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Nickel/microcapsules composite electrocoatings; the synthesis of water-containing microcapsules and preparation of the coatings

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Composite coatings, the product of electrolytic codeposition of solid particles in a metallic matrix have been developed and utilized in industry as wear resistant coatings. The work described in this paper concerns the development of water-containing metallic coatings prepared by the electrolytic codeposition of water-containing microcapsules from nickel Watts plating baths under pulse reversed current conditions. The water-containing polystyrene microcapsules employed in the codeposition experiments were produced by the complex emulsion/solvent evaporation technique. The influence of the use of two types of stabilizers on the size and the surface chemistry of the microcapsules is discussed. The microcapsules prepared in both cases are rigid spheres with compact walls and a smooth surface. The different stabilizers showed a significant influence on the dispersability of the capsules in the plating solution and their codeposition behaviour. The codeposition experiments carried out with the use of a rotating disc electrode revealed the influence of the plating parameters on the incorporation procedure and on the quality of the composite electrodeposits.

1. Introduction

Electrolytic codeposition, namely the incorporation of inert particles suspended in a plating bath, into a metallic matrix during electrolysis, has since 1969 been presented in the literature as an alternative method to conventional techniques for the production of composites (powder metallurgy, metal spraying, internal oxidation, coprecipitation). The method offers the possibility of producing smooth deposits with desirable dimensions and variable properties. The strong dependence of the physical properties of electrodeposits on plating conditions has been recorded in literature [1–4]. The conditions affecting the characteristics of the composites are; (a) the composition of the plating bath, (b) the current density, (c) the temperature and the type of stirring of the plating bath, and (d) the concentration of the particles. Composites having modified physical and mechanical properties in comparison to those of metals prepared by electrolysis, find considerable application in the space- and automobile-industries. Their applications can be classified into three categories depending on the type of incorporated particles, namely: (a) dry lubricant or wear resistant coatings, (b) corrosion or oxidation resistant coatings, and (c) dispersion-strengthened coatings [5].

The most commonly employed industrial technique for the electrodeposition of metals involves the application of a direct current (DC). Recently however, the pulse current (PC) and the pulse reversed current (PRC) techniques have been utilized, especially in fields involving the use of noble metals. The electrodeposition of metals by either a cyclic variation or by an interruption of the applied current, can be considered as an alternative for electroplating. Pulse plating is essentially an interrupted direct current plating technique, with limitations at high frequencies due to the capacitance effect on the electrodes, whilst at low frequencies the electrode potential does not differ essentially from the corresponding to DC conditions.

The composite coatings which have so far found wide industrial application have generally contained solid particles. In addition to the entrapment of solid particles, the incorporation of liquid-containing microcapsules into metallic coatings has been recently reported [6, 7]. The codeposition of liquid-containing microcapsules along with metals from electrolytic baths, leads to the development of a totally new type of material, *the liquid-containing metallic electrocoating*. In addition to the type of the liquid core, the polymeric wall of the microcapsules strongly affects the characteristics of the coating. A number of well known microencapsulation techniques can be applied for the encapsulation of an aqueous or organic phase into polymeric materials. The methods of microencapsulation can be classified into three main categories; (a) physical methods (phase separation–coacervation, solvent evaporation), (b) chemical methods (interfacial polymerization, *in situ* polymerization) and (c) mechanical methods (fluidized bed, spray drying). The selection of the appropriate technique is based on the specific requirements for the type of liquid to be incorporated, the wall thickness and the surface characteristics of the microcapsules.

The liquid-containing microcapsules employed in a codeposition process, must have a narrow size distribution, within a specific size range depending on the thickness of the coating. They must also be dispersable and stable under stirring, heating and the ionic strength conditions of the plating bath. The complex emulsion-solvent evaporation technique can be applied to the production of water-containing microcapsules with compact and rigid polymeric wall. The technique involves the formation of a water–organic (w/o) emulsion, where the organic phase is a solution of the polymeric wall material in a suitable volatile organic solvent and the aqueous phase is the aqueous solution that will be encapsulated. The w/o emulsion is subsequently dispersed in an aqueous phase containing a stabilizer, thus forming a complex (w/o)/w emulsion. The evaporation of the organic solvent at an elevated temperature or a reduced pressure leads to the precipitation and hardening of the polymer around the internal aqueous droplets, which thus form the microcapsules [8].

This paper presents some preliminary results concerning the incorporation of water-containing polystyrene microcapsules into nickel electrodeposits. Two types of polystyrene based microcapsules, prepared using different stabilizers, were employed in the codeposition experiments. The effect of the use of different stabilizers on the behaviour of the microcapsules in the plating solution is discussed. The influence of three variables of the codeposition process, namely; (a) the rotation velocity of the cathode, (b) the pulse frequency and (c) the capsule concentration have been investigated in order to elucidate their effect on the incorporation procedure and also on the quality of the composite electrodeposits.

2. Experimental

2.1. Materials

The following materials were used: polystyrene with a molecular weight 280,000 (Aldrich) and gelatin of type A, 300 bloom (Aldrich). The emulsifiers stabilizers included sorbitan sesquioleate (Sigma) and potassium oleate (Fluka). Dichloromethane (Merck) was of analytical grade. All chemicals were used as received.

2.2. Microencapsulation procedure

Water-containing polystyrene microcapsules were prepared by the complex emulsion-solvent evaporation technique. The experimental procedure included the following steps; a solution of polystyrene in dichloromethane was introduced into an homogenizer beaker. An aqueous solution of gelatin was added dropwise to the beaker and the mixture was vigorously agitated by a rotor-stator homogenizer (Polytron, Kinematika AG) to form a w/o emulsion. This emulsion was subsequently dispersed into an aqueous solution containing a predetermined amount of an o/w type stabilizer, using the homogenizing device. The (w/o)/w emulsion thus formed, was transferred into a glass jacketed reactor vessel, equipped with a mechanical stirrer. The complex emulsion was heated at 45 °C for 16 h, to allow the evaporation of the organic solvent. After the completion of the solvent removal the microcapsules were separated from the liquid by decantation or/and centrifugation.

Two variations on the basic procedure described above were performed. In the first case a w/o emulsifier, sorbitan sesquioleate, was dissolved in the organic phase along with the polymer and the anionic stabilizer potassium oleate was employed in the second emulsification step. In the second case no w/o emulsifier was used and a gelatin polymeric stabilizer was employed for the formation of the complex emulsion.

Samples of both types of microcapsules were thoroughly washed by repeatedly dispersing them in warm distilled water and centrifuging. In the screening experiments, the microcapsules were stirred in the plating solution for about 24 h. Microscopic observations were performed during these tests and also comparisons of their size distributions before and after the tests were carried out in order to assess the stability and dispersability of the microcapsules in the plating solution.

2.3. Particle size measurements

The size distribution of the microcapsules was measured by a Malvern laser diffraction particle size analyzer, model 2605 C interfaced with an Olivetti personal computer. The volume distributions were obtained by reference to a log–normal distribution model.

The optical observations were carried out using an optical microscope (Leiz Metallux 3) attached to a camera and a TV monitor. The system was connected with a 80286 IBM personal computer, supplied with suitable software (Image Pro Plus, Version 1.1) for advanced image analysis.

The size and the surface morphology of the microcapsules were examined by a scanning electron microscope (SEM). The microcapsules were thoroughly dried in a vacuum evaporator then coated with carbon and observed in a Jeol Model JFM-840A scanning electron microscope at an accelerating voltage of 15 KV.

2.4. Codeposition procedure

Experiments on the electrolytic codeposition of nickel with water-containing microcapsules were run out on a rotating disc electrode from a Watts type bath. A nickel-coated brass disc having an exposed area of 0.049 dm^2 was used as the working electrode. The flash nickel plating is necessary under DC conditions in order to prevent the brass from dissolving during the first anodic periods. A speed rotator was used to rotate the working electrode at a specific speed during the experiments. The rotation velocities employed were 1200, 600 and 400 rpm. The bath contained 300 gl^{-1} $NiSO_4 \cdot 7H_2O$, 35 gl^{-1} $NiCl_2 \cdot 6H_2O$ and 40 gl^{-1} H_3BO_3. The pH value of the electrolyte was fixed at 4.4, while the temperature was maintained at 50 °C.

A pulse generator (630 Minilab, BWD) was used to produce square reversed pulses and an oscilloscope (Storage Oscilloscope, BWD) to control the pulse frequencies and the current density. The pulse frequency (υ) was adjusted at 0.1 or 1 Hz and the duty cycle (θ) was kept constant and equal to 95%. The current density (J_p) was 11.4 A dm^{-2}.

3. Results and Discussion

3.1. Microcapsule size

The complex emulsion solvent evaporation technique involves two emulsification steps, one for the formation of a simple w/o dispersion and a second for the formation of a complex (w/o)/w dispersion. The method is consequently affected by phenomena occurring in the liquid–liquid dispersion processes. A liquid–liquid dispersion process taking place in an agitated vessel is characterized by two dynamic phenomena: drop breakup and coalescence. Droplet breakup can occur either in the regions of high shear stress encountered near the agitator blades or as a result of turbulent velocity and pressure variations along the surface of a single droplet. The rate of coalescence of droplets is determined by turbulent flow which can both increase or decrease the observed rate. The flow and mixing conditions obtained in stirred vessels depend on the geometry of the vessel and impeller, and also the physical properties of the mixed phases. These variables determine the relative breakage and coalescence rates that give rise to a distribution of droplet size of the dispersed phase [9].

In a liquid–liquid dispersion system the interfacial tension is a measure of the relative resistance of the droplets to breakage as compared to coalescence. Thus, a decrease in the interfacial tension results in a reduction of the average droplet size due to both a decrease of the resistance to breakage and also an increase of the resistance to coalescence. The interfacial tension between two immiscible liquids in a dispersion will depend on the temperature, as well as on the presence of surface-active agents. The function of surface-active agents is to adsorb on the monomer-water interface and prevent other drops from approaching because of steric repulsion forces. This causes a reduction in immediate coalescence, due to the increasing strength of the liquid film entrapped between two colliding drops. The formation of a protective film extends the contact time for drop coalescence, thus increasing the probability of droplet separation by agitation. However, some of the collisions do result in adhesion of the colliding drops. In this case the resulting film tends to decrease in thickness with time and finally collapses; thus permitting the coalescence of the droplets. Surfactants increase the interfacial viscosity and lower the interfacial tension thus making the interface more rigid and more deformable [10].

The first emulsification step results in the formation of a w/o dispersion, in which the dispersed phase is the aqueous solution that will comprise the liquid core of the microcapsules, whilst the continuous phase is a solution of the polymer in an organic solvent. The size distribution of the aqueous droplets must be narrow and below the desired size of the final microcapsules. The dissolution of gelatin in the aqueous phase improves the stability of the w/o emulsion. This is because aqueous droplets containing gelatin behave as hardened spheres and thereby exhibit better resistance to coalescence than the simple aqueous droplets [11]. The presence of a w/o type emulsifier in the organic phase further reduces the size of the aqueous droplets and enhances the stability of the w/o emulsion.

Two types of polystyrene microcapsules were investigated in this work. For the preparation of the first type of microcapsules the w/o emulsifier sorbitan sesquioleate was used, in addition to the inclusion of gelatin in the internal aqueous phase. This emulsifier significantly lowers the interfacial tension between the aqueous and the organic phase, resulting in the formation of aqueous droplets with a mean diameter of 1.5 μm. For the second kind of microcapsules no w/o emulsifier was used and the corresponding size of the aqueous droplets was about 10 μm for the same agitation conditions. The presence of the emulsifier sorbitan sesquioleate in the organic phase not only affects the formation of the w/o emulsion and the size distribution of the aqueous droplets, but also the formation of the complex emulsion. This in turn influences the interfacial tension between the intermediate organic phase and the external aqueous phase. When sorbitan sesquioleate, containing the sorbitan group which has a hydrophobic character, is present in the organic phase, the anionic stabilizer potassium oleate proved to be an excellent stabilizer for the complex emulsion. This is because it provides the complex droplets with anionic groups which produce electrostatic stabilization of the droplets. The microcapsules prepared in this case had a uniform size distribution with a mean diameter of about 6 μm. Gelatin on the other hand, did not provide sufficient stabilization and the final product exhibited agglomeration. When however the w/o emulsion was prepared without the use of sorbitan sesquioleate, gelatin was able to successfully act as a stabilizer. The microcapsules prepared in this case had a mean diameter of about 26 μm. The size distribution of the two types of microcapsules are depicted in Fig. 1.

Microcapsules prepared in both cases, appeared in SEM micrographs as perfect, rigid spheres, with compact walls and smooth surface (Fig. 2).

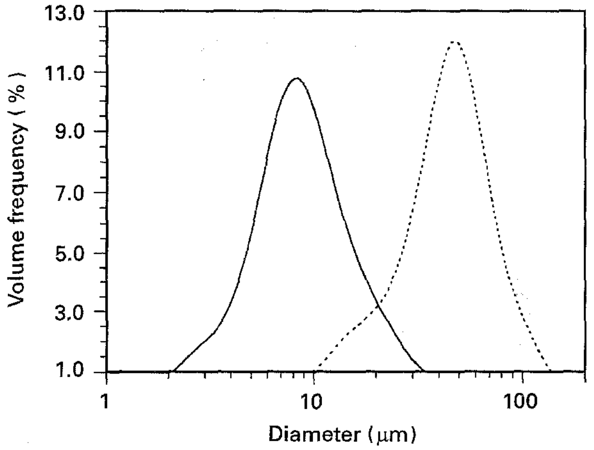

Figure 1 Particle size distributions of water-containing polystyrene microcapsules prepared using different stabilizers: a) (-) use of w/o emulsifier sorbitan sesquioleate and of o/w stabilizer potassium oleate, b) (- -) no w/o emulsifier used and employment of o/w stabilizer gelatin.

3.2. Dispersability of microcapsules in the plating solution

The stability and dispersability of the microcapsules in the plating bath solution is related to the reactivity of the surface groups with the bath components, i.e. ions, surface active agents, polymeric species, as well as to the effect of pH and temperature. The surface groups of the microcapsules arise from the polymeric wall material, and the stabilizers used for their preparation. Ions present in the core solution may also interact with the dispersion medium through the microporosity of the capsules. Ions from the electrolyte solution, as well as surfactants are adsorbed on the surface of the capsules and strongly affect their behaviour. Some of the surface groups of the microcapsules are ionized in the dispersion solution, and the microcapsules acquire charge depending on the composition and the pH of the solution. A number of ions from the solution phase are arranged close to the surface of the particle, in order to keep electroneutrality. The conformation of these counterions is known as the electrical double layer. As the particles approach, the double layers interpenetrate and rearrange. The interaction between the double layers determines whether a repulsive or an attractive force is exerted between the capsules.

Screening tests were carried out prior to the use of the microcapsules in the codeposition experiments, in order to assess their behaviour in the plating solution. The microcapsules were collected and washed in order to remove traces of the stabilizers, which could possibly contaminate the bath and inhibit metal deposition. The size distribution of the microcapsules was measured after each washing step and after stirring for a certain time in the plating solution. Comparison of these size distributions gives evidence about the stability of the microcapsules in the plating solution. The microcapsules were also observed in the optical microscope during the screening tests, to examine if they retain their spherical shape or collapse and are destroyed.

The first type of microcapsules exhibited signs of coagulation after the second washing step. This is attributed to the fact that these microcapsules have been prepared using the w/o emulsifier sorbitan sesquioleate, which enhances the hydrophobicity of the microcapsules. This leads to the coagulation of the capsules when the stabilizer is removed from their surface during the washing treatment. These microcapsules have been collected and redispersed in clear aqueous solution, using a sonicator, before their testing in the plating solution. Upon their addition in the plating solution strong coagulation of the capsules was observed, and the dispersion was not improved, even after stirring of the solution for 24 h with a magnetic stirrer. However, when a small amount of an anionic surface active agent, i.e. SDS was dissolved in the plating solution, the microcapsules were effectively dispersed and formed a stable suspension after 24 h stirring. The size distribution of a sample of microcapsules in the product withdrawn from the reactor and of a sample of washed microcapsules, after 24 h stirring in the plating solution containing sodium dodecyl sulfate (SDS) are depicted in Fig. 3.

The second type of microcapsules exhibited good stability during the washing procedure and no sign of coagulation was detected, even after repeated washing. These microcapsules were also effectively dispersed in the plating solution without use of any dispersing agent. On the other hand, when a small amount of SDS was added in the solution, the microcapsules were strongly coagulated and could not be dispersed even after 24 h stirring. Fig. 4 presents the size

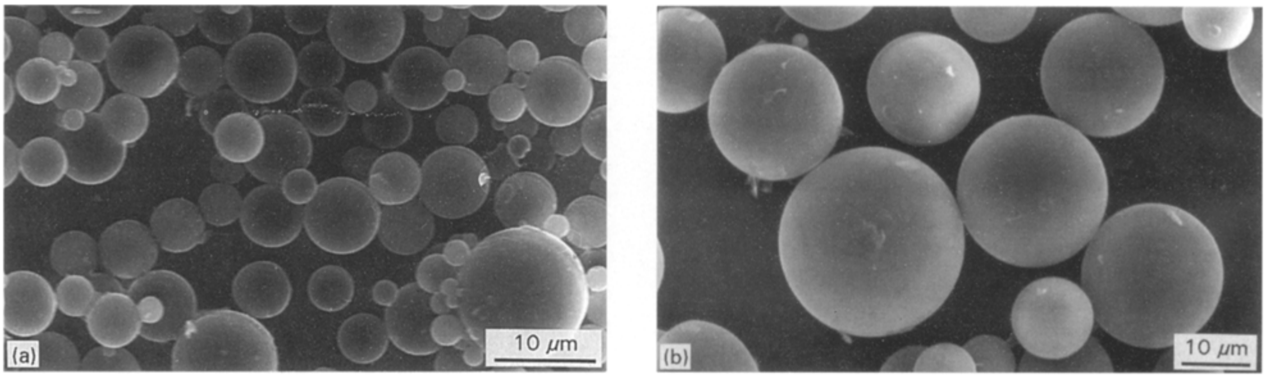

Figure 2 SEM photomicrographs of water-containing polystyrene microcapsules: a) use of w/o emulsifier sorbitan sesquioleate and of o/w stabilizer potassium oleate, b) no w/o emulsifier used and employment of o/w stabilizer gelatin.

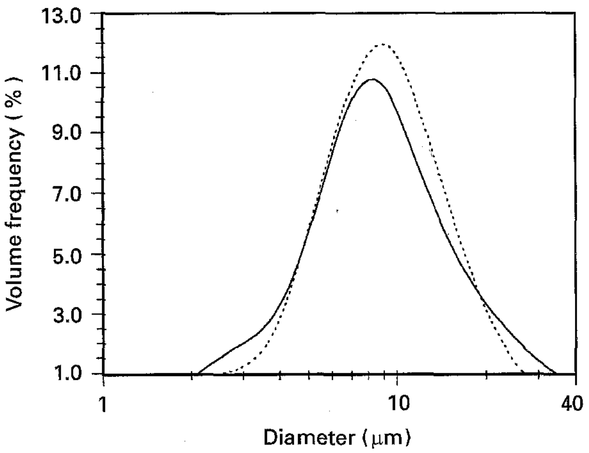

Figure 3 Particle size distributions of water-containing polystyrene microcapsules prepared using sorbitan sesquioleate and potassium oleate: a) (-) microcapsules in the product withdrawn from the reactor, b) (- -) microcapsules once washed, 24 h magnetically stirred in the plating bath solution.

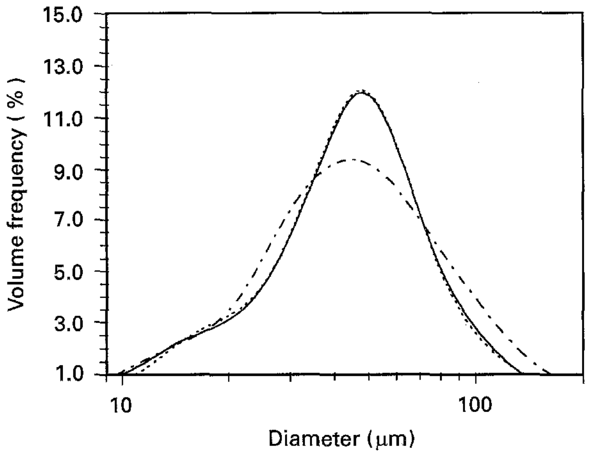

Figure 4 Particle size distributions of water-containing polystyrene microcapsules prepared using gelatin as stabilizer: a) (-) microcapsules in the product withdrawn from the reactor, b) (- -) microcapsules after the washing procedure, c) (----) microcapsules once washed, 24 h magnetically stirred in the plating bath solution.

distributions of a sample of microcapsules in the product withdrawn from the reactor, of a sample of microcapsules after the washing procedure and of a sample of washed microcapsules after 24 h stirring in the plating solution.

From the screening tests it is clear that the two kinds of microcapsules exhibit totally different behaviour under the conditions of the plating solution. Since both kinds contain the same aqueous solution and were prepared using the same polymer, the difference in their behaviour is attributed to the different stabilizers used in their preparation. On the surface of the first type some groups are introduced from the sorbitan sesquioleate and potassium oleate. The latter contains a hydrophobic chain oriented towards the surface of the capsules and also a carboxylate group, a hydrophilic moiety, oriented towards the aqueous solution. This group is negatively charged in aqueous solutions.

Surface groups on the second kind of microcapsules derive from gelatin, a high molecular weight polypeptide, containing amino-acids. Gelatin shows polyampholyte properties and can be either positively or negatively charged in aqueous solutions depending on the pH. The stabilization provided by gelatin results from its adsorption on the interface in a loop-and-train conformation. Although the molecules may bear a net electrical charge, the adsorbed layers are believed to stabilize by steric rather than electrostatic mechanism.

The different character of the surface groups has been experimentally confirmed by other researchers [12]. Measurements of the zeta potential revealed that the first kind of microcapsules has a positive zeta potential in $\mathrm{pH} < 3$. This indicates the presence of positive groups, probably arising from the gelatin in the core solution of the microcapsules. These microcapsules have an isoelectric point around 3 and then acquire a strong negative zeta potential in higher pH. This suggests the existence of a greater proportion of negative sites than positive on the surface of the capsules. The former are created by the stabilizer potassium oleate. The zeta potential of the microcapsules in the presence of nickel ions has also been measured. These measurements showed that at a pH of 4 nickel ions are adsorbed on the surface of the microcapsules and the zeta potential becomes less negative as the concentration of nickel ions increases, reaching a zero value. This indicates a neutralization of the charge of the microcapsules, resulting in their coagulation. When however SDS is present along with nickel ions, the surfactant molecules are adsorbed on the surface of the capsules together with nickel ions. Despite the fact that zeta potential becomes less negative as the nickel concentration increases, it never reaches zero, which explains why the capsules do not coagulate in the plating solution when SDS is present.

The second kind of microcapsules has a positive zeta potential in a $\mathrm{pH} < 6$ due to the presence of positive groups from gelatin in both the core solution and on the surface of the capsules. At higher pH values the zeta potential becomes negative due to the new negatively charged groups of gelatin. This kind of microcapsule does not show strong variation in its zeta potential in the presence of nickel ions, even for high nickel concentration, which is in agreement with the fact that these type of microcapsules are dispersable in the plating solution.

3.3. Codeposition behaviour

The pulse reverse plating (PRP) technique is an advancement in the electroplating field. The basic concept of this process is the periodic reversal of the plating current for appreciable lengths of time, thereby removing a substantial amount of previously plated metal [13]. In this way a metal is deposited for a period of time (cathodic or deposition time, T) and then some of the deposit is redissolved during the anodic period (anodic or dissolution time, T′). The anodic time is shorter than the cathodic [14]. The pulse frequency (υ) and the duty cycle ($\theta = T/T + T'$) are the parameters that intervene on the adsorption desorption phenomena occuring on the metallic surface and thus, perturb the crystal growth process. The cathodic and the anodic pulse current densities, J and J′ respectively are also important process parameters [15–19]. A reverse pulse of high anodic current enables the metal to dissolve into the electrolyte from high points such as burrs and dentrites [20].

It has been shown that in any system where the rate of cathodic metal deposition depends upon the concentration of metal ions in the solution adjacent to the electrode surface, the efficiency may be increased by carrying out the deposition in a cyclic manner with a pulse reversed current, provided that a certain limiting current density is exceeded.

Due to the reverse or deplating portion of the cycle, the overall electrical efficiency is reduced as compared with continuous direct current conditions. Metal deplated during the anodic part of the cycle is dissolved in the solution immediately adjacent to the electrode surface, i.e. in the metal-electrolyte interface (catholyte), so that abnormally high local concentrations of the metal ions are present when plating is reversed during the next interval of cathodic time. Accordingly, the plating part of the cycle can operate at maximum efficiency, and from a practical standpoint, much higher current densities can be achieved [14].

Incorporation of water-containing microcapsules in nickel coatings has been successfully accomplished as shown in Figs 5 and 6.

The first kind of microcapsules were very well incorporated in the metal, although a number of pits having the shape of craters were present on the surface of the deposits. Moreover the capsules seem to be preferentially incorporated in the vicinity of the craters (Fig. 7). Capsules are also emerged at the internal surface of the cavities. Craters give a dull or rough image to the deposits, even to the ones which appear to have a smooth surface in the SEM scale. The density of craters increases for high cathode rotation velocities (1200 rpm), low pulse frequency (0.1 Hz) and high microcapsule concentration (0.18 $g l^{-1}$).

Quantitative analysis of backscattering electron images gives evidence of a correlation between the pulse frequency and the quantity of incorporated capsules; the incorporation is generally weaker at 1 Hz than at 0.1 Hz. This could be attributed to the fact that when $\upsilon = 0.1$ Hz the dissolution time ($T' = 1$ s) is considerably larger than when $\upsilon = 1$ Hz ($T' = 0.1$ s), and the concentration of the metal ions in the catholyte, as well as of the capsules already incorporated, increases. If the deposition is held further during the next deposition period (T) then better adsorption of the capsules in the electrode is ensured.

For a concentration of capsules of 0.18 $g l^{-1}$ the surface coverage is approximately 15–18% for a pulse frequency of 0.1 Hz and rotation velocity of 600 rpm. It should be noted, that although there is no clear evidence of a correlation between the rotation velocity and the quantity of incorporated capsules, incorporation at 1200 rpm is generally weaker than that at 600 or 400 rpm. Although the percentage of incorporation does not significantly differ for rotation velocities 600 and 400 rpm, the higher coverage was obtained at 600 rpm. Table I presents the surface coverage for two pulse frequencies and three rotation velocities.

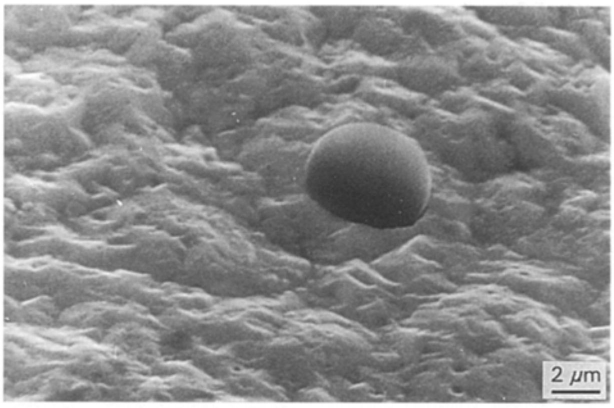

Figure 5 Codeposition of the first type of microcapsules in a PR nickel electrodeposit ($\Omega = 600$ rpm, $\upsilon = 1$ Hz, $\theta = 95\%$, concentration of capsules = 0.06 $g l^{-1}$, diameter of capsule = 6 μm).

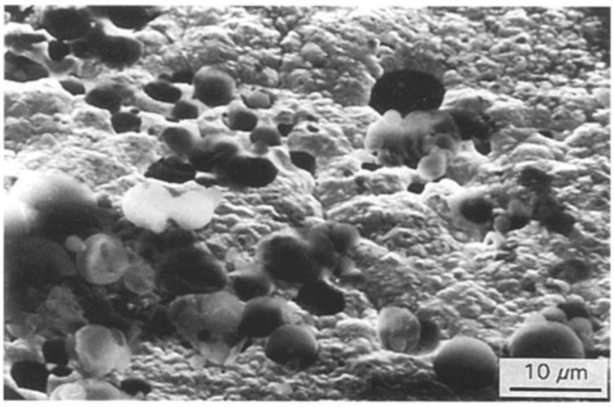

Figure 6 Codeposition of the first type of microcapsules in a PR nickel electrodeposit ($\Omega = 1, 200$ rpm, $\upsilon = 1$ Hz, $\theta = 95\%$, concentration of capsules = 0.18 $g l^{-1}$, mean diameter of capsules = 6 μm).

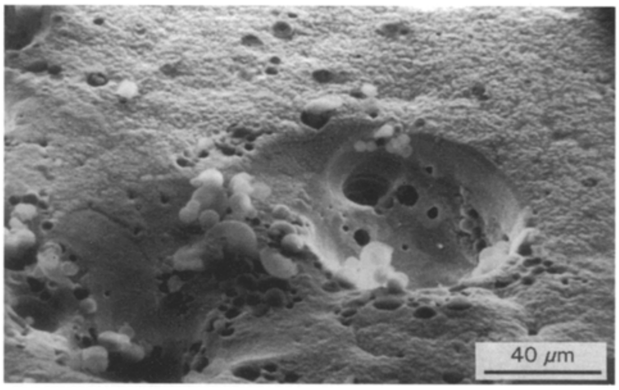

Figure 7 Codeposition of the first type of microcapsules in a PR nickel electrodeposit. Incorporation in the vicinity of the craters ($\Omega = 600$ rpm, $\upsilon = 0.1$ Hz, $\theta = 95\%$, concentration of capsules = 0.18 $g l^{-1}$, mean diameter of capsules = 6 μm).

Less satisfactory codeposition was achieved with the second kind of microcapsules. This is attributed to the thickness of the deposits; all deposits prepared did not exceed approximately 60 μm which could explain the difficulty of incorporation of large microcapsules. The number of microcapsules of the second type incorporated was relatively low and appeared to

TABLE I Percentage incorporation of microcapsules of mean diameter 6 µm.

Pulse frequency (H_2)	Rotation velocity (rpm)		
	1200	600	400
1	8.1%	9.2%	2.6%
0.1	10–12%	15–18%	9–14%

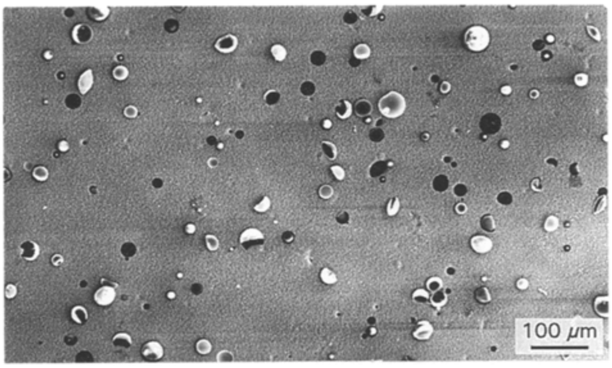

Figure 8 Codeposition of the second type of microcapsules in a PR nickel electrodeposit. Incorporation in the centre of the deposit ($\Omega = 400$ rpm, $\upsilon = 1$ Hz, $\theta = 95\%$ concentration of capsules $= 0.15\ \mathrm{g\,l^{-1}}$, mean diameter of capsules = 26 µm).

increase at small rotation velocities and low pulse frequencies. When the concentration was 0.05 $\mathrm{g\,l^{-1}}$, almost no capsules were codeposited at any rotation velocity or pulse frequency, as SEM micrographs revealed. When a higher concentration of capsules was applied (0.15 $\mathrm{g\,l^{-1}}$), they were incorporated mainly in the centre of each deposit (Fig. 8). The greater incorporation was achieved at 400 rpm and 0.1 Hz. When the pulse frequency was 1 Hz, the incorporation was not very successful even at 400 rpm; only a small number of capsules were observed in the centre of the deposit and they appeared deformed or broken.

4. Conclusion

This paper presents some preliminary results concerning the electrolytic codeposition of water-containing polystyrene microcapsules in nickel coatings. It was demonstrated that the parameters affecting the synthesis of the microcapsules as well as the plating conditions determine the codeposition behaviour of the capsules and the quality of the deposits. The stabilizers used for the preparation of the microcapsules affect not only their size but also their surface chemistry. The stabilizers anchored on the surface of the microcapsules have to be removed, prior to codeposition, in order to avoid contamination of the plating bath. Washing of the microcapsules however can cause their destabilization and aggregation. This problem was particularly observed when a w/o emulsifier enhancing the hydrophobic character of the microcapsules was present in the system. Another major problem encountered in this work was the efficient dispersion of the microcapsules in the plating bath, especially when the stabilizer used for their preparation was of ionic type. A number of additives (e.g. SDS) can be employed to improve the dispersability of the microcapsules but they may inhibit nickel deposition. These first results appear very promising. The application of the pulse reversed current technique gives better results than the direct current technique regarding the capsule incorporation. The electrolysis parameters as well as the size of microcapsules influence the codeposition procedure. Strong inhibition conditions (0.1 Hz) and low rotation velocities give deposits with well-incorporated microcapsules in the metallic matrix.

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