Ionic Liquids for Surface Finishing Processes

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Ionic liquids are known by a variety of names, including low temperature molten salts, liquid organic salts, non-aqueous ionic liquids and room temperature ionic liquids. They have been around for many decades. However, it is only more recently that there has been increased interest in using these liquids for surface finishing operations such as cleaning, electropolishing and the electrodeposition of reactive metals, such as aluminum. Figure 1 illustrates this trend in terms of the number of ionic liquid publications in recent years.[1]

In this column, we will briefly discuss what ionic liquids are, the benefits of using them instead of aqueous based processing baths, some possible applications and what might be some of the barriers to their more widespread adoption by the surface finishing industry.

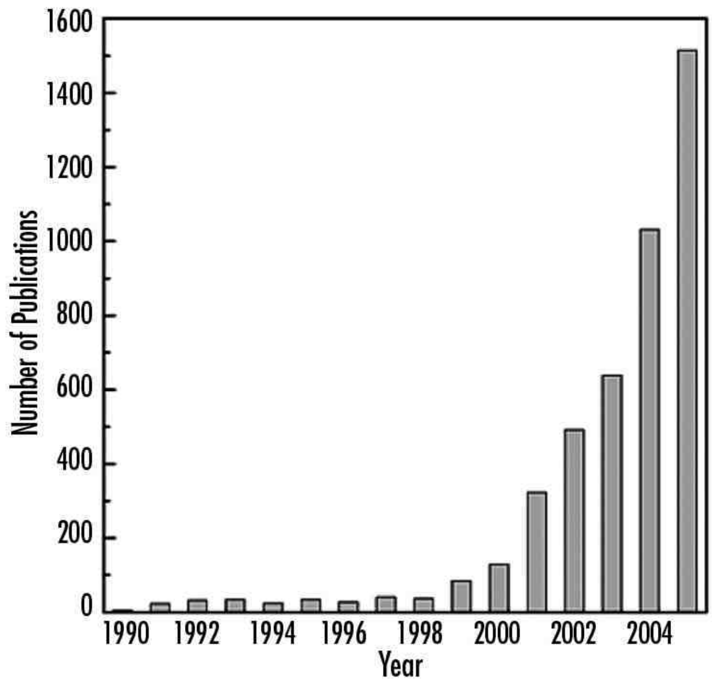

Figure 1—Trend in the number of publications on ionic liquids.[1]

What are ionic liquids?

Ionic liquids are defined as liquids consisting only of cations (+) and anions (-), and which by definition have a melting point of 100°C or below. The cations are large and irregular in shape, while the anions are smaller. Because of this disparity in shape and size, the ions do not form regular (crystalline) arrays and become solid salts (*e.g.*, $Na^+ + Cl^- \rightarrow NaCl$, as shown schematically below) but exist in liquid form.

Typically, the cations are organic chemicals (*e.g.*, ammonium-based compounds such as triethylammonium or tetraalkylphosponium) and the anions are inorganic chemicals (*e.g.*, tetrafluoborates) or more environmentally acceptable, complex organic compounds that do not contain halides, such as triflates.[2] There is a comprehensive database of ionic liquids and their properties where these and other compounds are listed.[3] Ionic liquids are electrically conductive, have a low vapor pressure, are highly solvating, have a wide voltage range where they are stable electrochemically and are not flammable below their dissociation temperature. With the right choice of ions, the properties can be "tuned" to provide the desired melting point, viscosity, density, pH, miscibility with water and so on, thus making them attractive for a wide range of uses.

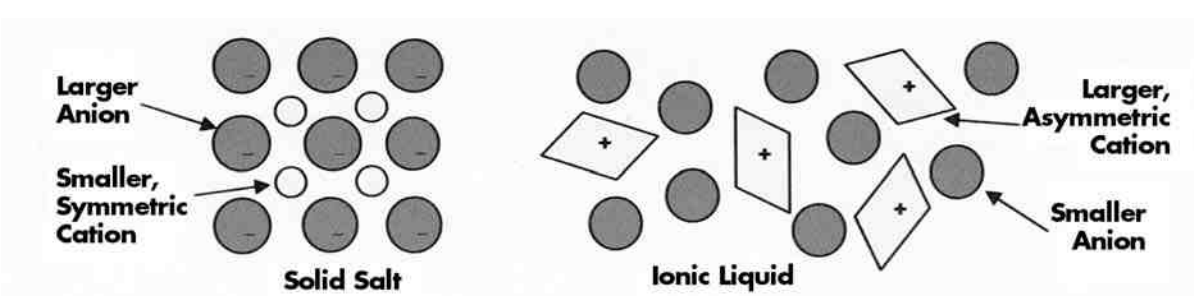

Figure 2—Solid salt compared to an ionic liquid.

What are some current and proposed uses?

About 300 ionic liquids are available commercially,[4] and those currently in use are mostly involved with chemical synthesis and production, such as described in Reference (1), where it is used to remove byproduct acid. Other chemical industry applications include use as a reaction medium or solvent, distillation, extraction and catalysis. Other applications described in the open literature[1,5] include use in the textile, paper and plastics industries; treatment of nuclear wastes; as battery and capacitor electrolytes; and in the oil and gas industries. Some more esoteric uses are being explored,[5] such as electrolytes in electrochemical mechanical actuator devices, dye-sensitized photo-electrochemical cells and as solvents for "electrowetting on dielectric micro-reactors" (also known as "lab-on-a-chip") to prepare very small quantities of dangerous, expensive or rare chemical compounds.

Possible surface finishing applications

As long ago as 1948, 1-butyl-pyridium chloride/aluminum chloride mixtures were investigated as electrolytes for electrodepositing aluminum coatings.[4] Since that time there has been sporadic interest in using ionic liquids for: (1) surface treatment of reactive metals (such as magnesium and titanium); (2) electrodeposition of reactive metals (such as aluminum and tantalum); (3) cleaning; (4) electrodeposition of nano-structured and nano-porous coatings (such as zinc, chromium, silver, nickel and their alloys); (5) electrodeposition of semiconducting materials; (6) electropolishing and (7) wastewater treatment. Table 1 lists some of these applications and their current stage of development and comments about some of them.

Some of this information was extracted from an editorial by the Managing Director of the European Institute of Printed Circuits,[6] and refers to the work being done under the auspices of IONMET, an integrated project in the European Community's 6th Framework Programme. Other information is from the sources provided in the given references.

Aqueous cleaning processes do not work well for reactive metals, and organic solvents are associated with health and safety issues, as well as environmental compliance limitations. Ionic liquids offer an alternative approach with some attractive features, such as low vapor pressure, low processing temperatures and the ability to remove polar and non-polar soils.[7] A disadvantage with their use is that residual liquid may remain on the surface, which may be good to prevent flash rusting on ferrous substrates, but it could interfere with subsequent processes such as electroplating.

Similarly, aqueous conversion coating processes do not work well for reactive substrates such as magnesium. However, an ionic liquid based process (using bis(trifluoromethane sulfonyl)amide (TFSA) as the anion) has been investigated[8] for providing a protective, corrosion resistant coating. The results were found to be promising.

The use of ionic liquids to electrodeposit aluminum coatings is of interest to the defense industrial base because ion vapor-deposited (IVD) aluminum coatings are the only qualified coatings as a replacement for cadmium coatings primarily used on steel components. However, the IVD coatings must receive post-treatments, such as chromium-containing conversion coatings, to provide the required corrosion protection properties.[9] Electrodeposited aluminum coatings have been shown to provide excellent properties,[10] and could be used to replace cadmium coatings. However, the bath is composed of hazardous organic chemicals (*e.g.*, toluene) and is difficult to operate, and has not been scaled up to be useful for the aerospace industry. An ionic liquid bath chemistry could overcome the problem with the use of toluene in the bath electrolyte, and academia and industry have been working to develop a robust process,[6,11] Preliminary results show promise, as seen in Figure 2.

Academia also has been investigating the electroplating of aluminum alloys and composite coatings from ionic liquids to improve coating properties. Examples of the alloys being studied are Al-Cr,[12] Al-Mn,[13] Al-Nb[12] and Al-Ti[12,14] and the composite is aluminum with dispersed 0.2-micron SiO_2 particles.[15]

Chromium may be deposited from a trivalent chromium electrolyte that is said to be more environmentally acceptable than conventional aqueous plating baths containing hexavalent chromium.[16] In addition, the current efficiency of this process is said to be greater than 90%!

The deposition of nanostructured silver coatings for printed circuit board (PCB) applications is of interest because the use an ionic liquid overcomes the problem of corrosion of copper at the solder mask interface when aqueous silver plating baths are used.[6] Deposition can be done at lower temperatures and solderability is excellent. This application is said to be at an "advanced stage" of development.

A number of zinc alloys have been deposited from ionic liquids in the laboratory on steel, nickel, tungsten, copper and glassy carbon substrates. The alloys include Zn-Cd,[17] Zn-Co,[18] Zn-Fe,[19] Zn-Mg[20] and Zn-Sn.[21] The corrosion protection provided by the Zn-Mg alloy on a steel substrate was stated to be twenty times better than a similar zinc coating. The work with the Zn-Sn alloy coatings on nickel is also of interest because it demonstrated that a composite coating could be obtained if alumina particles were added to the ionic liquid plating bath.

A few studies have been done on electrodepositing platinum metal group alloys for improved catalysts. One study focused on palladium-gold alloys[22] and another on platinum-zinc alloys.[23]

An ionic liquid can be used for electropolishing stainless steel, with the advantages that the electrolyte is non-corrosive and the current efficiency is higher.[6,16] As a result, this surface finishing process already has been scaled up to a "pre-production" scale.

It also may be feasible to deposit silicon, germanium and gallium arsenide from ionic liquid electrolytes,[6] which certainly cannot be done from aqueous electrolytes.

Figure 3—Aluminum deposited on a mild steel rod.[6]

Table 1
Ionic liquid applications and their current stage of development

Process	Substrate/Coating	Ionic Liquid Use	Comments/Status
Cleaning	Various	Solvent/extractant	Laboratory R&D scale; substrates include light (reactive) metals
Conversion Coating	Magnesium	Bath electrolyte	Laboratory R&D scale; avoids aqueous processing baths
Electroplating	Aluminum, copper, steel/**aluminum**	Bath electrolyte	Laboratory R&D scale up in progress; nanostructured coatings possible
	Various/**cadmium**	Bath electrolyte	Laboratory scale
	Various/**chromium**	Bath electrolyte	Pilot scale; trivalent Cr bath; nanostructured coatings possible on laboratory scale
	Various/**cobalt**	Bath electrolyte	Laboratory R&D scale; nanostructured coatings possible
	Various/**copper**	Bath electrolyte	Laboratory R&D scale; nanostructured and copper-tin alloy coatings possible
	Silver/**magnesium**	Bath electrolyte	Laboratory R&D scale; studied for battery electrode use
	Various/**manganese**	Bath electrolyte	Laboratory R&D scale
	Various/**nickel**	Bath electrolyte	Laboratory R&D scale; nanostructured coatings possible
	Various/**nickel-zinc**	Bath electrolyte	Laboratory R&D; zinc can be leached out to provide porous, high surface area electrodes for catalysis and fuel cells
	Glassy carbon/ **palladium-gold**	Bath electrolyte	Laboratory R&D scale
	Glassy carbon/ **platinum-zinc**	Bath electrolyte	Laboratory R&D scale
	Various/**selenium**	Bath electrolyte	Laboratory R&D scale; nanostructured coatings possible
	Various/**silver**	Bath electrolyte	Pre-production scale; immersion nanostructured coatings possible for PCBs
	Various/**tantalum**	Bath electrolyte	Laboratory R&D scale
	Various/**zinc**	Bath electrolyte	Laboratory R&D scale; other alloys also possible
Electropolishing	Aluminum	Bath electrolyte	Laboratory R&D scale
	Stainless steel	Bath electrolyte	Pre-production scale
	Titanium alloys	Bath electrolyte	Laboratory R&D scale
Lubrication	Various	Wetting agent	Laboratory R&D scale
Wastewater Treatment	N/A	Solvent/extractant	Laboratory R&D scale; can remove cations such as cadmium, mercury

What next?

Efforts are under way to deposit a wide range of metals, alloys and inorganic compounds for a number of industries requiring coatings with very specific properties for demanding applications. In addition, deposition from ionic liquid electrolytes is being used to prepare nano-structured and semiconducting materials, with the potential to produce micro-electro-mechanical systems. Interestingly, these are topics that have been discussed in previous columns.

While early indications from laboratory scale investigations have been promising, and the use of ionic liquids in surface finishing operations has potential, opportunities for commercialization have been limited. There are several barriers to commercialization, including:

- Only very small quantities of the ionic liquids being available
- The high cost of the chemicals used to prepare ionic liquids
- The need to establish safe working practices
- The need to establish compliance with existing and planned environmental regulations
- The need to identify the best applications with the potential for success in the marketplace
- The processes are not optimized, nor at a stage where they can be qualified for use in industry.

As markets develop and grow, some of these barriers will disappear. However, at present there is a "Catch 22" situation. But as experience is gained, and the cleaning, electrodeposition and electroplating processes near commercialization receive more publicity, others may be encouraged to invest resources in bringing technology incorporating ionic liquids to the marketplace. It will be interesting to see how this emerging technology will develop in the next five to ten years! *P&SF*

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