

A novel, two-phase medium for electrochemically induced conversion coatings

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A method to facilitate electrochemical coatings from a non-aqueous, poorly conductive (and therefore normally difficult to work with) electrolyte is presented. The process involves loading the electrolyte with pretreated ion-exchange beads to provide multiple low-resistivity paths for ionic but not electronic conduction between a counter-electrode and workpiece. Using the formation of iron phosphate conversion coatings from an oil-based lubricant as a test case, the effects of bead moisture content and oil additive concentration on the coating process are described. With this new approach electrochemical coating is possible, even in poorly conductive fluids, over a far larger range of electrode separations than could otherwise be accomplished.

1. Introduction

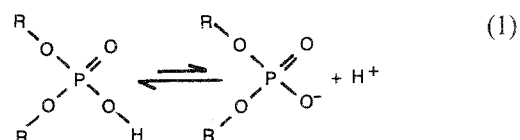
Electrical conductivity is an essential ingredient for any electrochemical process. To produce coatings electrochemically, the electrolyte/medium must allow an adequate flow of current. This paper describes a method of providing for this requirement when working with non-aqueous, poorly conductive electrolytes. The generation of low-friction coatings is the immediate application for this work.

It is known that lubricant additives can reduce friction and wear by reacting chemically with metal surfaces [1-4]; however, the process is generally very slow and reaction films thus formed in the metal-lubricant environment are typically not uniform. Therefore, it is desirable to precoat automotive parts with friction- or wear-reducing films before they reach the assembly line.

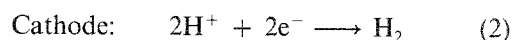
It has been disclosed [5] in a patented development at General Motors, called GM Electroslide™, that iron phosphate films, which have friction- and wear-reducing properties, can be coated electrochemically on the surfaces of cast iron or steel immersed in an oil lubricant containing a 2.5 wt % acid phosphate additive. However, due to the extremely high electrical resistance of such oil-based lubricants and the difficulty of passing current, this process can be used only for two parallel metal surfaces separated by a very thin film of lubricant; that is, less than 200 μm. Therefore, it would be difficult to coat complex or irregularly shaped automotive components, such as camshafts. If the resistance of the lubricant can be reduced, then the application of this coating technique can be broadened considerably. That was the purpose of this work.

2. Approach

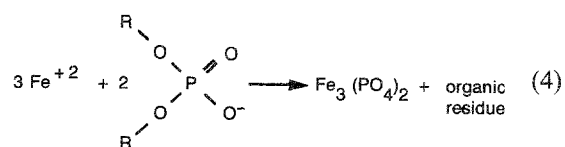
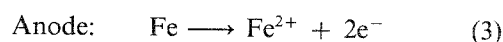
The mechanism for the GM Electroslide™ process is presently viewed as follows: an acid phosphate liquid additive dissociates in the base oil to a small extent according to



Dissociated hydrogen cations migrate to the cathode where they are reduced to hydrogen gas according to



The organic anions (Equation 1) migrate to the anode workpiece (cast iron or steel). There, electrochemical dissolution of iron (Equation 3) allows ferrous ions and the organic anions to form the desired amorphous iron phosphate on the workpiece surface (Equation 4). A thickness of 30 nm, achieved in 60 min, is typical.



(The organic residue can be detected by infrared spectroscopy.)

The limiting factor for this process is the inherently high electrical resistivity of the oil-based liquid (> 10⁹ Ω cm) which essentially restricts the process to

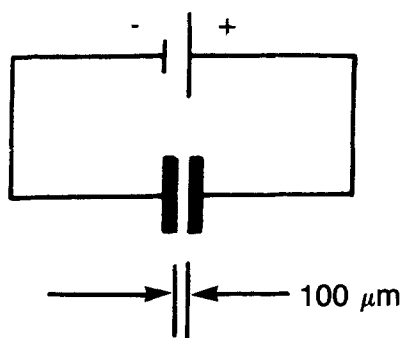


Fig. 1. Schematic diagram of the Electroslide™ process.

two parallel metal surfaces separated by a very thin film of lubricant; that is, less than $200\ \mu\text{m}$ (Fig. 1). At wider electrode separations only extremely low current, in the range of picoamperes, can be passed and no coating is observed.

Our approach to the above problem is based on the use of a two-phase electrolyte. Such electrolytes containing ion-exchange beads have previously been found to increase the conductivity of highly resistive aqueous solutions and to be useful as a means of enhancing metals recovery from dilute wastewaters [6]. Conductivity enhancement results from a relatively concentrated array of mobile ions (positively charged cations for cation-exchangers) within the pores of an ion-exchange bead which can carry current by migration in response to an applied electric field (Fig. 2).

Our approach in the present application was to load the oil-based liquid between the electrodes with hydrous ion-exchange beads and allow bead-to-bead contact to provide multiple low-resistivity paths for ionic conduction (Fig. 3). Hydrogen ion transfer through cation-exchange beads, from the anode to the cathode, is one possibility. With this arrangement it was thought that the electrical resistance could be greatly reduced, ionic current more readily passed and an electrochemically induced surface coating could be obtained on the workpiece over a far greater range of electrode separation than could otherwise be accomplished. For example, Electroslide™ coatings on an automotive part with a complex shape such as a camshaft lobe might be obtained by the use of ion-exchange beads (Fig. 4), whereas such a coating could not be applied uniformly without the beads.

3. Experimental details

3.1. Materials

Materials used in this work included a commercially available mineral oil base and for the phosphate-

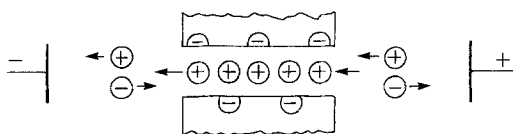


Fig. 2. Schematic of idealized pore through a cation-exchange bead and associated ion movement in response to an electric field.

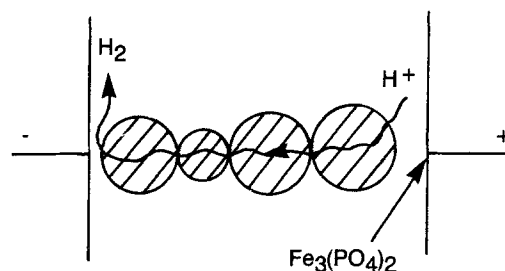


Fig. 3. Schematic showing current-carrying capability of cation-exchange beads between the electrodes of the Electroslide™ process.

producing additive, a commercially available mixed alkyl hydrogen phosphate (acid phosphate). Mild steel electrode specimens were cut from standard steel Hull cell panels. Because the ion-exchange beads were expected to allow current passage by hydrogen ion migration, a commercially available, hydrogen-loaded cation-exchange material was selected for this work. Physical and chemical properties from the manufacturer are shown in Table 1.

3.2. Equipment

A plastic electrochemical cell was designed and fabricated so that each individual test panel would demonstrate electrochemical deposition performance over a wide range of anode-cathode separation. This was accomplished by maintaining the anode workpiece at a wide angle to the cathode. The electrochemical cell is illustrated in Fig. 5. The electrode dimensions were $15\ \text{mm} \times 32\ \text{mm}$ for anodes and $15\ \text{mm} \times 26\ \text{mm}$ for cathodes (0.2 mm thick). The resulting electrode separation (gap) varied over two orders of magnitude, from approximately 0.25 to 25 mm. All tests were run with unstirred electrolytes with the exception that the sample shown in Fig. 8c was obtained by intermittent, manual stirring with a glass rod.

3.3. Procedure

Ion-exchange beads were washed repeatedly in distilled water to remove extraneous electrolyte before drying by one of the following treatments: (1) blotting on filter paper, (2) air-drying overnight, (3) drying over a CaSO_4 desiccant overnight; (4) drying in an oven at 100°C for 2 h.

Table 1. Physical and chemical properties of the cation-exchange resin

Type:	Strongly acidic, sulphonated polystyrene cation-exchange resin - medium porosity, RSO_3-H^+
Apparent density (average)	$0.77\ \text{g ml}^{-1}$
Bead mesh size (wet)	20-50 mesh
Void volume	35-40%
Degree of regeneration	98% minimum
Moisture holding capacity	52%
Total exchange capacity	
Volume	$1.75\ \text{meq ml}^{-1}$ minimum
Weight (dry)	$5.0\ \text{meq g}^{-1}$ minimum

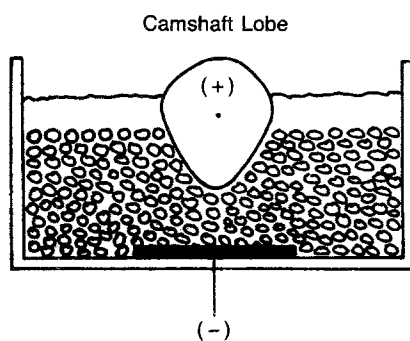


Fig. 4. Potential application of Electroslide™ utilizing ion-exchange beads.

Before each electrochemical test, steel anodes and cathodes were prepared by: (1) immersion in 50% HCl for 20 s; (2) water rinse; (3) wipe with water-wetted paper towel; and (4) wipe with acetone-wetted paper towel. All tests were performed at room temperature.

4. Results and discussion

A preliminary test of the concept involved merely adding ion-exchange beads to a beaker of commercial oil and allowing the beads to settle to the bottom. Platinum wire electrodes were then placed in the beaker at a separation of a few millimetres and 20 V dc was applied between them. When the electrodes were positioned in the upper, 'oil only' region, no current was detected. When the electrodes were lowered into the two-phase, oil-bead mix, detectable currents of 0.1–2 mA were readily obtained and the magnitude increased when the electrodes were moved to squeeze

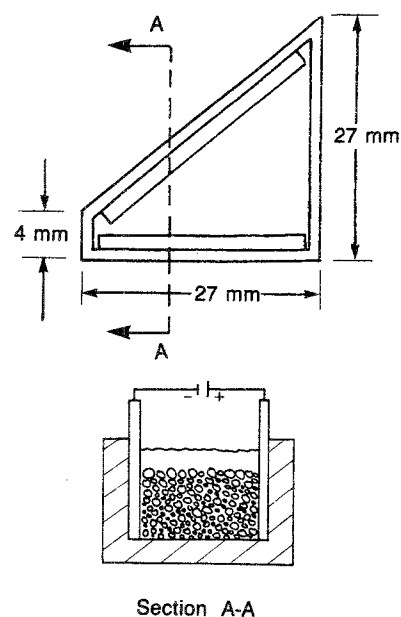


Fig. 5. Electrochemical test cell showing steel electrodes and bead-oil mix.

the beads together slightly and enhance bead-to-bead contact. These results indicated that significant conductivity enhancement occurred, which perhaps could be exploited.

The next step was to attempt to use this dual-phase electrolyte to obtain Electroslide™ coatings. Because the optimum percentage of the acid phosphate film-forming additive needed for an industrial Electroslide™ coating process was not known, we briefly investigated three different concentrations, covering a broad range — 100%, 50% and 2.5% additive.

Table 2. Representative experimental results

Material	Test conditions	Results
<i>100% Acid phosphate</i>		
No beads (fresh)	4 mA, 2 min, 108–130 V	Blue/brown deposit on left 6 mm only
No beads (stirred 5 days)	4 mA, 2 min, 56–53 V	No deposit observed
With beads, desiccated (fresh)	4 mA, 2 min, 24–45 V	No deposit observed
With beads, untreated (fresh)	4 mA, 2 min, 8–15 V	No deposit observed
<i>50% Acid phosphate–50% oil</i>		
No beads	74–100 μ A, 3.0 h, 300 V	Deposit on left 0.5 mm only (Fig. 8A)
With beads, desiccated	4 mA, 2.5 h, 178–225 V	Circular patches of deposit, 0.3 mm average diameter, over entire panel (Fig. 8b)
With beads, oven-dried, intermittent stirring	1.1–0.9 mA, 1.0 h, 300 V	Specked deposit, thin on right side (Fig. 8c)
With beads, oven-dried	1.4–0.5 mA, 3.8 h, 300 V	Circular patches of deposit, 0.4 mm average diameter, over entire panel; analysis indicated Fe, P and O as $\text{Fe}_3(\text{PO}_4)_2$ and film thicknesses of 32, 55 and 80 nm at electrode gaps 19, 10 and 4 mm, respectively (Fig. 9)
<i>2.5% Acid phosphate</i>		
No beads	0.1–3.0 μ A, 5.0 h, 300 V	Deposit on left 1.0 mm only
With beads, oven-dried	22–4.0 μ A, 1.5 h, 300 V	Small circular patches of deposit, 0.06 mm average diameter on left 12 mm only
With beads, desiccated	4 mA (unstable), 40 min, 80–200 V	Waxy, grey-black deposit over entire panel; analysis indicated S, C, Fe, P and O

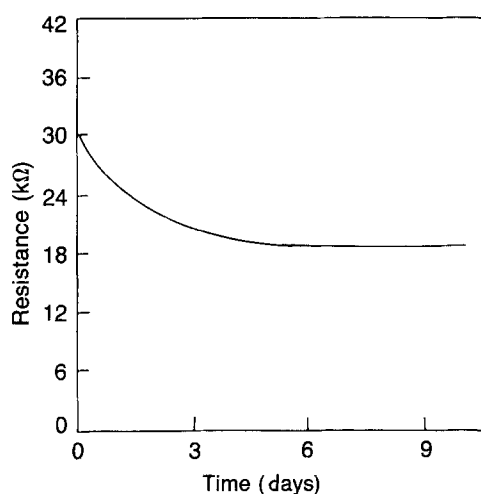
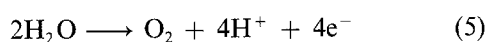


Fig. 6. Decrease in electrochemical cell resistance (E/I) with 100% acid phosphate caused by stirring and atmospheric exposure. A 2.0 mA cell current was used.

Using 100% acid phosphate additive (no oil), the desired blue-brown film was initially formed, but after exposure to the air for a period (days), this lubricant tended to lose its ability or provide such films, with or without the ion-exchange beads (Table 2). This behaviour is attributed to moisture uptake by the pure acid phosphate liquid. This moisture is thought to allow at the anode an alternative and competitive water oxidation reaction (see Equation 5) to occur preferentially rather than the desired anodic film-forming reactions (Equations 3 and 4):



This conclusion is supported by the observation that resistivities of the acid phosphate and acid phosphate-bead mix (as indicated by total cell resistance determinations, E/I , in the electrochemical cell) were found to decrease during this same period. Such decreases in resistance with time are shown in Fig. 6, obtained by stirring magnetically a sample of 100% acid phosphate to entrain air bubbles gently over an extended period. The decrease in resistance with time is apparent, and correlated with a similar decrease in the observed film formations. This instability problem with 100% acid phosphate liquid led to studies at the other additive concentrations.

A second series of tests was conducted with a 50% additive-50% oil mix. Because the previous studies suggested a moisture sensitivity effect on the Electroslide™ process, ion-exchange beads were prepared thereafter under a variety of drying conditions before use, so as to control the bead moisture content. The effect of this moisture content on the electrical resistance of the resulting bead-lubricant mix (again indicated by total cell resistance) is shown in Fig. 7. The resistance was determined to be extremely sensitive to the moisture content and to vary in inverse proportion. A variation over more than three orders of magnitude could be obtained (see Fig. 7). Electroslide™ coatings from these liquid-bead mixes were obtained with increasing ease as the moisture content

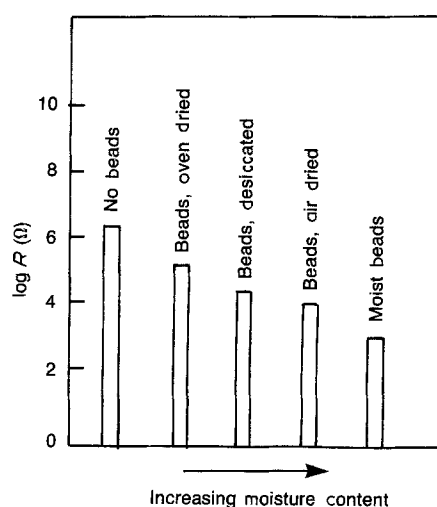


Fig. 7. Effect of bead moisture content on electrical resistance of 50% acid phosphate/50% oil mix.

increased, with the exception that the highest moisture content (moist beads-lubricant mix) provided no visible coating. Rather than coating formation, gassing was observed on this anode workpiece, which suggests that water oxidation (Equation 5) was again dominating. Thus a criticality in moisture content apparently exists for optimum performance with such a two-phase electrolyte.

Further inspection of these Electroslide™ films also demonstrated that, indeed, coatings over a much wider area were obtained by use of the two-phase electrolyte. Figure 8 shows representative samples. The test panel of Fig. 9a demonstrates the shortcoming of the Electroslide™ process without ion-exchange beads. A deposit is formed on the workpiece only at the smallest electrode gap; that is, only on the left side of the panel (the slender, about 0.5 mm wide deposit is just barely visible in the photograph). In contrast, Fig. 8b shows that with the dual-phase electrolyte the deposit can form across the entire test panel (across two orders of magnitude variation in the electrode gap!). Energy dispersive X-ray spectra confirmed the presence of phosphorous in the film and Auger electron microscopy and X-ray photoelectron spectroscopy further indicated that this coating was the desired iron phosphate, $\text{Fe}_3(\text{PO}_4)_2$. This film in Fig. 8b appears mottled and from microscopic examination is seen to be, in fact, an array of circular patches of the iron phosphate film. Due to the high resistivity of the oil-based lubricant, the film initially forms on the test panel surface only in the proximity of the ionically conductive particles. Further analysis indicated deposition rates of 21, 14 and 8 nm h^{-1} were obtained across one panel (see Table 2) at positions where the electrode gap was 4, 10, and 19 mm, respectively.

Figure 8c shows the effect during the film-forming process of occasional electrolyte stirring which tends to smooth out the discrete patches into a continuous film. The bare right side in Fig. 8c suggests that this movement tends to reduce the 'throw' or film formation on the widest electrode gap (lowest current

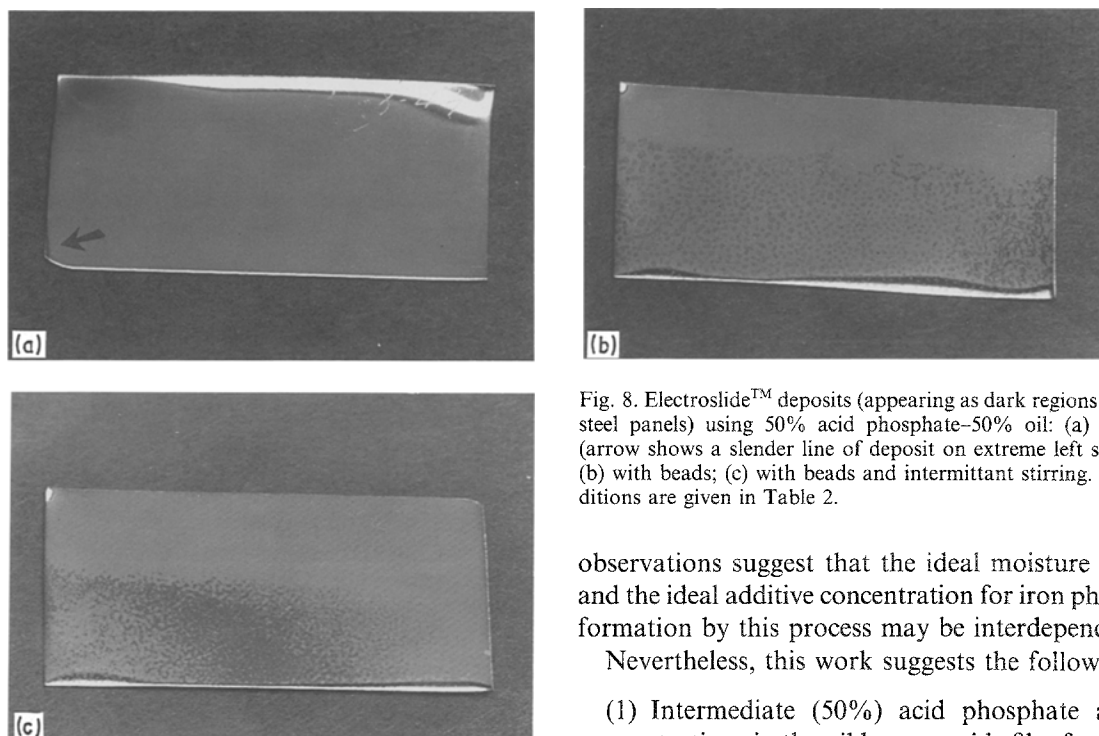


Fig. 8. Electroslide™ deposits (appearing as dark regions on bright steel panels) using 50% acid phosphate–50% oil: (a) no beads (arrow shows a slender line of deposit on extreme left side only); (b) with beads; (c) with beads and intermittent stirring. Test conditions are given in Table 2.

density) areas as well. Different bead sizes or size distribution may be an alternative method of achieving a more continuous film.

Figure 9 shows an Electroslide™ surface from a deposition similar to that shown in Fig. 8c but without stirring and for a much longer coating time (see Table 2). The micrograph shows the top edge of the coating; that is, the highest level on the steel specimen where ion-exchange beads settled against the steel surface and therefore allowed a coating to form. This magnified view shows the (previous) locations of individual ion-exchange beads and also shows that the separate, circular patches of film do, indeed, blend into a continuous coating in time. The different shades within the coating (the dark regions at both the periphery and centre of each individual patch of coating) are a result of thickness variations giving rise to interference colours which are quite evident with these very thin coatings.

A third, brief study was also made with 2.5% acid phosphate in oil plus ion-exchange beads (Table 2). Films could be obtained which were visually similar to the previous films but more difficult to obtain. Oven-dried beads produced very slowly forming films with this mix, apparently due to a high electrical resistivity resulting from low concentrations of both the acid phosphate and moisture. Air-dried or desiccated beads allowed higher currents, but with these higher currents provided an undesirable waxy, complex film composition which, from Auger and X-ray spectroscopy, was shown to include S and C as well as O, P and Fe. Apparently these conditions – low acid phosphate concentration and a relatively high moisture content coupled with high impressed current – allowed other competitive electrochemical reactions such as additive degradation or water oxidation (Equation 5) to dominate or coexist with iron phosphate formation. These

observations suggest that the ideal moisture content and the ideal additive concentration for iron phosphate formation by this process may be interdependent.

Nevertheless, this work suggests the following.

(1) Intermediate (50%) acid phosphate additive concentrations in the oil base provide film formations more readily than either low concentrations (2.5%) or the pure (100%) acid phosphate liquid.

(2) The 50% additive–50% oil mix plus beads can also provide Electroslide™ deposits over a wide range of electrode gap, up to at least 25 mm, the largest gap tested. Deposition rates of 8, 14 and 21 nm h⁻¹ were obtained at electrode spacings of 19, 10 and 4 mm, respectively.

(3) Moisture content in the ion-exchange beads affects significantly the film-forming process. Low moisture content increases the electrical resistivity and limits film formation. High moisture content prevents high-purity film formation by enhancing competitive electrochemical reactions.

5. Summary

A novel method of obtaining useful electrochemically induced coatings from highly resistive, non-aqueous

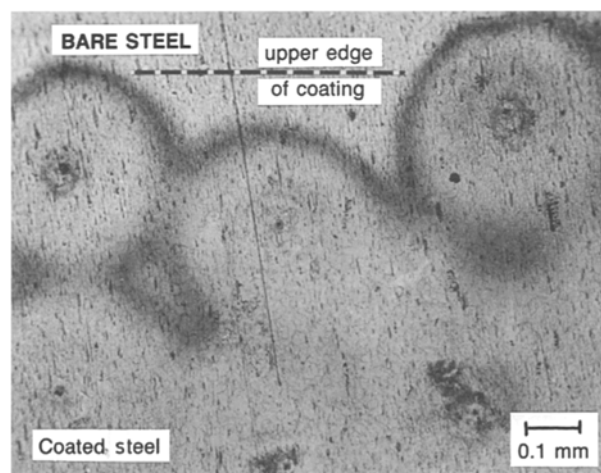


Fig. 9. Blending of discrete film patches with time to form a continuous coating. Test conditions are given in Table 2.

electrolytes was developed. The process involves loading the electrolyte with pretreated ion-exchange beads to provide multiple low resistivity paths for ionic but not electronic conduction between a counterelectrode and workpiece. Using the formation of iron phosphate conversion coatings from a poorly conductive oil-based lubricant as a test case, the process was demonstrated and the effects of the bead moisture content and the oil additive concentration on the coating process were noted. Further work is obviously necessary to establish optimum conditions for this particular application, not only concerning the additive concentration and the bead moisture content, but also regarding other important variables such as the temperature and current/voltage requirements.

Nevertheless, the success of this preliminary work has established the potential usefulness of this two-phase electrolyte. The enhanced ionic conductivity and resultant electrochemical coating so readily obtained from fluids which were previously difficult to work with may provide one basis for advanced coating materials and processes for the future.

Acknowledgements

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