SYNTHESIS REPORT

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TITLE: Modelling and Process Control of Liquid-containing Metallic Electrocoatings

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Modelling and Process control of liquid-containing Metallic Electrocoatings

Final report of Project Work
performed in the period 1/8/1991 - 31/7/1995

The participants to this basic research *projects express their gratitude to the CEC for the financial support that made* this *research possible and for the strong collaboration that was created among the partners. This research has resulted in a substantial scientific and technological insight for the further development of advanced composite plating in European industries. The consortium has acquired a unique know how that is put at the disposal of European industries involved with composite plating in general*

At the end of this project it is a *great pleasure* for *the research partners to thank especially Mr. Jean-Claude Toussaint* of *the CEC-DGXII for his permanent and stimulating* interesting *this project.*

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1. Objectives of the project

This project, was a multidisciplinary research effort focussed on the development of liquid-containing metallic electrocoatings. The following objectives were selected initially:

1. optimization of the synthesis of liquid-containing microcapsules suited for composite plating,
2. development of appropriate in-situ process control procedures for composite plating in the case of codeposition of liquid-containing microcapsules,
3. investigation of the structure and functionality of liquid-containing electrocoatings and the development of appropriate testing procedures,
4. interdisciplinary action allowing a major breakthrough in the modelling of the Production of liquid-containing metallic electrocoatings.

2. Overview of the achievements of this basic research project

Task 1: Production and Characterization of **Microcapsules**

The techniques of interracial polymerization and solvent removal from complex emulsions have been identified as the most promising ones for the production of liquid-containing microcapsules. The work was focussed on the development of oil-containing microcapsules because of potential applications in the area of self-lubricating coatings. Main problems that had to be solved were the achievement of a dense polymeric wall, dimensional stability of the microcapsules after washing and on mixing with the plating solutions, as well as the achievement of a surface charge to avoid agglomeration of particles and finally obtaining an electrolytic codeposition. The interracial polymerization technique was extended to the synthesis of oil-containing polyamide and poly(phenyl ester) microcapsules with a mean diameter in the range of 1 to 85 µm. By phase separation (coarcervation) oil-containing polyvinyl alcohol microcapsules of 10 to 800 pm have been successfully produced. oil-containing polystyrene microcapsules (5 to 15 µm), PMMA microcapsules (5 to 50 µm) and cross-linked polystyrene/divinylbenzene microcapsules (4 to 10 pm) were successfully produced by microsuspension polymerization. Batches were distributed among the partners for further investigation of the surface properties and the codeposition behaviour. In the final stage of this project, polystyrene (100 to 2000 nm) and PMMA (100 to 400 nm) nanoparticles were produced by emulsion polymerization, and a few attempts were made to obtain gelatin microparticles (1 to 50 µm) by the suspension cross-linking method"

During the project, emphasis was put on the identification of the important physical and chemical factors affecting the synthesis of oil-containing microcapsules, being the use of the proper type of oil-soluble initiator and the use of appropriate anionic surfactants.

Task 2: Surface Reactivity and Dispersibility of **Microcapsules**

This work involved the selection of additives for the improvement of the stability and dispersibility of the oil-containing microcapsules in a nikkel Watts' plating solution operated at

55 "C. In that respect it was demonstrated that the presence of a volatile organic solvent in the interior of the microcapsules, caused the capsules to collapse during ageing in the bath due to the swelling of the membrane by the surrounding electrolyte. A large effort was done to characterize the surface hydrophobicity of the microcapsules. The role of this hydrophobicity on the electrolytic codeposition was investigated in a study of the adsorption of ions onto polymeric particles having different surface functional groups. This has allowed a first expiration of the complex matter of surfactants and additives in the control of the electrolytic codeposition process.

Task 3: Application of Electrochemical Techniques to the Study of **Codeposition**

A major concern was the development of specific in-situ electrochemical techniques to detect the presence of particles on the electrode and to quantify the residence time of particles onto the electrode. Two techniques were explored, namely the quartz crystal microgravimetry which allows in-situ mass changes to be detected, and the electrochemical noise analysis technique which gives information on the stochastic perturbations of the potential field by moving particles. A submerged impinging jet cell (SIJ) was developed and the performance of this electrode was characterised in detail by electrodiffusion analysis and electrochemical impedance analysis on microelectrodes and trisegmented microprobe. A quartz crystal microbalance was adapted for operation in electrolytic environments. Oscillations of the resonant frequency were observed when microcapsules adsorb on the microbalance and these oscillations were identified as characteristic of a soft mechanical coupling between the polymeric membrane and the electrochemical quartz crystal microbalance (EQCM). That effect was shown to depend slightly on the polarization potential. The principle of the EQCM/SIJ device was patented.

The electrochemical noise analysis was developed as a codeposition process control. The stochastic fluctuations of the current (or potential] were linked to fluctuations of the ohmic drop at the electrode resulting from the perturbations of the potential field by the presence of non-conductive particles in the vicinity of the electrode. The analysis has been developed in both the time domain and the frequency domain which is of interest in the case of concentrated suspensions. Experimental data have been shown to be in excellent agreement with a mathematical model developed within this project. This investigation is a first step towards the development of an electrochemical sensor for the in-situ control of codeposition in industrial composite plating cells.

Task 5: Production and Performance of Oil-containing Nickel Coatings

The electrolytic synthesis of oil-containing metallic coatings from nickel Watts' solutions was investigated. The focus was on the code position behaviour of the different types of microcapsules produced in Task 1. This involved the following:

- codeposition tests on a rotating disc electrode for the production of composite coatings.,
- determination of the amount of adsorbed and incorporated microcapsules (SEM and carbon analysis).

- performance of sliding and reciprocating tests in order to evaluate the friction and wear behaviour of coatings as a function of the type and amount of microcapsules codeposited.

Major outcome of this investigation was the demonstration of the influence of additives in the prevention of agglomeration of certain types of microcapsules. However, the presence of additives in the plating bath lowers or even hinders the codeposition process, Data on the adhesion force keeping particles in contact with the electrode have been derived based on a trajectory analysis worked out for the codeposition of non-Brownian particles. Adhesion forces in the range of only a few nanoNewtons were derived and the large role of the hydration force was clearly demonstrated. This low adhesion force is at the origin of the frequently experienced difficulties in this project to obtain large amounts of codeposited microcapsules.

With respect to the functional properties of these oil-containing nickel coatings, this project has for the very first time allowed the demonstration of the interesting friction and wear properties of this new type of composite coating. Indeed, extensive ball-on-disk tests have shown that:

- a minimum amount of oil-containing microcapsules in nickel coatings is necessary to achieve a reduced friction against steel in comparison to pure nickel in hen-lubricated sliding tests,
- the friction coefficient decreases with increasing amounts of microcapsules. The coefficient of friction in unlubricated sliding tests of steel against oil-containing nickel can be as low as 0.1 in comparison to 0.8 for sliding against nickel.

At the end of the project a limited number of components were coated with oil-containing nickel coatings and tested by industrial companies. These test results are partly available and indicate the need for a careful selection of contact conditions to get a full benefit of the incorporated oil-microcapsules.

Task 6: **Modelling** of the Composite Plating Process

Within this project the mathematical modelling of the composite plating process was advanced. Two topics were addressed namely:

- the modelling and experimental verification of the adsorption forces keeping particles in rest at electrodes,
- the mathematical derivation and the experimental verification of the boundary effects in composite plating, namely the potential and fluid flow disturbance fields induced by particles in the vicinity of electrodes.

From the modelling it was shown that the electrolytic codeposition of micron-sized particles is governed by colloidal interactions that can, in first order, be approximated by the Derjaguin-Landau-Verwey-Overbeek interactions plus an additional short range repulsion that was associated with the hydration force. The difficulties to codeposit particles arise from the low adsorption forces between particles and electrodes in plating solutions of high ionic strength. A methodology to derive this adsorption force from rotating disk electrode experiments was proposed. In the case of polystyrene particles codeposited from copper sulphate solutions, an adsorption force of only a few nanoNewton was calculated.

A quantitative basis for the interpretation of electrochemical noise generated by particles approaching an electrode was worked out. The method was based on the addition of fundamental solutions of the Laplace equation that conform to the particular geometry of electrodes and particles. A solution was obtained through the boundary collocation technique. Out of this, an algorithm was developed that finds the position of a particle based on the current flowing to a set of electrodes. Theroretical and experimental values were found to be in excellent agreement, the deviations being due to the limited experimental accuracy of resistance measurements,

3. European Benefit and Industrial Impacts - Exploitation Plans

This project initiated a close cooperation between French, Belgian and Greek research centers having complementary experience in composite plating. This cooperation was a novel one since none of the partners have cooperated before in the specific field of composite plating although three of them had been involved previously with industrial applications of composite plating. The novelty of the project was the development of a new type of" composite coatings namely oil-containing nickel coatings. At present it can be stated that the consortium has acquired a worldwide unique theoretical and practical know how

. on the synthesis of oil-containing microcapsules with surface characteristics suitable for electrolytic codeposition;

• *on* the synthesis of oil-containing metallic coatings exhibiting low friction, and

• on the modelling of the codeposition process.

From this research, the complexity of the development of a new type of composite coatings became evident and it was recognized by the industrial endorsers that further research is necessary before a successful introduction of this technology can be considered. Main points of attention in the future should be directed onto:

- the synthesis of oil-containing microcapsules on a pilot scale. The requirements to be imposed on the microcapsules were clearly identified. The biggest challenge in this respect is the synthesis of oil-containing sub-micron microcapsules or particles with appropriate surface characteristics,
- the development of an electrochemical sensor suitable for an in-situ control of the codeposition process. Potential fields of applications are the mapping of the fluid hydrodynamics of reactors in general and plating cells in particular, the control of 2 phase "flow, the detection of solid contaminants in fluids e.g. of interest in clean room related operations, the control of plating bath performance in case of composite plating like actual industrial Ni-SiC coatings in the automotive industries. During this project CNRS has protected the sensor related work by patents. A first application introduced for funding in VALUE was recognized for its technological quality but the limited field of application was the reason for not funding it.

- the extensive performance of Laboratory and field related tests to elaborate an insight on the potential field of application of low friction and wear resistant oil-containing metallic coatings. In this respect the optimization of microcapsules codeposition and metallic matrix is of prime interest.

The outcome of this project is of interest for further industrial exploitation in mainly two areas:

- specifically in the area of the development of materials which can be operated under dry (lubrication) conditions or under strongly reduced lubrication, and
- in the area of the actual industrial practice of composite plating in general where there is a need for the development of appropriate in-situ and on-line control techniques like for instance in the production of Ni-SiC composite coatings which is in use at a large scale in the French and German automotive industries.

The expertise developed within this four year project is unique and partly mature for further valorization. It should find uses in support to the improvement of the industrial field practice of composite coatings in general, and provides the European industries with a new type of coating. The present partners are considering the possibilities to work out future BriteEuram actions proposals within the area of codeposition for both basic and industrial research. Contacts with European research centers and industries have been initiated in that respect and it is foreseen that in 1996 proposals could be submitted as a follow up of this project.