A Novel Dynamic Process for Chemical Reduction Plating

By A. Fares Karam & G. Stremsdoerfer

This paper discloses a novel metallizing process utilizing sequences of simultaneous spraying of two aqueous solutions. The first acts as an electronic energy source (reducing agent); the second acts as a material source (metallic salt ions). The novelty of this technique is based on the sequential spraying procedure. It allows the electron exchange reaction to occur in a very thin aqueous layer next to the surface, exerting the influence of its characteristics and properties. The principle, the apparatus and several results are described, demonstrating the potentialities and the capabilities of this new process, as well as its convenience for many industrial applications.

Research in electroless plating and the development of new applications for this unique method of metal deposition has continued since 1946, when Brenner and Riddell described the mechanism of this process.[1]

Most developments achieved to date are related to bath composition. This composition has undergone several modifications, but has not basically changed since inception of the process.[2,3] The field of metals capable of this type of deposition has been moderately enlarged. Binary and ternary alloy baths, as well as a few composite coating baths, are now commercially available.[4]

If electroless plating has many advantages, such as uniform deposition on complex and intricately shaped parts, and features several economical aspects, such as the absence of an external current source,[3] there are still several practical problems.

The treatment of parts having large dimensions requires the use of enormous baths and large quantities of reactants. It is useful to note also the agitation, filtration and bath regeneration difficulties, as well as the auto-contamination problems. In the case of composite coatings, the baths are often unstable. This causes many economic and technical difficulties. Most baths used now operate at high temperature, especially nickel baths[2,5] (>60 °C), causing an energy consumption disadvantage for this technique. Those operating at a relatively low temperature generally have a very low deposition rate.

All these difficulties have led to development of a new procedure[6] for chemical deposition that permits avoiding most of the problems in many different cases. This new method allows metallic film deposition by projecting simultaneously, in a very accurate proportion and a specific spraying procedure, two, or several, solutions onto an adequately activated surface, vertically positioned.

The only existing comparable procedure is the old silver spray coating for metallizing non- conductors.[7-11] It consisted of projecting a silver nitrate aqueous solution, with glucose or formaldehyde as a reducing agent, on a horizontally positioned non-conducting substrate. The result was a very thin silver deposit and, when using glass, a bright silver film on the opposite side. This procedure was used for manufacturing mirrors[12] and as a first step for electroplating on plastics.[7-9,11] Gold was another metal deposited this way[2,10] and there was an unsuccessful extension to plate copper.[8,9] No development and no more extensions of this method to other metals have succeeded because of the technical difficulties in reproducing correct and adherent metallic films.[8] Even though such films were very thin (<0.3 μm), the deposition kinetics were too low.[8,9] A recent patent[13] described a procedure of metallizing that uses brushing or spraying aqueous solutions similar to the old technique. This indicates the need for such direct metallizing systems in the metal finishing industry.[14] This paper describes a new procedure for metallizing called “Dynamic Chemical Plating” **(**DCP**)** and emphasizes its potentialities and applications.

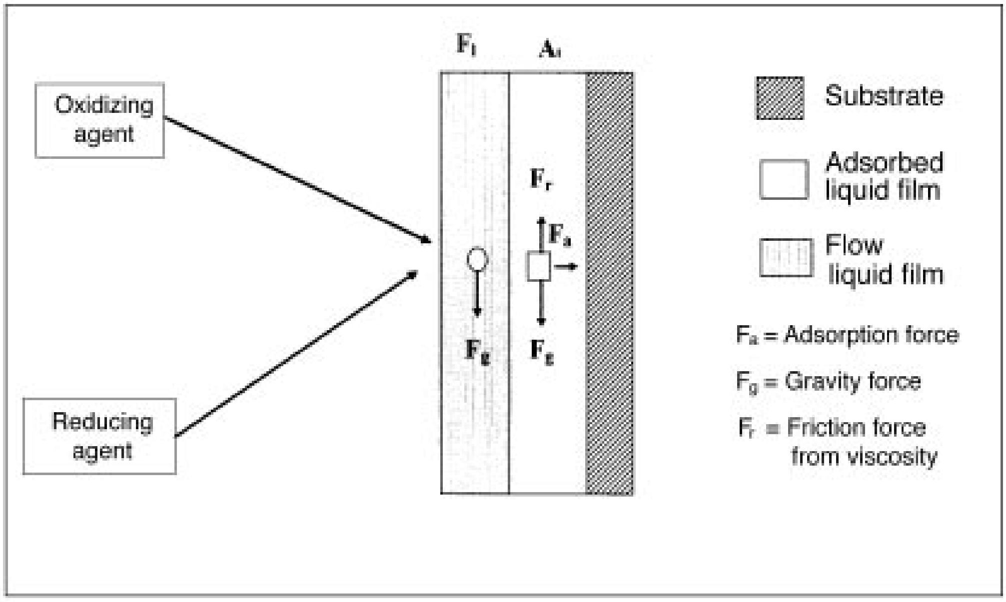

Fig. 1—Schematic representation of principle of dynamic chemical plating (DCP).

Experimental Procedure

Treatment of the substrates prior to metal plating consisted of degreasing with an appropriate organic solvent, depending on the nature of the material. The non-conducting substrates were activated by a 15-min dip in a mixed Pd-Sn colloidal solution, *SolMeb*,[15,16] then rinsed in a 1 M HCl solution.

The surface morphology of the substrates and the deposited films were

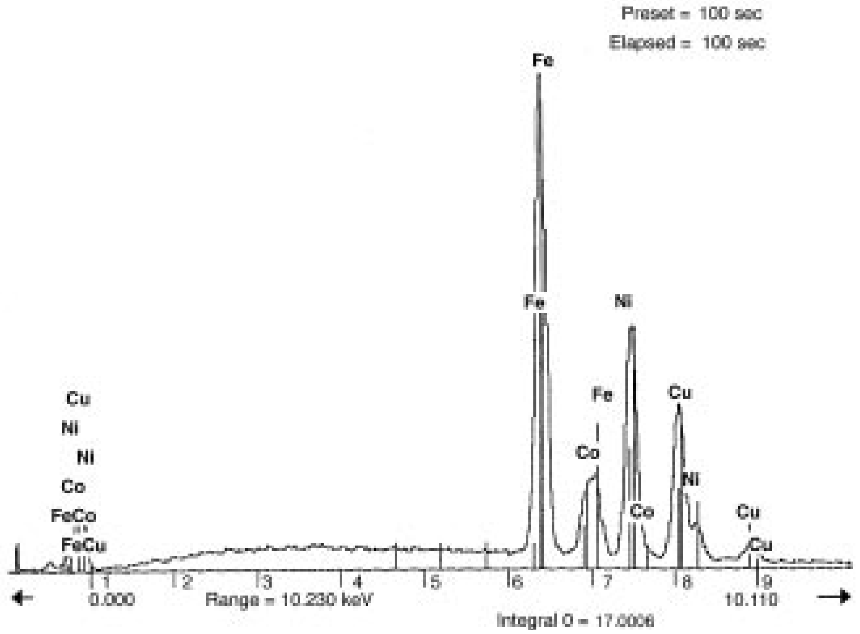

Fig. 2—EDS spectra of a Ni-Co-Cu alloy film deposited on steel. (Flow air pressure of copper, 0.6 bar)

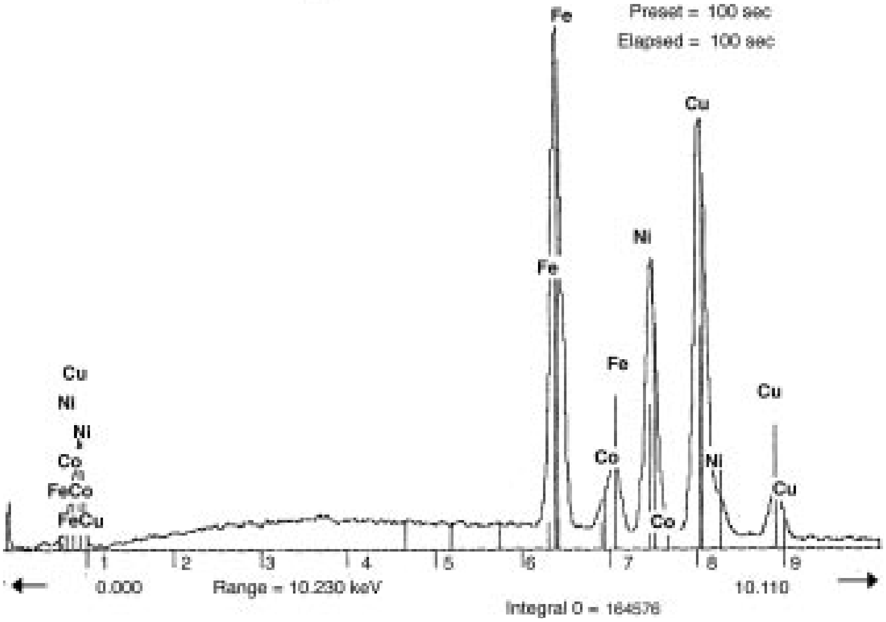

Fig. 3—EDS spectra of a Ni-Co-Cu alloy film deposited on steel. (Flow air pressure of copper, 1 bar)

observed by scanning electron microscopy, using a micrograph coupled to an X-ray probe for qualitative and semi-quantitative elemental analysis. Full quantitative elemental composition was determined using an X-ray energy dispersion spectrometer (EDS). An optical micrograph was used to evaluate homogeneous coverage of the substrate. The optical quality of the deposits was evaluated by a reflectivity measurement, using a near infrared (NIR)-visible-UV spectrophotometer.

Results and Discussion

The "Dynamic Chemical Plating" Process

The principle is to spray in sequence and simultaneously two, or several, aqueous or organic solutions onto an eventually catalytic substrate. The first solution contains a reducing agent and the other(s) contain(s) one or several metallic ion(s) to be deposited. If the composition is adequate, the oxidizing and reducing agents, which are mixed in the jet, will react on the catalytic substrate's surface. A continuous one-metal pure film, or a polyalloy coating, is then produced. The catalytic effect of the surface or the adequate surface modification[16] is absolutely necessary to plate a high-quality adherent film. Otherwise, coarse dark grains are obtained that are the result of an uncontrolled anarchic oxy-reduction reaction. The spray system uses any propellant gas that does not interfere with the oxy-reduction reaction. It could be a common aerosol, an inert gas or compressed air.

Spray Principle

The novelty of this method and the most important factor consist of the way of carrying out the spraying. All the other processes report continuous spraying. With them, there is a continuous supply of liquid solution to the substrate. Because these solutions have a relatively low viscosity, they will run off the surface, and a very small volume will actually reach the substrate to be plated. The reaction occurs on the substrate and partially inside the liquid film, which has a defined thickness, making dark, coarse grains, adsorbed on the surface. The result is a very thin deposit and waste of a large part of the plating solution.

With DCP, the spraying is done intermittently, using successive liquid projections. The two solutions are sprayed together, using a dual nozzle gun for specific times (several msec), followed by off times of perhaps hundreds of msec. This could be described as a two-phase procedure:

1. The liquid spray phase, and
2. The relaxation phase.

In the first phase, the reagents are sprayed with specific concentrations, proportions, and quantity, to form a very thin liquid film, adsorbed on the surface. The projection is done under a specific spray pressure and the flow effect is negligible. It is essential to note that the sprayed quantity is a function of the surface energy, Es, and the wettability of the surface. Consequently, the oxy-reduction reaction will occur on the surface and will be influenced by the physico-chemical properties of the material to be plated.

The relaxation phase is a function of the reaction kinetics and is inversely proportional to the kinetic constant. This is illustrated in Fig. 1, where (A_1) represents the DCP adequate thin liquid film and (F_1) represents the flow film when spraying continuously. It can be observed that next to the substrate (A_1) there is an equilibrium for each volume unit that permits the species to react adequately, while in (F_1), gravity controls the liquid film. This succession of phases permits a full reaction on the surface, allowing maximum output of the spray system, plus high efficiency for this receipent technique.

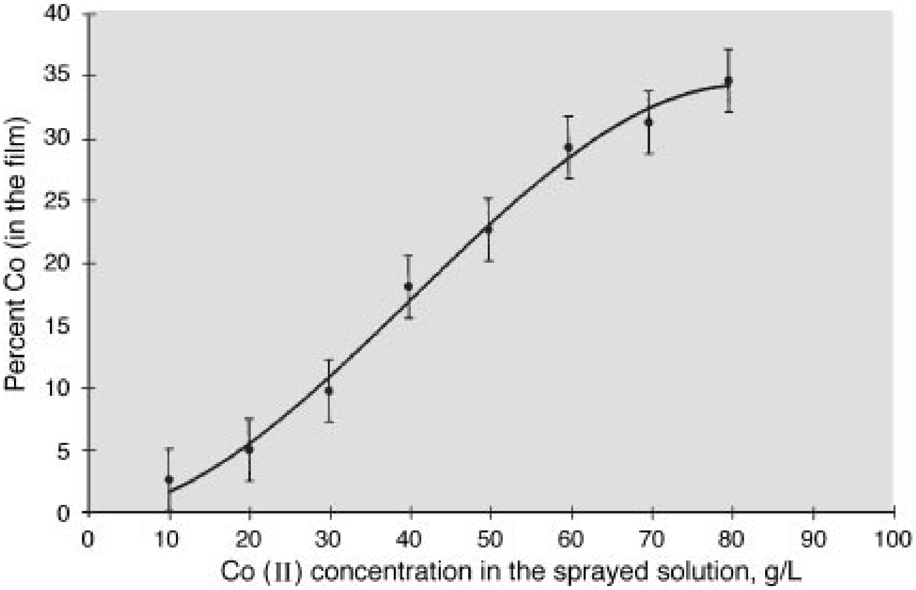

Fig. 4—Cobalt percentage in the deposited film as a function of Co(II) ion concentration the spray solutions.

Apparatus

A commercially available concentric double-nozzle spray gun† has been modified and used to obtain the deposits. The nozzle diameters have been diminished, and the system functions using an electric valve controlled by a microcomputer running "homemade" software. This has enabled operation of both spraying and relaxation phases covering the range of 50 msec to 10 sec. An air compressor was used as a spray system during the experiments. It supplied compressed air to two different stainless steel tanks that contain, respectively, the reducing agent solution and the oxidizing metal salt solution. A very precise air pressure on the different compartments is necessary to obtain a homogeneous, conical and straight jet. Fog-dispersed jets and the substrate wettability are important for high-quality coating films. Both tanks are linked to the automated spray gun.

Potentialities of the Process

Substrates

Several types of substrates have been used to demonstrate the large capabilities of the method. Steel, copper, titanium and aluminum were used as conducting substrates. A wide range of non-conducting materials was investigated, such as epoxy, polycarbonate, acrylonitrile-butadiene-styrene (ABS), polymethylmethacrylate (PMMA), polyvinyl chloride (PVC), polypropylene (PP), semi-crystalline polyesters and glass. It is important to note that all substrates were vertically set when plating. High-quality adherent and homogeneous films were deposited. Experience led to the conclusion that once the surface is well prepared and modified, any material can be plated using this process.

Deposits

Nickel, copper and cobalt were chosen because of their industrial importance and because their electroless and electroplated film properties have been extensively studied (microstructure, mechanism of formation, morphology, applications...).[3,4,18,19] Conventional metal salt reagent grade chemicals were used for metal deposition. The reducing agents used were sodium borohydride, KBH_4, and formaldehyde. Benzene sulfonamide and saccharin were used optionally as brighteners with the metallic salt solution. The solution composition for each component was variable. The optimum conditions depended on each type of deposit and on the material to be plated, but all types of deposits were plated at room temperature. The films obtained could be classified in four types:

1. The pure metal films: nickel, cobalt and copper
2. Binary alloys, such as Ni-B and Co-B
3. Ternary alloys, such as Cu-Co-B, Cu-Ni-B and Ni-Co-B
4. Quaternary alloys, such as type Cu-Ni-Co-B

Polyalloy coatings were investigated because industrial demand for ternary and quaternary alloys is increasing[20] for different applications, especially corrosion resistance. These films were obtained by projection of different metal ion solutions simultaneously. Unlike electroless deposits, the quantitative EDS patterns (Figs. 2 and 3) indicate that we can reach easily, at ambient temperature, a high percentage ratio of any desired element by simple variation of the different metal ion proportions in the spray solutions. For example, simply by changing the flow proportions of the copper solution, a considerable variation in the elemental composition of a Cu-Ni-Co-B alloy film is obtained. The copper proportion jumps from 43 to 67 percent, the cobalt proportion is diminished from 9 to 2.5 percent, and the nickel percentage decreases from 48 to 32 percent. Another example, illustrated in Fig. 4, shows the cobalt percentage variation in a Co-Ni-B ternary alloy film. The nickel salt concentration and propor-

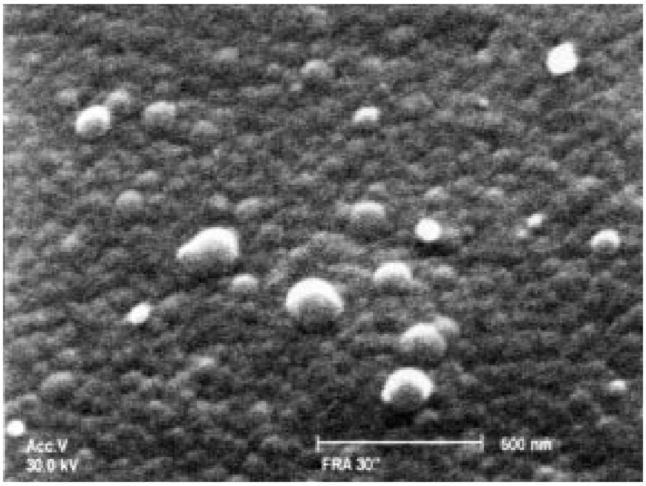

Fig. 5—Scanning electron micrograph of Ni-B deposit on PMMA polymer.

tion were kept unchanged at 40 g/L in the spray solution. The cobalt salt concentration was varied between 0 and 80 g/L for a constant spray proportion. It can be seen, consequently, that a high Co percentage can be obtained either by changing the flow rate or by changing the initial ion concentration. This is an interesting demonstration of the flexibility and convenience of the new process for industrial demands.

General Morphological Characteristics

Semi-bright deposits of Ni-B, Co-B, Cu-B alloys were obtained on conducting substrates. On non-conducting substrates, similar deposits were obtained. On glass, polycarbonate and PMMA, where a dark, coarse deposit was expected, mirror-bright thick films (> 15 µm) were formed. The brilliance of the films on the sprayed side is similar to the brilliance of the side that is bonded to the transparent substrate. This is a result of the very small size of metallic grains deposited homogeneously on a plane surface, as revealed by the scanning electron micrograph (Fig.5) of a Ni-B film on PMMA polymer. The surface morphology of the metallic grains is finer than that obtained with conventional electroless bath deposits. The diameter of the grains ranges between 45 and 90 nm. This demonstrates the high-quality coalescence of the film. To evaluate the optical properties of the plated films, we have used the reflectivity measurement. The percentages of different wavelength reflection are shown graphically in Fig. 6. The percentage climbs to 60 percent in the near infrared. This is similar to the optical properties of conventional electroless bright deposits after polishing.[4] To our knowledge, no really bright electroless Ni-B baths are available in the industry.

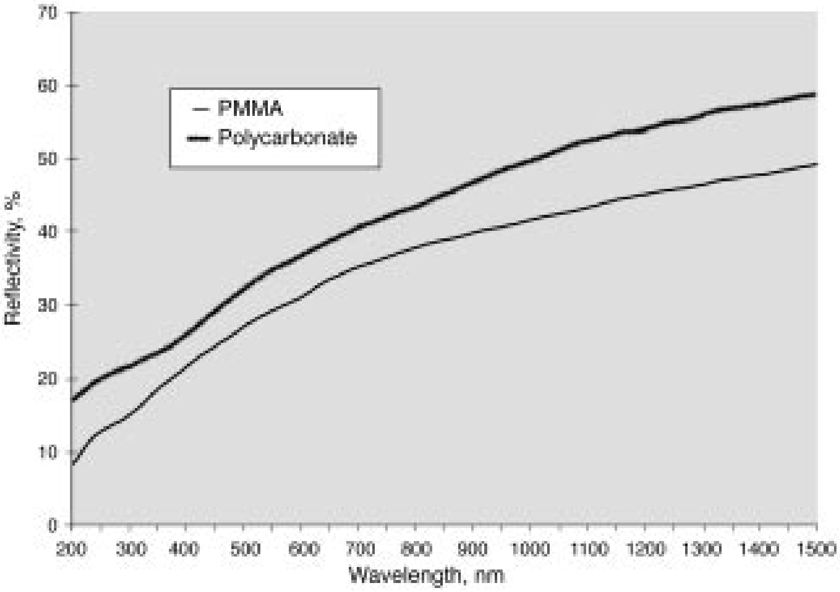

Fig. 6—Reflectivity of different wavelengths of a nickel-boron alloy deposited on PMMA and polycarbonate polymers.

Density and Kinetics

Figure 7 shows a transverse section of a Ni-B deposit obtained on a PVC substrate. It reveals a thick, compact and dense film. It is interesting to note that by changing the spray conditions, we can change the film structure. The deposit shown was obtained by spraying 425 mL of Ni(II) solution at a concentration of 18 g/L. The resulting thickness was 20 ±1 µm. This is equivalent to 52.4 percent in nickel weight, which is comparable to conventional electroless nickel baths. For waste treatment, this is advantageous. The effluent contains the Ni ions that did not react on the surface, plus the metallic nickel particles corresponding to the ions that reacted in the effluent with potassium borohydride. By simple filtration, the solid particles are separated and the resulting solution can be analyzed for adjustment of the Ni(II) ion concentration for reuse. The precipitated particles are not environmentally harmful, especially inasmuch as this reducing agent is used in the treatment of electroless nickel wastes.[21]

Figure 8 shows the same film with high porosity, just after changing the spraying air pressure. These kinds of deposits are reproducible and the different conditions are controllable. This shows the facility for depositing different types of films at once with the same solutions and apparatus. Unlike electroless deposition baths, the kinetics of the film formation are appreciable because deposits of several µm could be obtained in a few min. The deposition rate is about 40 µm/hr.

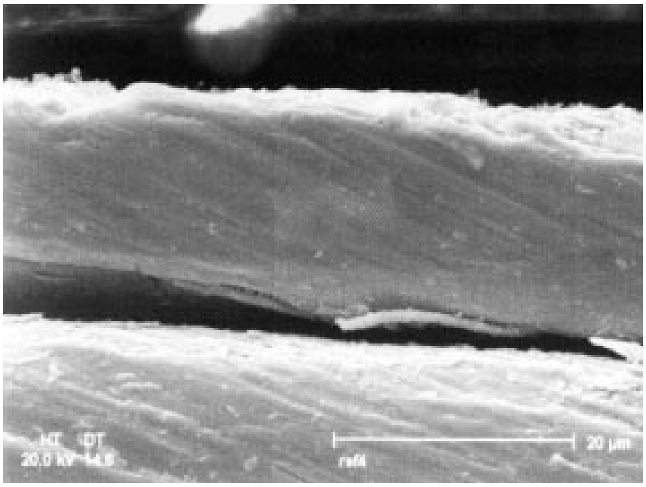

Fig. 7—Cross section of compact, dense Ni-B film deposited on PVC polymer. (Spraying air pressure, 1.2 bar)

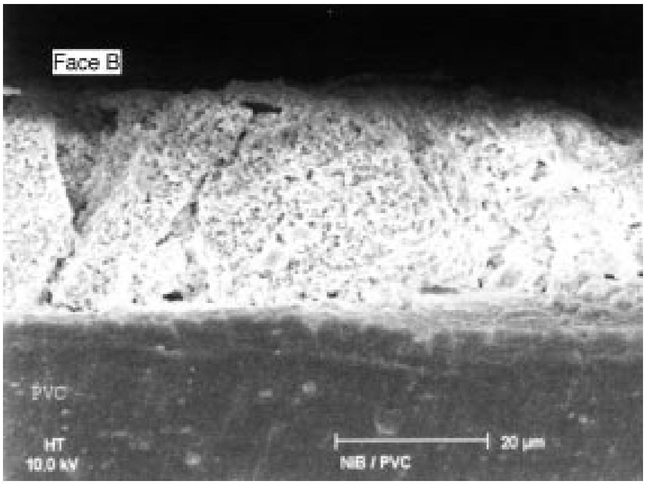

Fig. 8—Cross section of a porous Ni-B film deposited on PVC polymer (Spraying air pressure, 0.6 bar)

Conclusion and Applications

Traditionally, most of the physical and chemical methods of metal deposition have been unable, or at least inadequate, for metallizing large parts. The rare exceptions have resulted in a high-cost coating. Using this new procedure, a wide range of metal coatings can be deposited on any surface adequately prepared or modified. The films produced are analogous to electroless coatings, so may confer anti-corrosion properties, protect against wear, offer a lubricative surface... but they are simpler, faster and easier to prepare. Moreover, the apparatus is portable, simple and low in cost. That makes the procedures very practical because siting is possible anywhere and plating is done at normal ambient temperature. It is then possible to repair any damaged surface in the field for a gain in cost and time. The fact of working at room temperature makes this procedure energy economizing. Use of this technique will allow avoidance of the stability problems of electroless solutions, especially for composite baths where filtration is not feasible.

This process can replace the actual methods used in the aircraft, automotive and construction industries. The usual organic coatings could be replaced by long-life metallic films. The procedure may also be convenient for small pieces, because very specific localized films can be obtained without using chemical masking. More details and properties of the different types of deposits will be published in future studies.

† Type AGPV569/579, ITW Surfaces & Finitions S.A., France.

Editor's note: *Manuscript received, July 1997; revision received, October 1997.*

Acknowledgment

The authors wish to thank ITW Surface & Finitions S.A. France, and ETAP Industries, France, for their technical contributions and support of this study.

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