracting specific molecules from a solution.

Ionic liquids have the potential to increase chemical reactivity and thus lead to more efficient processes with higher product yields and reduced waste. They are electrically conductive, non-inflammable and have very low vapour pressure, which makes them less toxic than conventional solvents.

Ionic liquids are not new. Ethyl ammonium nitrate for example, which has a melting point of 12° C, was first described in 1914. But it has been during the last decade that research and development has accelerated to a point where a huge number of novel ionic liquids and associated applications have been developed.

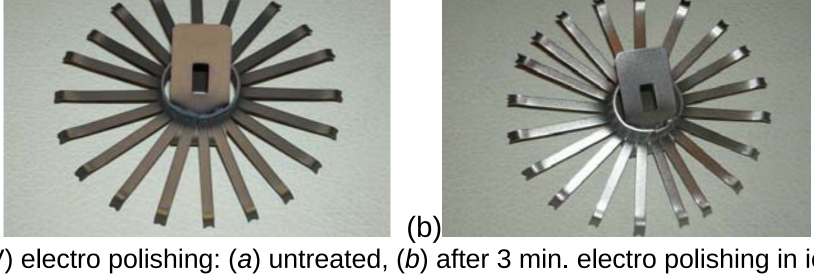
One particularly active research group is the team led by Professor Andrew Abbott at the University of Leicester in UK, a partner in the IONMET project. They have recently developed a range of ionic liquids based on choline chloride (chemically N-[2-Hydroxyethyl]trimethylammonium chloride). Choline chloride is also known as Vitamin B4 and is produced commercially in high volume as an additive for chicken-feed! The ready availability of this material enables the cost-effective preparation of choline-chloride-based ionic liquids in industrial, rather than laboratory, quantities and the university has set up a joint venture with a major chemical manufacturer to provide a production, marketing and licensing facility whilst fundamental and applied research is carried out. The joint venture company holds three worldwide patents that cover over a million ionic liquids and it has made 1 ton batch of ionic liquids that it is selling internationally, making it currently the world's largest manufacturer of ionic liquids.

The research group is currently studying fundamental aspects of solvation in ionic liquid media to determine solubility and reaction mechanisms, and developing applications in metal finishing, ore processing and chemical synthesis.

One metal finishing project which has already reached pre-production scale, developed with the support of UK government funding, has been a revolutionary way of electro polishing stainless steel using ionic liquid electrolyte in place of mixtures of phosphoric and sulphuric acids. The new electrolyte is non-corrosive and exhibits improved current efficiency.

As a partner in the IONMET project, the Leicester group is exploring the properties of ionic liquids as replacement technologies for the metal finishing industry, and investigating the underlying science, physical chemistry and electrochemical properties of the new processes which include zinc, nickel and chromium electroplating as well as electro polishing and other electrochemical dissolution processes.

(a) (b)



Ti alloy (Ta6V) electro polishing: (*a*) untreated, (*b*) after 3 min. electro polishing in ionic liquid bath.

Elsewhere in the IONMET partnership, there is a huge amount of international cooperation in the evaluation and development of metal finishing processes, some of which may offer direct replacements for existing processes, but with improved properties and more cost-effective and environmentally acceptable operation, electro polishing and hard chromium plating being examples, and some of which could provide means of achieving what has been impossible with aqueous technology. Examples are the electroplating of water-sensitive substrates such as magnesium and titanium or water-sensitive finishes such as aluminium and tantalum. Processes are at various stages of development from early laboratory trial to pilot-scale commercialisation. There is considerable scope for the deposition of nano-structured coatings of metals such as aluminium, nickel, copper, chromium, cobalt, silver and selenium from ionic liquid electrolytes, and for alloys such as nickel-zinc, from which the zinc component could be subsequently leached-out to leave a nano-porous nickel for use as a high-surface-area electrode. Moreover, it is feasible to electroplate semiconductors such as silicon, germanium and gallium arsenide for microelectronics and photovoltaic power generation, and these opportunities are also being explored. The possibilities are truly infinite.

Although the majority of the work of IONMET is ultimately directed towards the general and specialist metal finishing industries, there are significant potential applications in printed circuit technology, particularly in protective and solderable finishes. A nano-structured immersion silver based on ionic liquid technology is at an advanced stage of development, and is being evaluated by the only PCB fabricator in the partnership, PW Circuits, based in the East Midlands of the UK. CircuiTree visited PW Circuits for a practical end-user's view from managing director Cecil O'Connor.

O'Connor is a hands-on engineer who founded the company 35 years ago and continues to maintain an active technical involvement in his manufacturing process. He has been working in close collaboration with Professor Abbot's group at University of Leicester since the inception of IONMET, and his interest in the silver process is more than academic. Since RoHS legislation put severe constraints on the use of tin-lead HASL, PW had adopted a leading proprietary immersion silver as a mainstream solderable finish. A serious cause for concern had been the well-documented phenomenon of corrosion of copper at the solder mask interface during immersion tin deposition. PW Circuits had minimised the effect by careful process optimisation and control, but the supplier was unable to overcome it because this type of corrosion is a natural consequence of the aqueous base chemistry of proprietary immersion tins. The fundamentally non-aqueous nature of alternative ionic-liquid chemistries presented a potential route to eliminating the problem at source. Additionally, the nano-structure of the deposit offered possible benefits in the performance of the deposit.

Extensive trials have been conducted by PW Circuits with immersion silver formulations based on ionic liquids developed at University of Leicester. (Because of intellectual property considerations, formulation details cannot be disclosed at this stage). Results have been very positive. Deposition rates are comparable with those of proprietary aqueous-based processes, at lower process temperatures, with no corrosion of copper at the solder mask interface. Solderability is excellent, at lower soldering temperatures than those recommended for the proprietary processes. A team at "Katholieke Hogeschool Sint-Lieven" in Belgium is co-operating in the development of brighteners and additives to improve the cosmetic appearance and the shelf life of the deposit, and C-Tech Innovation, based in UK, is developing a pilot-scale horizontal line for demonstration and further evaluation. It is likely that a marketable process will be available in the foreseeable future. An associated area of development is the substitution of traditional aqueous-based cleaner and micro-etch with ionic-liquid-based pre-treatment chemistry, to give an integrated non-aqueous process.

Two years in: the IONMET project has established a strong network of co-operation between its partners and yielded some very promising initial results. New ionic liquids have been made in industrial quantities. Some significant progress has been made in the electro deposition of chromium, zinc and zinc alloys.

a bright deposit of aluminium on a rod of mild steel.

Aluminium has been successfully deposited on steel, and the scale-up of some plating and polishing processes has begun. Important advances in solderable finishes for printed circuits are being realised. The IONMET project has another two years to run. If “exciting” is an adjective which is appropriate in the context of metal finishing, expect some quite exciting innovations!

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