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## Session O - Dispersion Coatings I

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DISPERSION COATINGS I

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# Dispersion Coatings I
# Session 0

## Is The Electrolytic Codeposition of Solid Particles A Reliable Coating Technology?

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# IS THE ELECTROLYTIC CODEPOSITION OF SOLID PARTICLES A RELIABLE COATING TECHNOLOGY ?

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The electrolytic codeposition of fine solid particles with metals has been recognized over the last decade as a technique which offers the possibility of producing coatings with unique properties. Up to now industrially developed applications are mainly restricted to the Ni-SiC system. Based on an analysis of the electrolytic codeposition process, the present paper attempts to explain this fact. The reliability status and the limitations of the composite plating technique are illustrated with experimental results.

The first time research laboratories got interested in the codeposition of particulate matter during electrolysis can be situated in the early sixties (1). Since that time a lot of research and development work has been done and in recent years this has led to some interesting industrial applications of composite coatings. The major break-through of composite plating is actually taking place in the automobile industry with the use of electrolytic nickel-silicon carbide coatings in a new generation of motor engines made of weight-saving aluminium alloys (2). Some of these nickel-silicon carbide coatings have been introduced under trade marks as e.g. Nikasil, Elnisil ... . A few European and Japanese automobile companies have already introduced this technology in their most recently developed motor-car models. This break-through of Ni-SiC composite coatings is probably the best guarantee for a further increasing interest of platers and designers to introduce other composite coatings as well with unique physical, chemical and/or mechanical properties. Besides the successful electrolytic codeposition one should also note the upcoming electroless composite plating offering the possibility to produce a wide range of coatings like Ni-SiC or Ni-PTFE having an outstanding wear resistance (3, 4). Reading through the open literature on electrolytic composite plating from 1968 till now some interesting features come to our attention. So e.g. the number of representative papers for the most frequently cited composite coatings systems are compiled in fig. 1 in which a differentiation is done in terms of the affiliation of the authors being either associated with universities or with industrial research laboratories. From this figure it seems at a first glance that nickel based composite coatings have received a marked preference in industrial research. The growing importance of industrial applications of Ni-SiC and, although in a more limited way, Ni-PTFE composite coatings is a logical result ! The industrial interest for the cobalt-chromium carbide coatings has solely to be related to intensive research and development work of a British company which promotes this type of composite coating for its favourable high temperature behaviour on aircrafts parts (5). Although research work on copper-based composite coatings has been intensively reported, there is presently and as far as we know no prospect for its commercial application. A potential application of copper-alumina coatings could be based on the dispersion-strengthening effect obtained (6). Related to the dispersion strengthening obtained by the incorporation of submicron particles in a metallic matrix and/or the as-

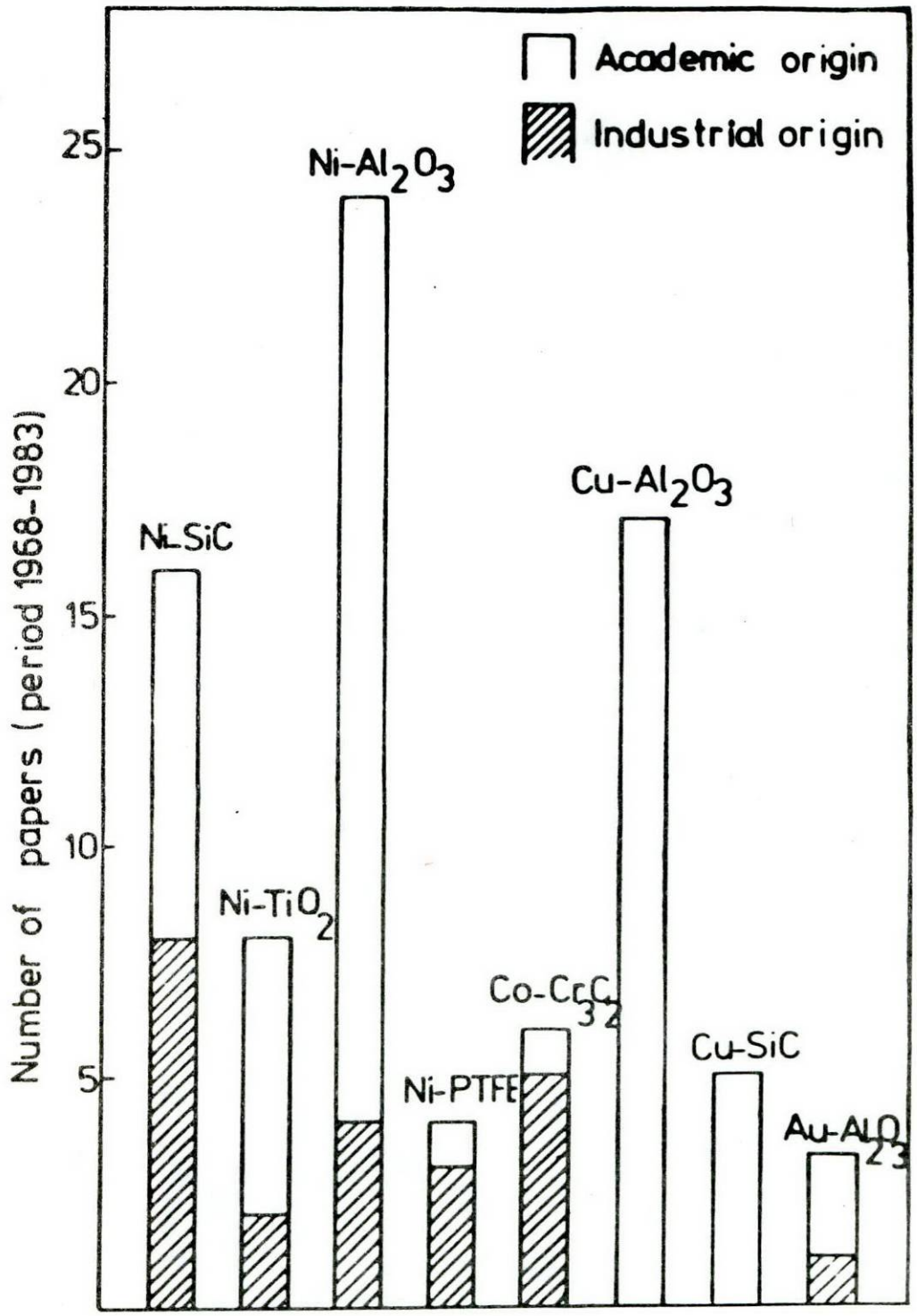



Fig. 1 : Compilation of published papers for some electrolytic composite coating systems.

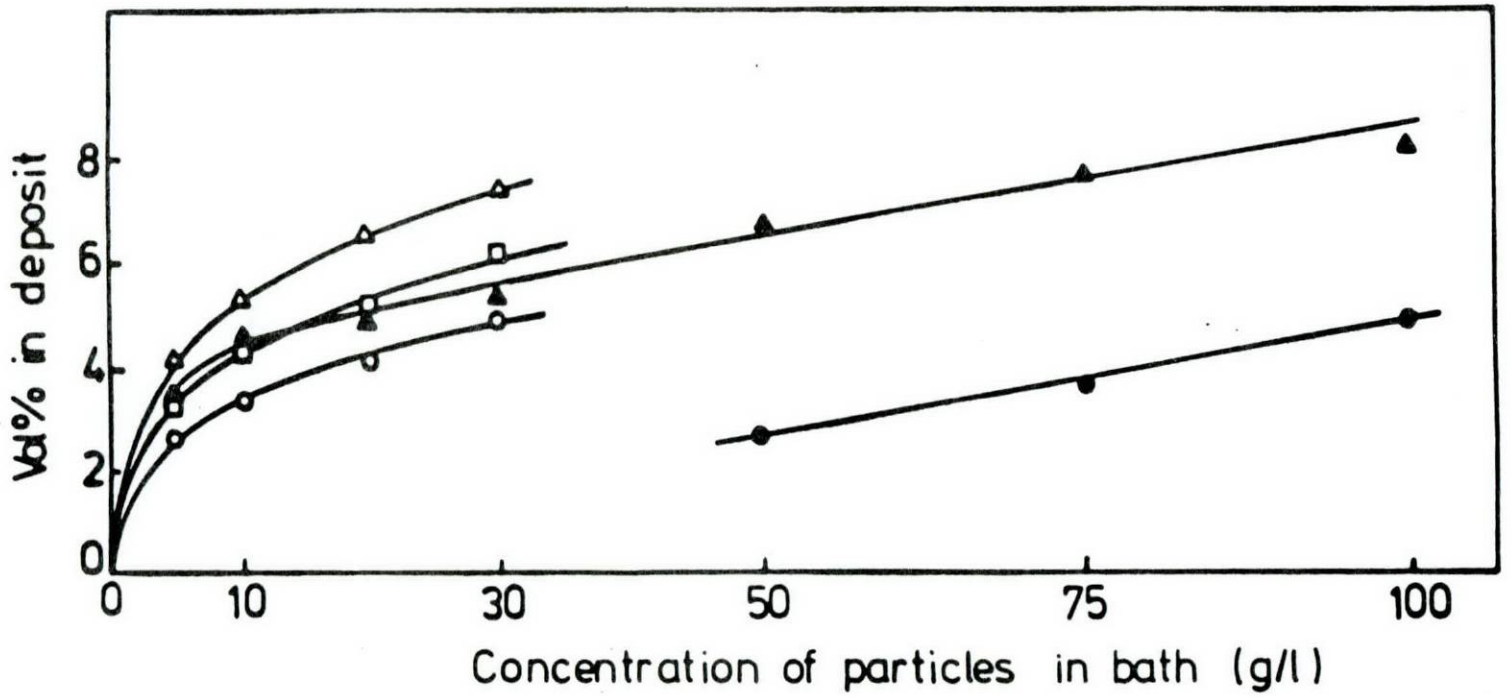



Fig. 2 : Codeposition of $TiO_2$ with Ni from nickel sulfamate solutions as reported in literature.

sociated self-lubricating effect, composite plating allows a non-negligible raw materials saving. In this respect the composite gold and silver plating seem to gain interest in the electronics applications (7). Besides open literature information an other interesting source of information on the potential future development of composite plating are the patents recently granted in the field of composite plating. Three major fields of interest can here be indicated, namely

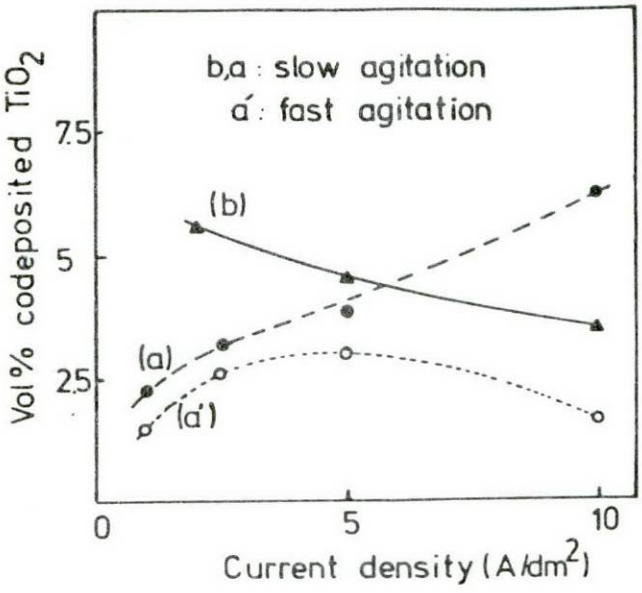
- self-lubricating coatings as e.g. the electrolytic deposition of silver-graphite composites (7)
- coatings for nuclear applications as e.g. the production of copper-boron carbide composites (8, 9)
- wear and oxidation resistant coatings (10) and the manufacturing of abrasive tools by the occlusion plating of diamond (11, 12).

From the above we can conclude that the electrolytic and electroless codeposition of solid particles with metals actually offers interesting industrial applications and that progress can be expected into new fields. Composite plating seems thus to be accepted from a technological standpoint as a valuable technique for the design of new coatings. Although much attention is paid to the Ni-SiC system, today questions which ask for an answer are : what is the reliability of the composite plating process for Ni-SiC and other systems ? And what are the fundamental reasons for the preferential break-through of Ni-SiC coatings ?

## The Mechanism of Codeposition : State of the Art

A first potential reason for the break-through of Ni-SiC composite plating can be brought back to the mechanism of codeposition. Based on a survey of the open literature starting in the early sixties, it is possible to follow the successive steps taken in the insight into the mechanism of incorporation of small particles in metals during electrolysis. In the period 1961-1967 three possible mechanisms were proposed namely electrophoresis, based on research on Cr-ZrC by Whithers in 1962 (13), mechanical entrapment of particles by Martin in 1964 from a research on copper-silica fibres (14) and adsorption of particles on the cathode by Brandes in 1967 as a result of a research on Ni-$Al_2O_3$ and Cr-$Al_2O_3$ (15). Tomaszewski et al. (16, 17) demonstrated in the period 1969-1976 the effect of anions and cathions on the electrolytic codeposition of solid particles like $BaSO_4$ and $SiO_2$. An important step forwards in the understanding of the mechanism of codeposition has been the publication by Guglielmi (18) in 1972 of a mathematical model based on a two-step adsorption process, namely a loose-adsorption step of particles on the cathode followed by a strong-adsorption step of these particles on the cathode. The main feature of this model is that it gives a mathematical equation which relates the amount of codeposited particles versus the amount of particles suspended in a plating bath. This equation is derived from the Langmuir adsorption isotherm and the Tafel equation governing electrode processes. This mathematical model was proven to be valid by Guglielmi for the Ni-$TiO_2$ and Ni-SiC systems (18). Guglielmi's model correlated well with the at that time generally accepted and in the meantime confirmed relationship (19, 20, 21) between the amount of codeposited particles at a given current density and the amount of particles suspended in the plating bath (see fig. 2). Where Guglielmi's model fails is where it does

not allow any prediction of the amount of codeposited particles versus the current density for quite comparable plating baths and versus the hydrodynamic flow conditions in the neigbourhood of the cathode. This is illustrated in fig. 3 for the codeposition of $TiO_2$ with nickel from sulphamate solutions based on data published by different researchers (18, 22). Increasing as well as decreasing codepositions at increasing current density have been determined for codeposition tests performed in at first glance quite similar conditions. One explanation herefore can be the important role played in codeposition by anions and cathions present in the plating bath as well as by the role of ions adsorbed onto the particles. These two facts have been put forward since 1977 by Foster et al. (23, 24) for $Ni-Al_2O_3$ and $Cu-Al_2O_3$ codeposition and by our own research on $Cu-Al_2O_3$ codeposition (25, 26). Although Guglielmi mentioned the potential role of adsorbed ions, he did not include their effect into his model.




| | a,a' | b |
|---|---|---|
| nickel sulphamate | 400g/l | 400g/l |
| nickel chloride | 5g/l | 5g/l |
| boric acid | 50g/l | 30g/l |
| pH | 4-4.5 | 4±0.2 |
| temperature | - | 50°C |
| size $TiO_2$ | 0.7µm | 1µm |

Fig. 3 : Effect of current density on the codeposition of $TiO_2$ with nickel (18, 22).

The importance of the growing insight into the mechanism of codeposition can be illustrated with a historical survey of the codeposition of alumina from acidified copper sulphate solutions, a system investigated in our laboratory since 1972. Till 1971 it was stated in literature e.g. by Sautter (1) and Hoffmann (27) that the codeposition of alumina was not feasible in such plating baths. In 1971 the importance of the phase structure of the alumina was shown by Chen (28) but it was still stated that only $\alpha$-alumina could be codeposited and in 1974 Foster (29) demonstrated that codeposition in such a plating bath is only possible if a positive surface charge is present. In 1977 we demonstrated the feasibility of the codeposition of either $\alpha$- or $\gamma$-alumina and we proved the validity of Guglielmi's model for both types of alumina (30). Moreover from our research it was shown that the relative effects of various electrolysis conditions as current density, pH, type and concentration of addition agents on the codeposition of $\alpha$ and $\gamma$-alumina are identical to those for Ni-SiC codeposition. In fig. 4 the dependency of the volume percent embedded alumina with copper versus current density is given based on data we published in 1977 (30) and which were recently confirmed by Foster et al. (31).

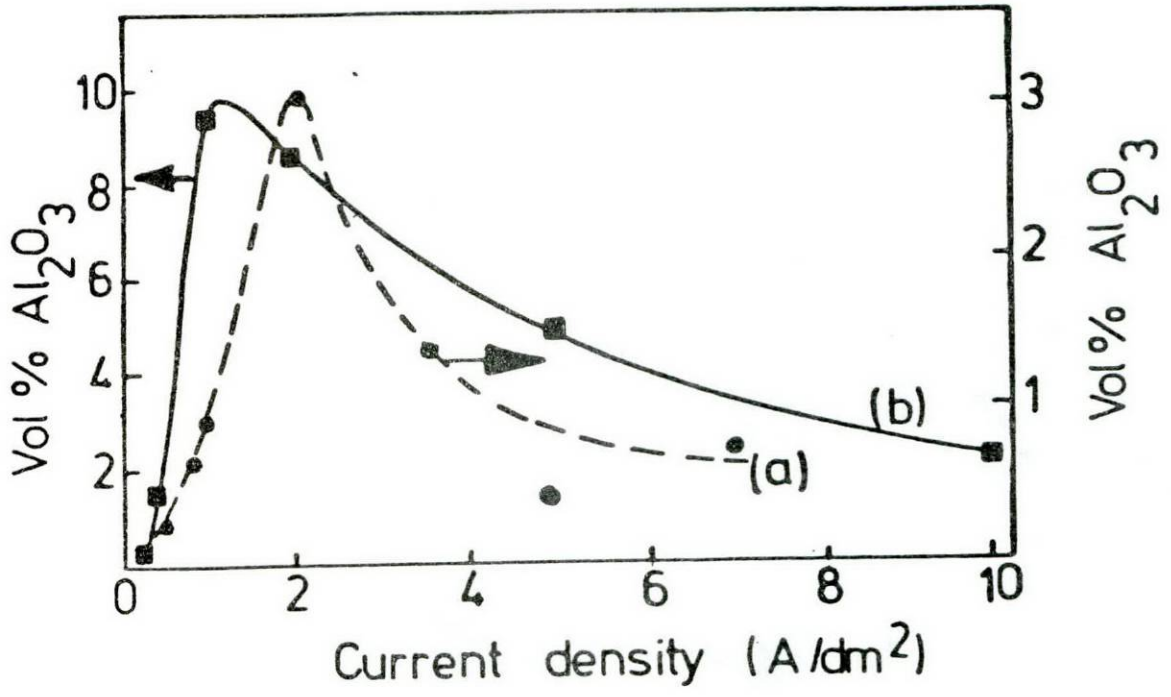



Fig. 4 : Dependency of the vol. % codeposited $Al_2O_3$ with Cu versus current density
(a) copper sulphate pH 0.3 + 10 g/l $\alpha$-$Al_2O_3$ (30)
(b) copper sulphate pH 1.4 + 50 g/l $Al_2O_3$ (31)

Based on data on the adsorption of $H^+$ and $Cu^{++}$ on alumina and on an analysis of polarization curves, we demonstrated that as long as the reduction of copper ions is under charge-transfer overvoltage control a considerable increase in the amount of embedded alumina particles is obtained with increasing current density (in fig. 4 up to $\sim$ 2 A/dm$^2$ at pH 0.3). When concentration overvoltage becomes predominant the amount of codeposited particles decreases with increasing current densities. The adsorbed layer on alumina particles plays a double role. Firstly if cathions are adsorbed the attraction of such particles towards the negatively charged cathode is increased, but at the same time these adsorbed cathions act as a screen between cathode and particles. As long as some of these adsorbed cathions are not reduced at the applied cathode potential only a loose adsorption condition is realized limiting the chance of codeposition of alumina particles. Based on recent literature, a quite similar process of codeposition may be put forward for the Ni-SiC system.

The mechanism of codeposition of SiC with nickel thus does not seem to be essentially different from the electrolytic codeposition of other carbides and oxides with nickel or other metals. This constitutes a first reason for the feasibility of Ni-SiC electrocodeposition.

## Generalities concerning the choice of codeposition parameters

A second reason for the break-through of Ni-SiC plating could be related to aspects of reproducibility. Although the modelling of the electrolytic codeposition process is far from being well-developed, it is possible based on the present scientific and field experience to describe to some extent the effect of several important electrolysis parameters. A schematic representation of the influence of four main parameters is given in fig. 5. The relative position of the curves is determined by the characteristics of the ionic layer adsorbed and of the particles themselves principally determined by the combined effect of

- the type of particles suspended

  e.g. * conductive particles give much higher codeposition than non-conductive ones,
  * large particles give per embedded particle much higher vol. % than small particles (proportional to $\Delta r^3$).

- the composition of the plating bath

  e.g. * addition of anionic surfactants reduces or even impedes codeposition, where cathionic surfactants can considerably increase the codeposition,
  * low pH increases the adsorption of hydrogen at the cost of metallic ions reducible at the applied cathode potential.

At this point it is important to point out that this discussion refers to electrolytic codeposition on vertical or even on the underside of horizontal cathodes. In such cases the sedimentation of particles by gravity forces

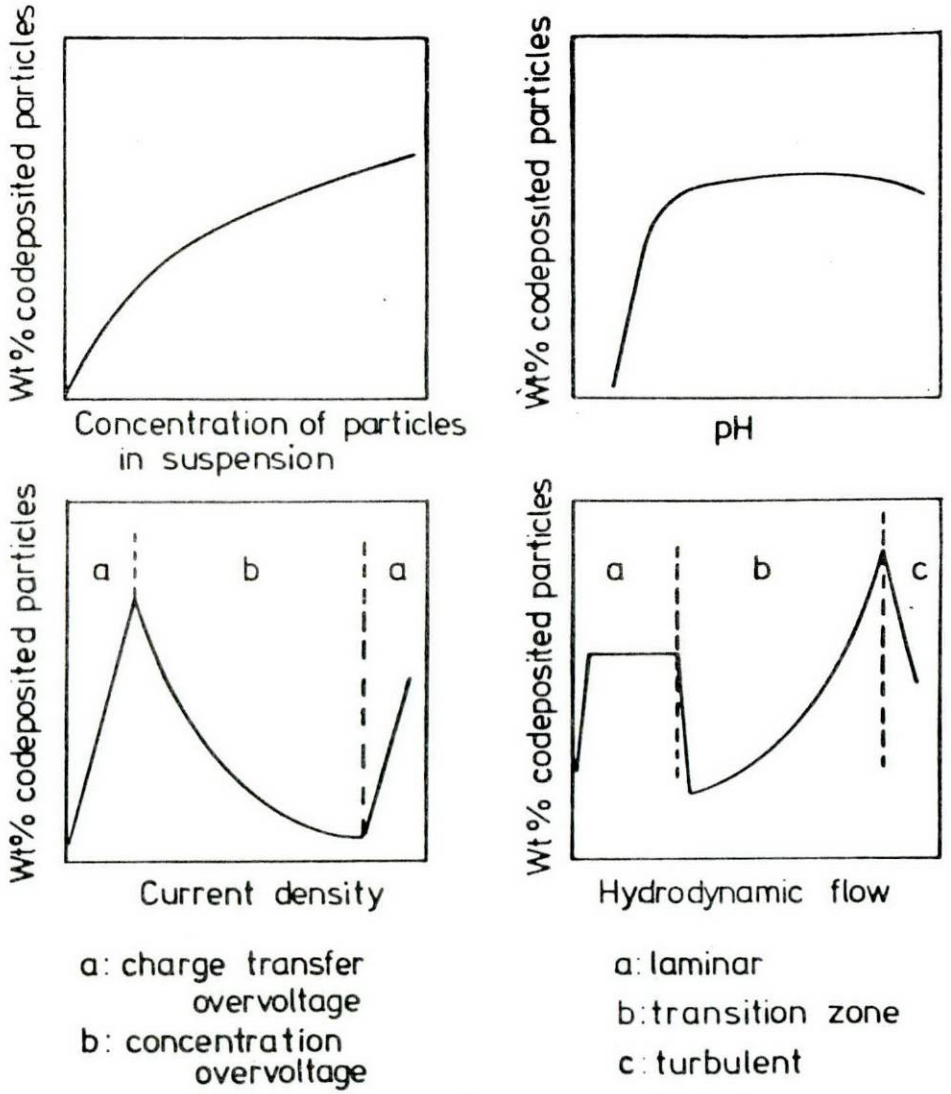



Fig. 5 : Schematic representation of the dependency of the amount of codeposited particles versus some electrolysis conditions.

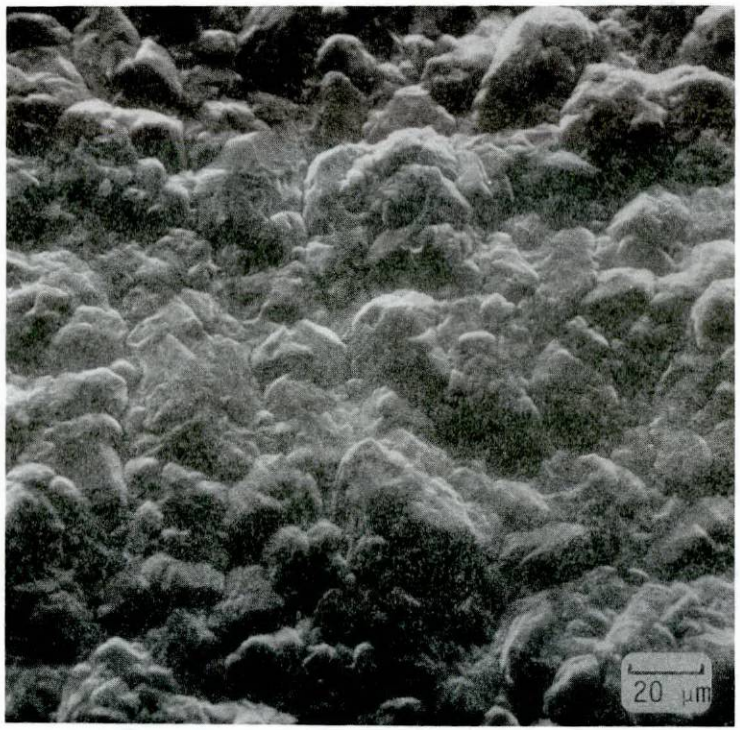
cannot be responsible for codeposition of particles. In sediment codeposition or occlusion plating sedimentation on the upperside of horizontal or sloped cathodes takes place. It is evident that in such cases the bath agitation and the shape and position of the cathode mainly determines the volume present of codeposited particles. This technique which cannot be considered as an electrochemically controlled process is frequently applied in industrial composite plating.

The effect of ageing of the composite plating bath on the relative position of the curves given in fig. 5 has received very little attention in the open literature (28). As far as we experienced no ageing effect occurs in Cu-$Al_2O_3$ plating from acidified copper sulphate baths, the Ni-$Al_2O_3$ and Ni-diamond codeposition in sulphamate plating baths, the Au-$Al_2O_3$ plating from neutral and acid gold cyanide solutions. In relation to the Cu-SiC codeposition from acidified copper sulphate baths we reported earlier (32) an ageing effect on the morphology of the composite coating (fig. 6). Present research (33) allows us to relate this change in morphology to a time-dependent codeposition as shown in fig. 7. The cause is probably a time-delayed ionic adsorption-desorption process at the surface of suspended SiC particles. A similar investigation for the Ni-SiC system is under progress.

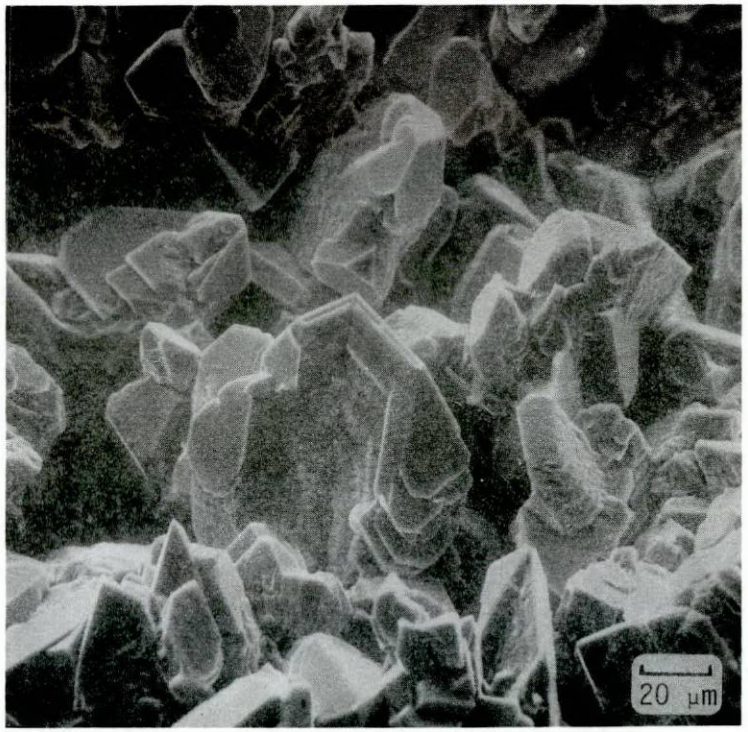
It may thus be put forward that composite plating is indeed a reproducible process on condition that important electrolysis conditions as local current density, bath composition and fluid flow along the cathode are constant. No ageing effects have been experienced in case of codeposition of oxides, the codeposition of carbides on the contrary could be time dependent. In industrial plating baths this ageing effect will probably be minimized due to the presence of large amounts of cationic surfactants.

## Conclusion

Our answer to the question : "Is the electrolytic codeposition of solid particles a reliable coating technology ?", can be that indeed the codeposition of solid particles during electrolysis is reproducible on the condition that hydrodynamic and electrochemical conditions under which the electrolysis process is carried out are constant. The actual industrial success of Ni-SiC composite plating should be considered as a stimulus to designers and platers to develop new composite plating systems since no difference neither from a fundamental nor from a practical point of view is apparent between Ni-SiC codeposition and other systems. The biggest remaining limitation today is certainly a lack of insight into the functional properties of composite coatings, and research and development in this field should be stressed in the future.




(a)




(b)

Fig. 6 : Surface morphology of composite Cu-SiC coatings deposited at 2 A/dm$^2$ from a copper sulphate bath containing 20 g/l SiC (mean size 3 µm)
(a) from a freshly prepared bath
(b) from a 5 day-old bath

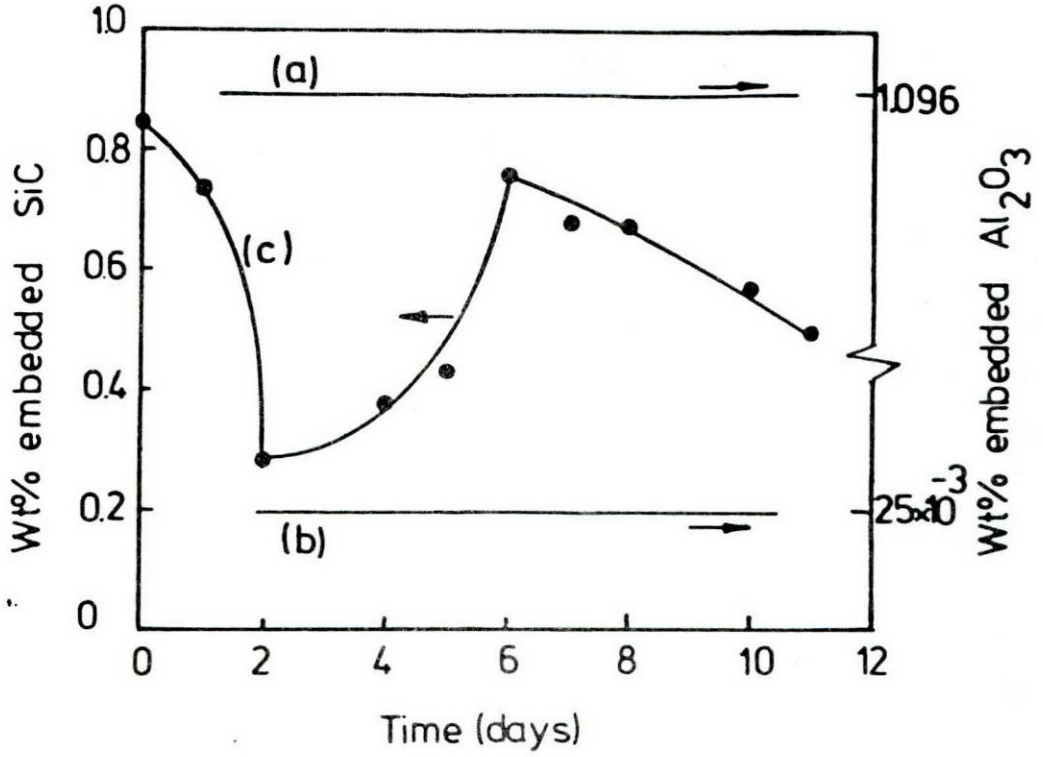



Fig. 7 : Effect of the ageing of the composite plating bath on the electrolytic codeposition of solid particles.

| (a) | (b) | (C) |
|---|---|---|
| copper sulphate | gold cyanide | copper sulphate |
| 35 g/l $\alpha$-$Al_2O_3$ 0.3 µm | 20 g/l $\gamma$-$Al_2O_3$ 0.05 µm | 20 g/l SiC 3 µm |
| pH 0.3 | pH 7 | pH 0.3 |
| 3.5 A/dm$^2$ | 3 A/dm$^2$ | 3 A/dm$^2$ |
| 25°C | 60°C | 25°C |

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# Dispersion Coatings I
# Session 0

## Deposition of Galvanic Dispersion Layers on Inner Surfaces by a Tampon Technique

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# DEPOSITION OF GALVANIC DISPERSION LAYERS ON INNER SURFACES BY A TAMPON TECHNIQUE

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## 1 Statement of problem

When one looks critically at a mechanical appliance used in daily life, as for instance a car, one observes an enormeous number of friction points. Most of them are located in tubular holes which have a bearing function. Apart from the motor and driving system, where friction and wear are obvious, there are many other points of friction in a car, such as door hinges, wind shield scrapers with various parts, switches, levers and so on.

The mechanical load acting at these friction points varies greatly, depending on the forces involved, the rate of the movement, frequency of operation, access of abrasive dirt and corrosive media.

Also, the degree and rate of wear at these friction points is quite different.

Therefore, the countermeasures taken by the designers to prevent or to reduce friction and wear in a car have a broad range. In some cases, no countermeasure is necessary at all. In many cases, however, some type of lubrication is adopted: a rather complicated system of oil distribution in the motor, a simple application of fat at the door. In some cases, where play and tolerances determine the satisfactory function, lubrication may not suffice and special measures have to be taken, such as switching from a sliding to a rolling motion by installing ball bearings. Another measure is to put special materials onto the surfaces under friction. One example is the construction of journal bearings. Another, rather recent, example is the application of galvanic dispersion layers. Such layers are now routinely applied to cylinders of motors of bicycles and chain saws.

As there are several other lectures of this conference which deal with galvanic dispersion layers, only a short comment will be made on galvanic dispersion layers: They constitute a composite material consisting of small particles in a metal matrix. The particles - mostly hard ones - act against abrasion while the metal matrix remains ductile and can be subjected to deformation without fracture. Also, in many cases, the corrosion resistance of the metal matrix is of great importance.

Because of this unique combination of properties of dispersion layers, it is desirable to apply them to many of the loci of friction as hinted at above and in many other machines and apparatuses. However, there are several obstacles that have so far presented their widespread usage:

- In most cases, the dispersion layer is to be applied to only a small fraction of the total area of a workpiece. Dipping it into a galvanic bath after lacquering the surface not to be coated is sometimes impossible or to say the least, very cumbersome.

- It is often the interior surface of a small tubular hole to which the dispersion is to be applied. This entails two problems:

  a) In order to achieve the incorporation of a sufficient number of particles into the layer and to obtain a homogeneous and agglomerate-free dispersion of the particles in the matrix, the suspension of the powder in the galvanic bath is to be continuously agitated. This is very difficult to accomplish in narrow cavities. The particles tend to agglomerate an to sediment out.

  b) In the conventional galvanic technique, the anode has to be placed very accurately in the center of the hole in order to obtain a homogeneous layer thickness and good layer quality. Otherwise, the current density would be different at different areas of the surface of the hole.

## 2 Description of the technique

For many years, Battelle Frankfurt has been actively engaged in the application of various types of galvanic dispersion layer for a broad variety of friction and wear problems. Apart from a general increase of interest in dispersion layers, there was an increasing number of demands for means of improving the wear resistance of just such small tubular cavities. They came not only from motor and car manufacturers but also manufacturers of various types of machinery for the chemical industry, hydraulic equipment and others.

We now have found that by a modified tampon or brush technique it is possible to deposit good galvanic dispersion layers homogeneously in small tubular holes. By "small" we mean diameters of a few centimeters down to - at present - five millimeters. We are confident, however, that it will be possible to produce satisfactory dispersion layers in even smaller holes. The principle of our technique is demonstrated by Fig. 1: The anode is covered by a sponge, which is filled with the suspension

electrolyte. The sponge is in close contact with the cathodic surface of the workpiece. The suspension is continuously pumped from a reservoir through the hollow and perforated anode into the sponge and flows back into the reservoir.

The flow of the suspension through the many irregular channels of the sponge ensures a good agitation - on a microscopic scale - of the suspension. The structure of the sponge is a very critical element of the process. If the channels of the sponge are too small, one observes the build-up of some sort of filtering cake inside the sponge until the flow of the liquid almost stops. If the channels are too wide, only part of the sponge is filled with the suspension.

Fig. 2 shows the behaviour of several types of suspensions at various concentrations in steady state flow through a typical sponge material. With the small size $\alpha$-$Al_2O_3$ and WC the flow rate is only little dependent on the particle concentration. With the rather coarse SiC and BN, however, the sponge cannot be used, if high suspension concentrations are required. So it follows that one has to select the structure of the sponge according to the desired dispersion coating.

In addition to its structure, the sponge has to have a good chemical resistance against the electrolyte and against mechanical abrasion by the dispersion layer.

During the deposition, the anode and the sponge which is fastened to the anode, are rotated and, if necessary, oscillated in the axial direction. It was found that it was not necessary to locate the anode accurately in the center of the hole in order to obtain a very homogeneous layer thickness. It was somewhat to our surprise that the wiping or scratching of the surface by the sponge did not prevent the incorporation of the particles into the metal matrix. Perhaps the sponge, or at least the type of sponge we used, contacts the cathode surface at very few spots only. Hence, there is time enough for the powder particles touching the surface to form a strong bond with the growing metal matrix before coming in close contact with the sponge. On the other hand, the sponge seems to have a profound disturbing effect on the galvanic diffusion layer. This conclusion is based on the observation that a rather high current density can be maintained without the layer surface becoming rough.

Fig. 3 shows a more detailed schematic drawing of the set-up used by us:

5 is the main suspension reservoir. The suspension is kept from settling by a stirrer. By the pump 6 , the suspension is circulated at a high rate through the container 7 and back

into the reservoir. Part of the suspension flows into the hollow anode and through the sponge as described below. The anode and the attached sponge is rotated by the motor 8 by means of the flexible shaft 9 . The best results were obtained by using a platinum coated titanium anode. The current flows from the source 10 through a meter 11 into the anode via a rotary contact, through the electrolyte to the cathode (workpiece) and back to the source.

## 3 Results

Fig. 4 summarizes the experimental conditions and results of a typical deposition process.

Fig. 5 is a light micrograph of another result: SiC in a Ni matrix. It demonstrates the good distribution of the particles in the metal matrix and the flawless adhesion of the galvanic layer to the substrate.

With high-speed electrolytes it is possible to deposit dispersion layers within a few minutes. Fig. 6 is a section of a layer of cobalt with dispersed aluminium oxide. The thickness is 50 µm, deposition time was 2 min. In spite of the high deposition rate, a satisfactory amount of particles is incorporated, the adhesion of the dispersion layer to the substrate is excellent, the layer surface is quite oven. The heat generated by the ohmic energy loss is easily removed by the flowing electrolyte.

There is no special difficulty in depositing by the tampon technique galvanic dispersion layers to various "difficult" base metals like aluminium or zinc alloys or stainless steels provided that they are appropriately pretreated.

## 4 Outlook

Because of the short electrolysis time, the process lends itself to the incorporation into a process line of a mechanical manufacture. The pretreatments necessary for good adhesion of the galvanic dispersion layer to the base material, such as degreasing, rinsing and etching can be carried out by apparatuses very similar in appearance to the galvanic apparatus. Fig. 7 shows a concept of an integrated pretreatment-deposition machine which is moved past a heavy workpiece such as a block of a truck engine. It is not necessary to coat the workpiece by a lacquer, to tilt it into a, perhaps, awkward position, and, as we think, most important of all, to move it to another place to have a relatively small area of it covered by a galvanic dispersion layer.

In conclusion it may be said that this modified tampon technique provides a convenient means for the application of antifriction, antiwear and anticorrosion galvanic dispersion layers to the interior surface of tubular holes. Of course, depending on the type of base metal, cavity size and shape as well as the load acting on it, more or less work is necessary to find the optimum layer and optimum deposition parameters.

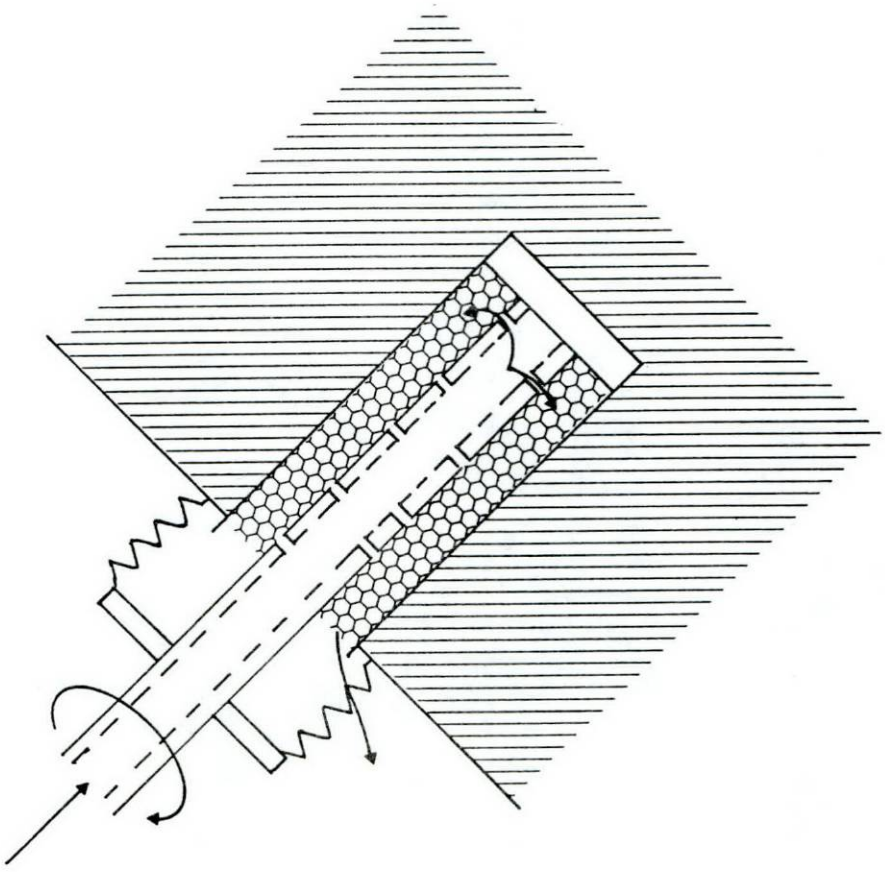

Fig. 1: Flow of suspension electrolyte through anode and sponge

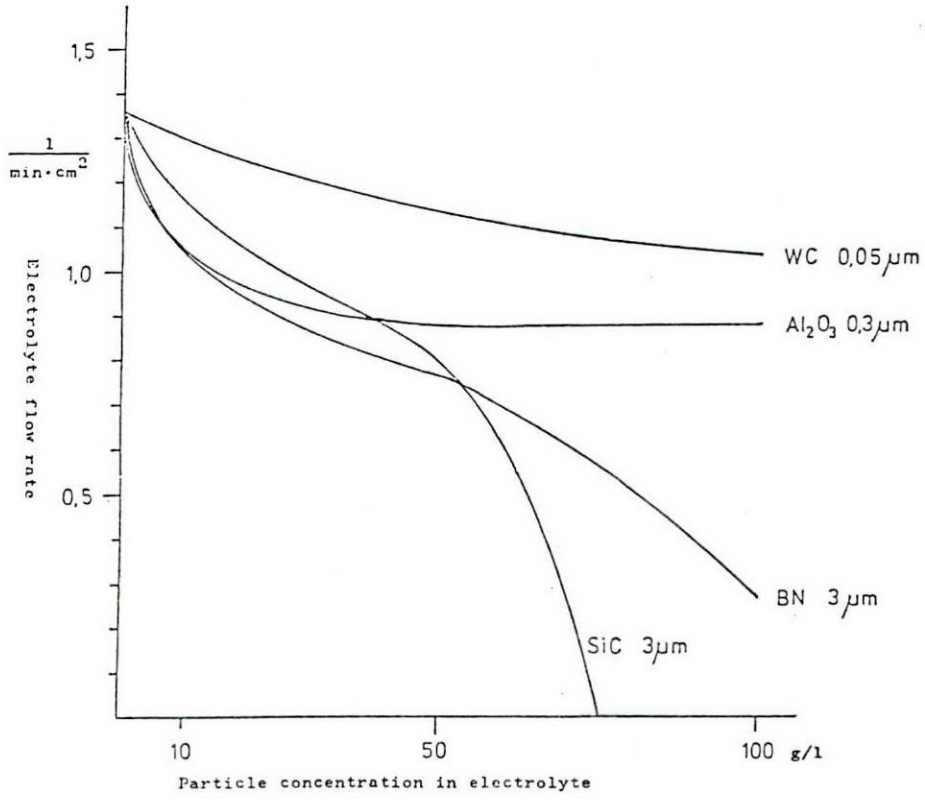


Fig. 2 Steady state flow through a tampon material rate of suspensions in Watts' bath

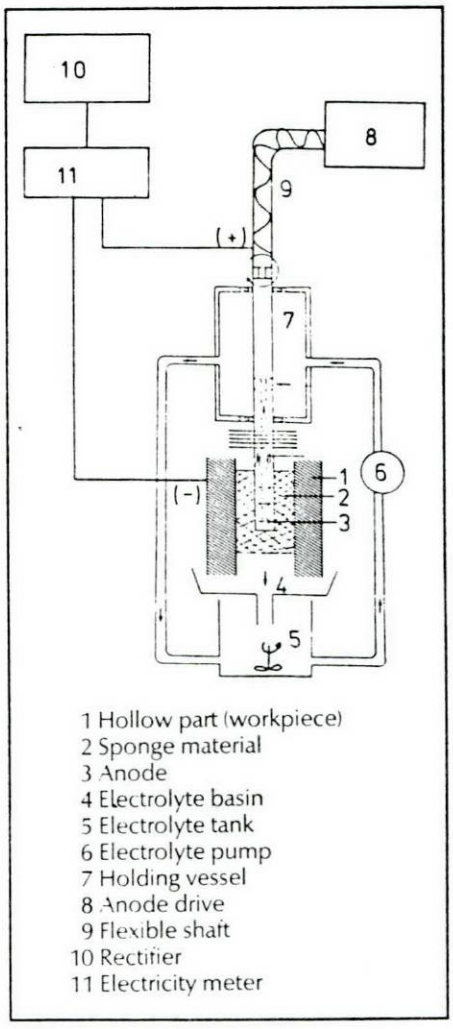


Fig. 3 Sketch of tampon galvanizing apparatus for dispersion coating

| | |
|---|---|
| Composition of bath: | 600 g/l $Ni(NH_2SO_3)_2.4H_2O$<br>40 g/l $H_3BO_3$<br>5 g/l $NiCl_2.6H_2O$<br>3 g/l NaF<br>60 g/l $\alpha$-$Al_2O_3$ |
| Grain size of aluminium oxide: | 0,3 µm |
| Current density: | 20 $A/dm^2$ |
| Cathode: | low carbon steel tube, inner dia. 10 mm |
| Pretreatment: | conventional |
| Rotation speed at the circumference of the sponge: | 167 mm/s |
| Average flow rate at the tampon surface: | 30 l/h |
| Layer thickness: | 95 to 105 µm |
| Concentration of $Al_2O_3$ in Ni: | appr. 10 vol.% |
| Appearance: | bright |

Fig. 4: Experimental conditions (example)



Fig. 5 Ni-SiC dispersion layer on brass deposited from Watts' bath

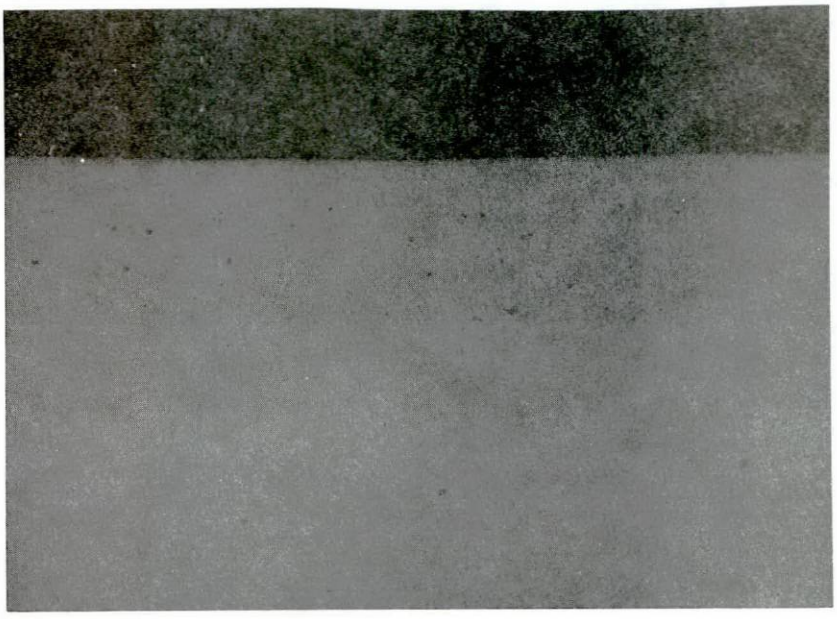

Fig. 6 Co-$Al_2O_3$ dispersion layer on brass deposited from high speed electrolyte

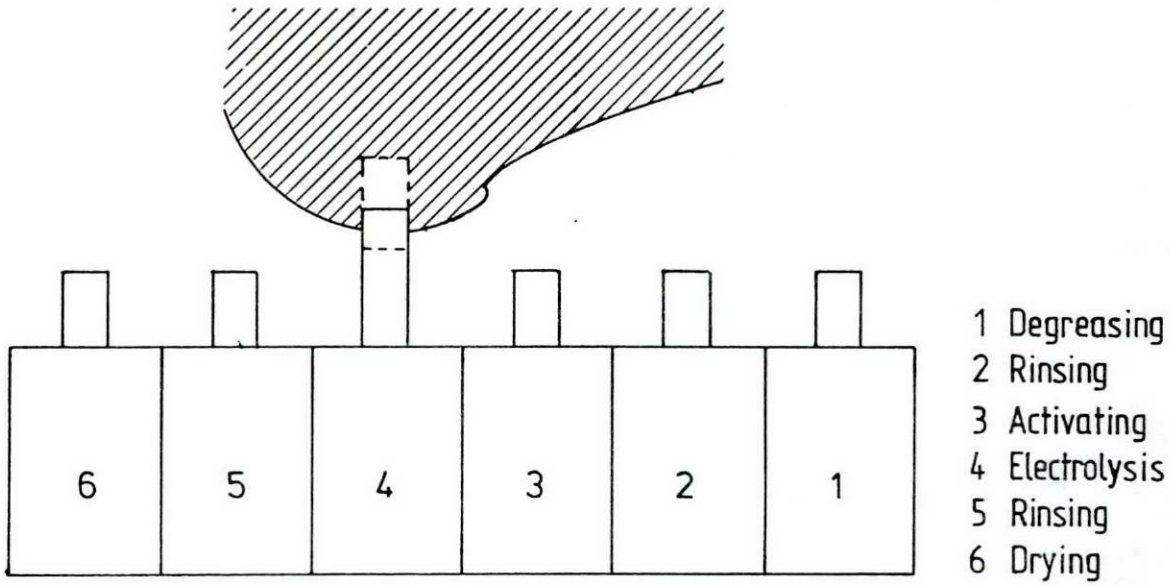


Fig. 7: Complete pretreatment, electrolysis and after-treatment apparatus

# 0-3

# Dispersion Coatings I
# Session 0

## Formation of Ni-$Al_2O_3$-$CaF_2$ Composite Coating on Inner Surfaces

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# FORMATION OF Ni-$Al_2O_3$-$CaF_2$ COMPOSITE COATING ON INNER SURFACES

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## Introduction

Recently considerable efforts have been made in producing commercially applicable electrodeposited composite coatings with improved chemical, physical and mechanical surface properties.

These deposits are metallic coatings containing dispersed solid particles such as carbides[1,2], diamonds[3], oxides[4-7] and polymers[8], incorporated so as to increase resistance to wear, corrosion and oxidation, by dispersion hardening and self lubrication respectively. The embedment of the various particles into the deposits took place directly from the plating solution where they were kept in suspension during the electrodeposition process.

Coating characteristics and properties are affected directly by particle type, size, concentration and their distribution in the coating. Therefore, it is of considerable importance to characterize the basic factors associated with particle incorporation into the deposits during their formation.

Electrodeposition conditions such as type of electrolyte, pH, current density, particle concentration in the electrolyte, mode of agitation and additions of surface active agents into the plating solution have been investigated by several authors[1-5]. However, no major effort has been made in evaluating and understanding the formation of composite coatings in inner surfaces of tubes at various electrolyte flow conditions[9].

The purpose of this study was to examine the feasibility of formation of composite coatings under laminar and turbulent flow conditions. Furthermore, this study was aimed at studying the relationship between electrolyte flow rate and particle size, concentration and distribution in Ni-$Al_2O_3$-$CaF_2$ composite coatings and of deposit properties.

## Experimental

The coatings were carried out in an experimental system designed and built so as to provide for the following needs:

- Maintaining the suspension in the cylinder to be coated
- Installment of an internal anode
- Rotation of the cylinder around its axis to assure a more uniform particle distribution in the coating
- Provision of electric contact to the rotating cylinder and internal anode
- Means for control of c.d., temperature, concentration of particles and their distribution.

The system is described schematically in Fig. 1 and its main features are:

- A 2-liter glass container with a conical outlet for the electrolyte (16)
- A mechanical mixer located in the electrolyte to maintain the suspension (14)

- A thermostatically controlled water bath surrounding the electrolyte container for temperature control at ±1°C (18).
- A peristaltic pump (Magna M-80) for circulation of the electrolyte through the coated cylinder with provision to vary flow rates by varying its rotation speed between 40-400 rp/m (13).
- A system for holding of the coated cylinder which enables rotation of the cylinder around its axis and variation of its position from horizontal to vertical. The rotation is induced by a separate motor and rotation speed can be varied between 2 to 4 rp/m(2-10).

The electrolyte for Ni plating was of the following composition:

Ni sulphamate - 450 g/l
Boric acid - 30 g/l
Ni chloride - 10 g/l
Antipitting agent - 0.5 cc/lit
Temperature - 50°C

Various sources of aluminia and calcium fluoride particles were tested in the optical microscope for size distribution and shape. The particles which had the narrowest size distribution and rounded shape were AlCOa A-17 particles with an average size of 1 μ. The $CaF_2$ had a similar size.

The first series of experiments was carried out with a Ni anode in the form of a 2 mm diameter wire. In view of frequent ruptures of the wire an inert anode made of a 1 mm diameter platinum wire was further used.

The coatings were applied on cylindrical specimens made of copper with an internal diameter of 8 mm and an external one of 12 mm and a length of 30 mm.

Surface preparation of the Cu-specimens prior to plating included the following stages:
- Degreasing with TCE in an ultrasonic bath,
- Abrasion with MgO,
- Acid pickling in 10% HCl followed by
- Alkalinic cleaning in a solution of NaOH, $Na_3PO_4$, $Na_2CO_3$ and $Na_2SiO_3$ at 80-90°C and finally dipping in 10% HCl.

The following parameters were applied in the experiments:

| | | |
|---|---|---|
| Particle concentration: | | $CaF_2$ 20 g/l + $Al_2O_3$ 40 g/l |
| | | $CaF_2$ 50 g/l + $Al_2O_3$ 100 g/l |
| Current density | : | 1 and 2 A/dm$^2$ |
| Solution flow-rate | : | 0.22 - 1.25 1/min |
| Coating duration | : | 30-240 min |
| Specimen position | : | horizontal and vertical |

The coatings obtained were evaluated by the following criteria: distribution of coating thickness, surface roughness, microhardness, surface morphology, particle distribution and faradeic efficiency.

The coating thickness and its distribution were measured on metallographic specimens prepared from crossections of the coated cylinders. Coating hardness was measured with a Wilson Tukon tester with a 100 g weight. Surface roughness was measured with a Talysurf instrument and surface morphology

was evaluated with a JEOL SEM. Particle distribution was evaluated from metallographic specimens by optical inspection assisted by microanalysis.

## Results and Discussion

The first series of experiments was carried out in a Ni-plating solution without particles. The results obtained for this stage are summarized in Table 1. Initial experiments were carried out with a Ni-wire anode. During plating pitting of the anode was detected which finally lead to rupture of the Ni wire. The uneven dissolution of the anode was enhanced by the relatively high anodic c.d. due to the discrepancy in cathodic and anodic area. Therefore, further experiments were carried out with Pt-wire anodes. For industrial purposes platinized titanium anodes can be used. The use of inert anodes has, however, an adverse effect on the faradeic plating efficiency which is reduced from 90% to 60% when the inert anode is used. This reduction may be related to the effect of the gaseous oxygen evolved on the inert anode. Oxygen bubbles may mask part of the cathodic area increasing the cathodic c.d. and thus reducing the plating efficiency. However, another factor related to the use of an inert anode reduces the efficiency. The anodic reaction which in this case is

$$2H_2O \rightarrow O_2 + 4H^+ + 4e$$

causes a lowering of the pH of the plating solution and therefore leads to an increase of hydrogen evolution. Coating thickness varied up to 20% from the mean value, both in the circumferential and longitudinal directions. No correlation was found between this variation and any parameter studied (such as flow rate or c.d.). However, the reason for it seems to be variations in distance between the anode and the coated area due to some excentricity of the anode wire. Symmetric and steady location of the anode is therefore of utmost importance in this coating technology. Coating hardness is measured more reliably in the thicker coatings (~40 μ) and for these it was in the range of 500-700 Knoop units. This is bigger than the hardness obtained in conven tional Ni plating (200-300 Knoop) and may be characteristic of coatings obtained under flow conditions.

Surface roughness was in the range of C.L.A.-0.4-0.6 μm and no relation of this criterion to experimental parameters was found. However, the surface morphology on a finer scale was affected by flow rate. At laminar flow both stream-lines and dimples are seen on the surface (Fig. 2). Both features are less frequent under turbulent flow rates (Fig. 3). In view of a possible lowering of solution pH due to oxygen evolution on the anode a series of plating experiments was carried out in the same solution without pH correction. The pH changed from 4.5 to 1.0 during seven consecutive experiments. In parallel, the plating efficiency was reduced from 79.3% to 38.3% and the thickness was reduced from 29 to 14 μm (see Table 3).

The coating thickness varied within 15% of the mean value along the longitudinal axis, however it was quite constant along the circumference. As before, no dependence on flow rate or c.d. was found.

The concentration of particles and their distribution were not affected by their concentration in solution for the two concentrations studied, nor by c.d. However, the specimen (cylinder) orientation and the flow rate, when in vertical position, had a strong effect. In the horizontal posi ion a higher

and more even incorporation of particles was observed (see Figs. 4,5) independent on flow rate or c.d. However, when the cylinder is in a vertical position, the flow rate affects the number and size of incorporated particles. Thus, at lower flow rates (0.73 vs. 1.25 1/min) less particles are incorporated and their average size seems larger (Figs. 6 vs. 7) than at higher flow rates. The absence of an effect of concentration on the concentration of particles in the coating may be explained on the basis of previous findings in the study of composite coatings, which showed an asymptotic dependence of particle concentration in the coating on that in the solution. It is possible that both concentrations tested are in the asymptotic range. The surface roughness is slightly larger than that for coatings without particles (0.7-0.8 μ vs. 0.4-0.6 μ). Microhardness measurements reflected the hardness of the Ni matrix and were in the range of 400-500 Knoop.

A semiquantitative microanalysis of a composite coating obtained at $2A/dm^2$, 0.73 1/min, horizontal position and particle concentration in solution of 40g/1 $Al_2O_3$ + 20 g/1 $CaF_2$ is as follows:

Al - 2-5%, Ca 0.5-1%, Ni - rest

(O and F are not detected by EDS microanalysis).

The high throwing power of the Ni-plating solution is preserved in the composite system as reflected in Fig. 8, where the substrate had an uneven contour.

TABLE 1: Coating properties as function of plating parameters for Ni coatings (no particles)

| Expt. No. | c.d. $A/dm^2$ | t min | flow rate 1/min | Position | Anode | Thickness (μ) av | Hardness Knoop | Surface roughness (av) C.L.A μm |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 65 | 0.75 | horiz. | Ni | 24 | 290-325 | 0.54 |
| 2 | 2 | 65 | 0.22 | " | " | 24 | 200-260 | 0.58 |
| 3 | 2 | 65 | 0.50 | " | " | 23 | 220-280 | 0.46 |
| 4 | 1 | 96 | 0.22 | " | " | 16 | - | 0.53 |
| 5 | 1 | 96 | 0.50 | " | " | 19 | 180-230 | 0.40 |
| 6 | 1 | 96 | 0.75 | " | " | 19 | 230-310 | 0.43 |
| 7 | 2 | 120 | 0.50 | vert. | " | 39 | 600-730 | 0.43 |
| 8 | 2 | 90 | 0.22 | " | " | 29 | 540-640 | 0.45 |
| 9 | 1 | 240 | 0.22 | " | " | 46 | 620-700 | 0.44 |
| 10 | 2 | 60 | 0.22 | horiz. | Pt | 16 | 160-240 | 0.45 |
| 11 | 2 | 120 | 0.75 | " | " | 29 | 160-320 | 0.45 |
| 12 | 2 | 120 | 0.50 | " | " | 27 | - | 0.77 |

TABLE 2: Composite Coating properties as function of plating parameters

| Expt. No. | c.d. A/dm$^2$ | t min | Flow rate l/min | Position | Thickness av. µ | Hardness Knoop | Surface roughness C.L.A. µ | Faradeic efficiency % |
|---|---|---|---|---|---|---|---|---|
| 40 g/l $Al_2O_3$ + 20 g/l $CaF_2$ | | | | | | | | |
| 1 | 2 | 90 | 0.85 | horiz. | 30 | - | 0.66 | 82 |
| 2 | 1 | 180 | 0.73 | " | 29 | 390-420 | 0.67 | 79 |
| 3 | 1 | 180 | 1.00 | " | 21 | 280-400 | 0.88 | 57 |
| 4 | 1 | 180 | 1.25 | " | 21 | 330-440 | 0.67 | 57 |
| 5 | 1 | 180 | 0.73 | vert. | 21 | 290-360 | 0.74 | 57 |
| 6 | 1 | 180 | 1.25 | " | 14 | 180-210 | 0.82 | 38 |
| 7 | 2 | 90 | 0.73 | horiz. | 26 | 390-440 | 0.83 | 71 |
| 8 | 2 | 90 | 1.25 | " | 18 | 230-290 | 0.64 | 49 |
| 9 | 2 | 90 | 0.73 | vert. | 31 | 320-370 | 0.60 | 85 |
| 10 | 2 | 90 | 1.00 | " | 29 | 390-500 | 0.55 | 79 |
| 11 | 2 | 90 | 1.25 | " | 31 | 570-770 | 0.45 | 85 |
| 100 g/l $Al_2O_3$ + 50 g/l $CaF_2$ | | | | | | | | |
| 1 | 1 | 180 | 0.73 | horiz. | 37 | 340-470 | 0.37 | 100 |
| 2 | 1 | 180 | 0.73 | vert. | 36 | 340-470 | 0.30 | 98 |
| 3 | 1 | 180 | 1.25 | " | 38 | 470-550 | 0.47 | 100 |
| 4 | 2 | 90 | 0.73 | horiz. | 33 | 390-470 | 0.09 | 90 |
| 5 | 2 | 90 | 0.73 | " | 37 | 340-420 | 0.21 | 100 |
| 6 | 2 | 90 | 1.25 | " | 38 | 470-550 | 0.43 | 100 |

TABLE 3: Coating parameters and Faradeic oefficiency for a composite coating without adjustment of solution pH (40 g/1 $Al_2O_3$ + 20 g/1 $CaF_2$)

| Expt. No | pH | c.d. $A/dm^2$ | t min | Flow rate l/min | Posi-tion | Thick-ness av. µ | Efficiency % | Hardness Knoop | Surface roughness C.L.A. µ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.5 | 1 | 180 | 0.73 | horiz. | 29 | 79 | 425 | 0.67 |
| 2 | | 2 | 90 | 0.73 | " | 26 | 71 | 406 | 0.83 |
| 3 | | 1 | 180 | 1.00 | " | 21 | 57 | 330 | 0.88 |
| 4 | | 1 | 180 | 1.25 | " | 21 | 57 | 386 | 0.67 |
| 5 | | 1 | 180 | 0.73 | vert. | 21 | 57 | 323 | 0.74 |
| 6 | | 2 | 9 | 1.25 | horiz. | 18 | 49 | 261 | 0.64 |
| 7 | 1.0 | 1 | 180 | 1.25 | vert. | 14 | 38 | 198 | 0.82 |

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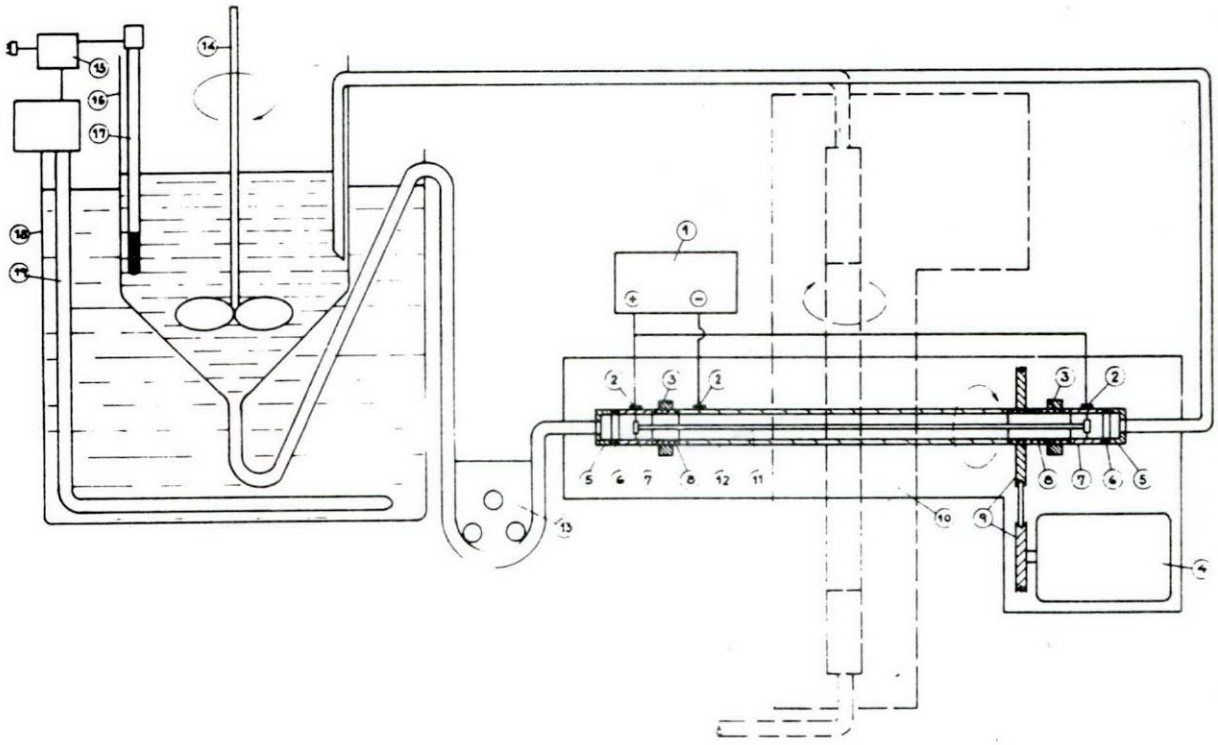

Fig. 1: Experimental set-up for deposition of composite coatings.

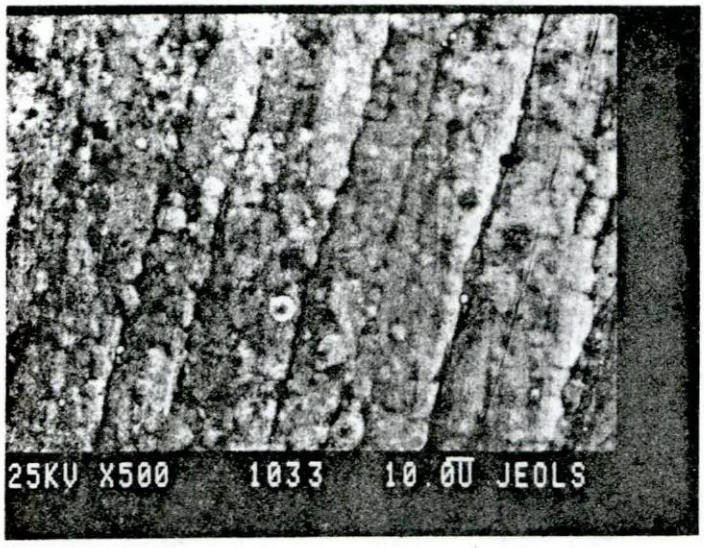


Fig. 2: Morphology of coating surface (2 A/dm$^2$, 0.22 l/min).

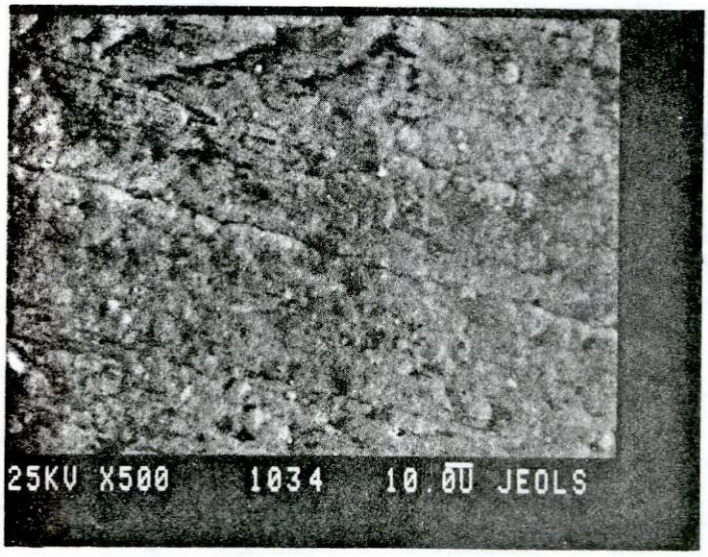


Fig. 3: Morphology of coating surface (2 A/dm$^2$, 0.75 l/min).

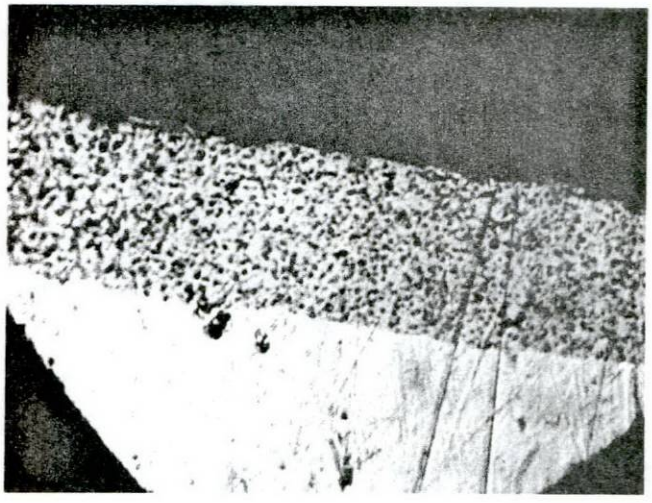

Fig. 4: Crossection through composite coating (horizontal, 1 A/dm$^2$, 0.73 l/min)

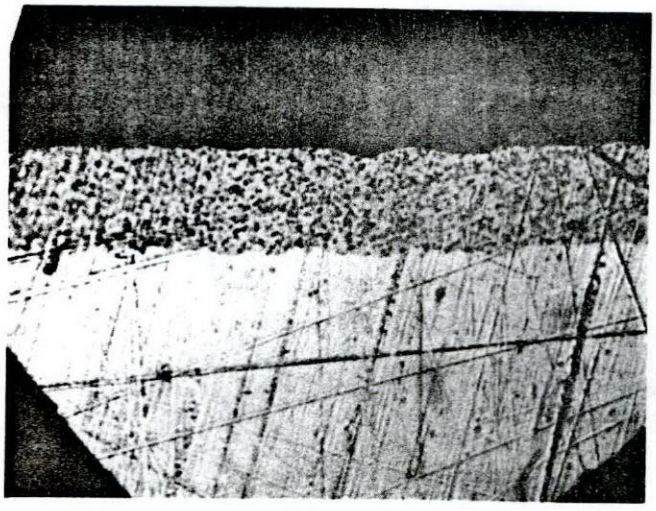

Fig. 5: Crossection through composite coating (horizontal, 1 $A/dm^2$, 1.25 l/min)

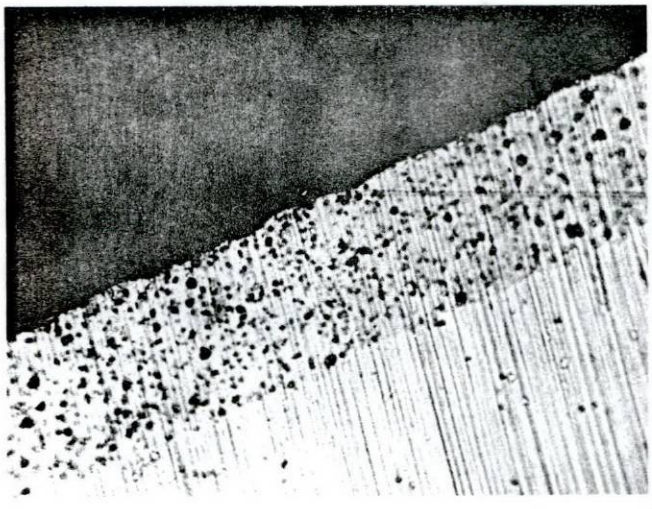

Fig. 6: Crossection through composite coating (vertical, 2 $A/dm^2$, 0.73 l/min)



Fig. 7: Crossection through composite coating (vertical, 2 A/dm$^2$, 1.25 l/min)

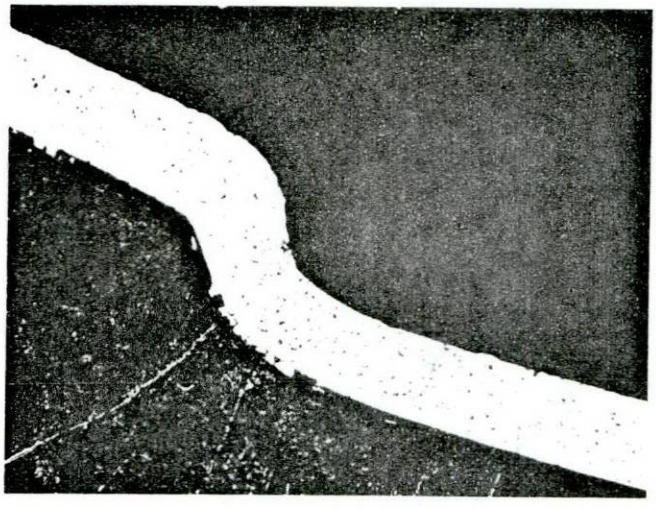

Fig. 8,

# 0-4

# Dispersion Coatings I
# Session 0

## A Fully Automatic Operating System for Applying an Electrolytic Dispersion of Nickel Silicon Carbide to In-Line Multiple Cylinder Motor Blocks

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# A FULLY AUTOMATIC OPERATING SYSTEM FOR APPLYING AN ELECTROLYTIC DISPERSION OF NICKEL SILICON CARBIDE TO IN LINE MULTIPLE CYLINDER MOTOR BLOCKS

G. A. LAUSMANN

Automobile manufacturers have been attempting to reduce weight for several years, in order to improve fuel economy. One important approach to this problem is to exchange light materials for heavy ones. Combustion engines and particularly their motor blocks are usually made of cast iron. When aluminium is used instead of cast iron, the weight of a medium-sized 6 cylinder block can be reduced by approximately 30 kgs (approx. 66 lbs). But the use of aluminium requires different treatment for wearing surfaces such as cylinder walls.

The system described here operates to fully automatically deposit nickel silicon carbide in cylinders of motor blocks. Not only does the system work fully automatically, but also provides for the optimal simultaneous concentric placement of the anodes in each of the cylinders. This is required to minimize the amount of material deposited on the cylinder walls and to make the approach practical from a mass production standpoint.

# A FULLY AUTOMATIC OPERATING SYSTEM FOR APPLYING AN ELECTROLYTIC DISPERSION OF NICKEL SILICON CARBIDE TO IN-LINE MULTIPLE CYLINDER MOTOR BLOCKS

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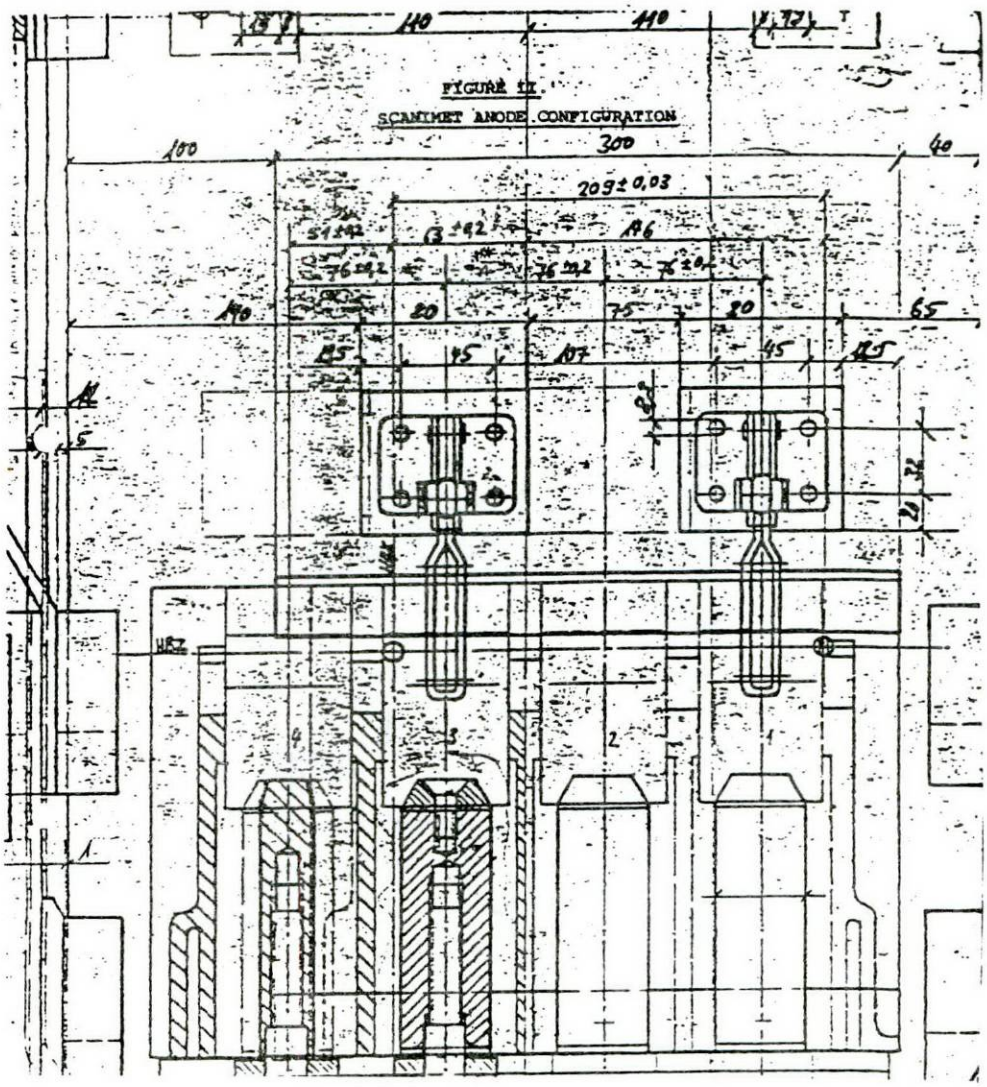



GRAPH O

The remainder of the paper is organized along the following lines:

- pretreatment
- bath characteristics
- management of hardness and stress
- control aspects
- industrial acceptance.

The system will probably be of greatest interest to large volume engine manufacturers, particularly those undergoing a fundamental engine redesign.

The pretreatment needs to be tailored for the specific alloy. To achieve good adhesion, pretreatment is a very important step. The pretreatment sequence is as follows:

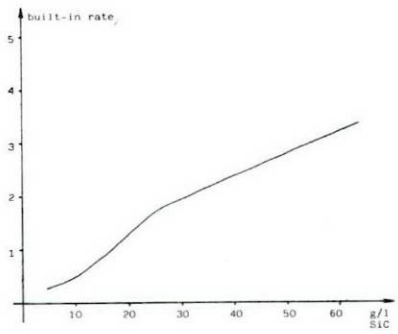
Soak Cleaner
Rinse
Acid Pickle
Rinse
Acid Pickle
Re Dip
Rinse
Scanimet* I
Scanimet* II
Rinse

* Scanimet is a trade mark of M&T Chemicals.

After pretreatment the anodes are attached and plating can commence. The plating speed averages 0.5 thou./min. The typical thicknesses deposited are 2 - 5 thou. The basic solution is a modified Watt's type. A special grade of silicon-carbide

is selected depending on the desired proportion of silicon-carbide desired in the deposit. The silicon-carbide content in the solution can be up to 80 g/l; higher contents usually lead to problems. A typical silicon-carbide proportion (by surface) in the deposit is 3 %. Aside from other parameters such as agitation, current density, pH, temperature and addition agents, the proportion of silicon-carbide in the deposit basically depends on the silicon-carbide content in the solution as shown in the following graph:

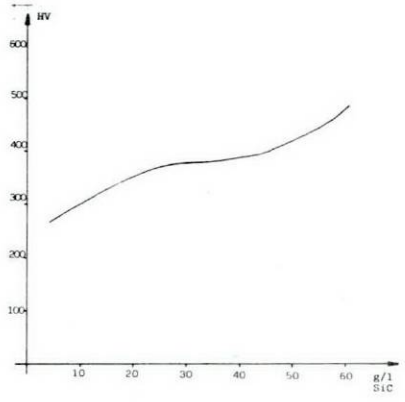
GRAPH 1




GRAPH 1

The hardness of the deposit is adjusted to meet wear and honing requirements. The basic hardness of a newly made up solution is approx. 300 HV. The hardness increases with increased silicon-carbide content.

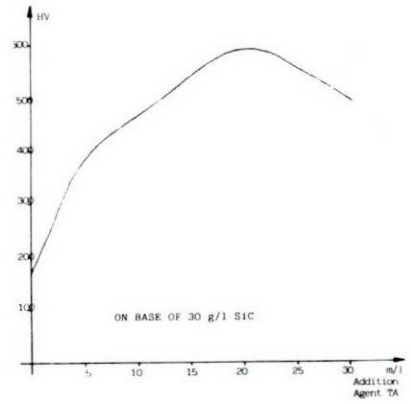
GRAPH 2




GRAPH 2

Alylsulfonic acid based special addition agents or mixtures of agents are required to keep the hardness at desired level and within desired range. Typical addition agents influence the hardness as shown in the following graph:

GRAPH 3

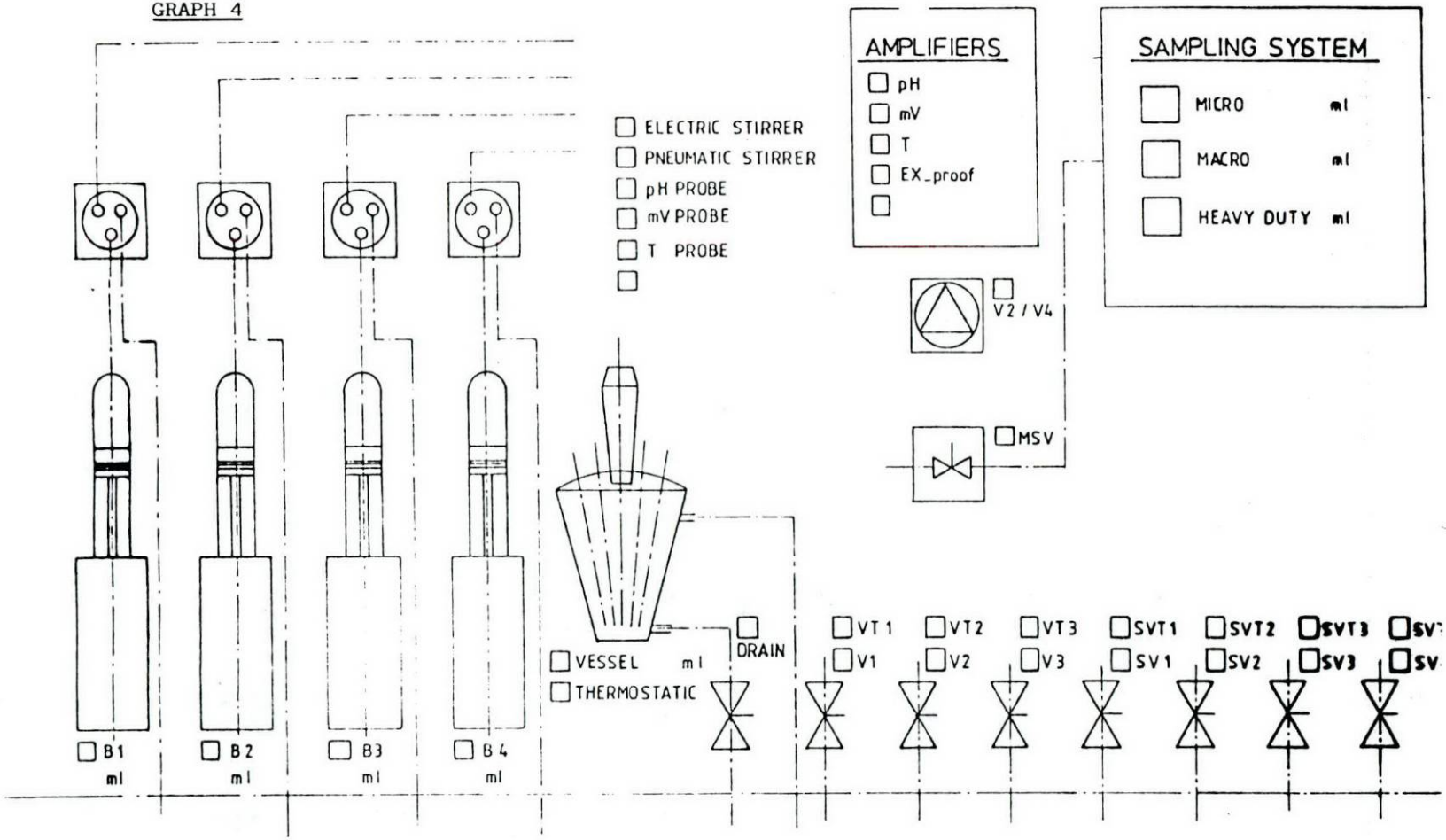



GRAPH 3

Depending on the alloy, hardness can also be strongly influenced by foreign metals entering the solution. Impurities of copper, lead, zinc and tin usually tend to increase the hardness. Impurities of aluminium tend to reduce hardness. Operating the solution under prescribed conditions, the resulting deposit will have a compressive stress characteristic. The internal stress can strongly be influenced by the addition agents used. It will also be influenced by impurities. Impurities seem to reduce the compressive stress. Tensile stress must be avoided, therefore it is necessary to control the parameters of the solution very carefully. Preferably a fully automatic analytical control with a recorder should be employed. The typical system is shown in the following graphs:

GRAPH 4 / GRAPH 5

GRAPH 4


AMPLIFIERS
pH
mV
T
EX_proof
SAMPLING SYSTEM
MICRO ml
MACRO ml
HEAVY DUTY ml
ELECTRIC STIRRER
PNEUMATIC STIRRER
pH PROBE
mV PROBE
T PROBE
V2 / V4
MSV
VESSEL ml
THERMOSTATIC
DRAIN
B1 ml
B2 ml
B3 ml
B4 ml
VT1
VT2
VT3
SVT1
SVT2
SVT3
V1
V2
V3
SV1
SV2
SV3

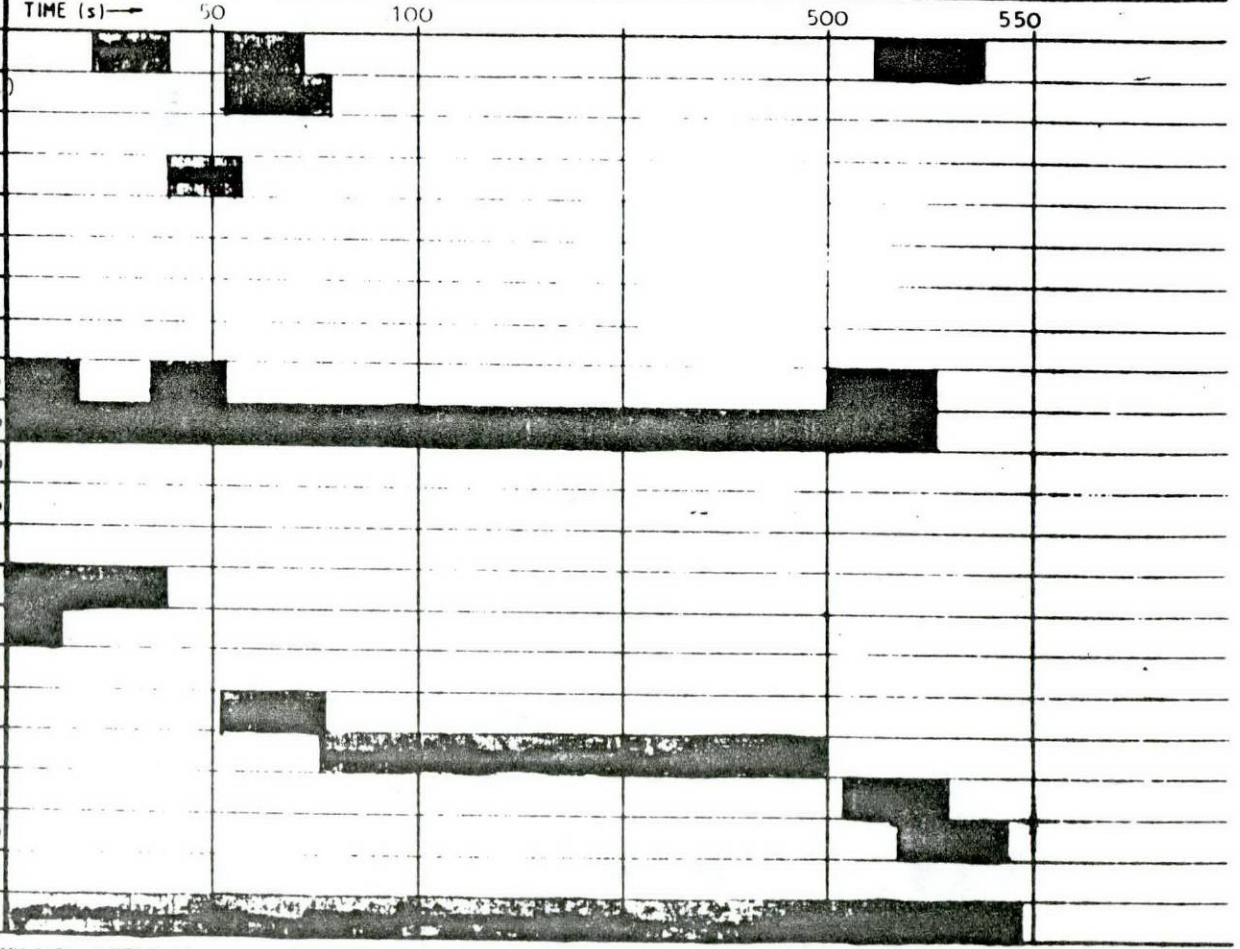
GRAPH 5

Applikon dependable instruments

ADI 2020 time programming sheet 1

**ANALYSIS:** Bestimmung von Phosphorsäure | PAGE: 1 | VERSION: 1 | DATE: 04.11.8

| LINE | FUNCTION | TIME BLOCKS |
|---|---|---|
| 1 | VALVE 1($H_2O$,dest) | 16 |
| 2 | VALVE 2(Prob.Tran) | 16 |
| 3 | VALVE 3 * | 16 |
| 4 | VALVE 4 (Pumpe)* | 16 |
| 5 | VALVE 5 * | 8 |
| 6 | VALVE 6 * | 8 |
| 7 | VALVE 7 * | 8 |
| 8 | VALVE 8 * | 8 |
| 9 | DRAIN | 16 |
| 10 | STIRRER | 16 |
| 11 | BURETTE 1 | 16 |
| 12 | BURETTE 2 | 16 |
| 13 | BURETTE 3 * | 8 |
| 14 | BURETTE 4 * | 8 |
| 15 | SAMPLE SELECT** | 8 |
| 16 | SAMPLE COMMAND | 8 |
| 17 | SAMPLER | 8 |
| 18 | ANALYSIS | 8 |
| 19 | CALCULATE | 16 |
| 20 | OUTPUT | 16 |
| 21 | PRINT | 8 |
| 22 | TIME SPAN | 4 |



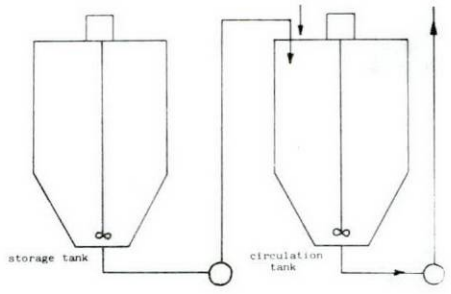

* ONLY ACTIVE WITH I/O EXTENSION INTERFACE

** IN BASIC VERSION FOR 2 SAMPLES, WITH I/O EXTENSION INTERFACE FOR 6 SAMPLES

Based on the continuous analytical control, the necessary chemicals are fed into the solution according to requirements. Only very pure liquid chemicals should be used in order to avoid a build-up of impurities in the solution, in that filtration of the solution is not applicable.

GRAPH 6

GRAPH 6




It is required to transfer a relatively high current absolutely equally onto all areas of the respective cylinder bore in order to get a highly uniform deposit. Thus design of the jig becomes very important. Depending on the size of the cylinder and the precision of the deposition thyristor controlled rectifiers for the individual bore can be applied. Jigs can be designed to enable using either one rectifier per motor-block or for complete bar. Asolutely precise contacting is essential. Automatic current density control must be applied.

With the prescribed system large series of single or multiple cylinders can be finished rapidly and automatically, and therefore economically. The precision of the deposition is

better than that of the casting and machining operations. The deposited dispersion of nickel-silicon carbide adheres perfectly. The wear resistance of the cylinder wall is optimal. Several leading European engine and automobile manufacturers already apply this type of deposit successfully over a period of time, thus its efficacity is established. With features of automation, control and jigging now worked out, the deposit can be viewed as appropriate for a mass production industrial setting.

# 0-5

# Dispersion Coatings I
# Session 0

## Dispersion Coatings - Its Technical Problems

Shigeru Ishimori, Shinjiro Otsuka, and Masayoshi Takama
Suzuki Motor Co., Ltd., Hamamatsu, Japan

# DISPERSION COATINGS - ITS TECHNICAL PROBLEMS

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Hamamatsu-Nishi P.O. Box 1 432-91 Hamamatsu, Japan

## 1. Preface.

Suzuki Motor Co., Ltd. is at present mass producing automotive parts plated using Ni-P-SiC and Ni-P-BN electrolytic dispersion coating methods. Ni-P-SiC dispersion coated parts are used to plate the cylinders for the reciprocating engines of such vehicles as motorcycles and snowmobiles, and Ni-P-BN dispersion coating is being used for the pistons for the engines of the Japanese "light" class of automobiles.

In this paper, the functional characteristics of both methods will be discussed. It is also important to take into consideration the fact that vehicles such as motorcycles and snowmobiles are made using aluminum alloy castings, and that they must function under extremely rigorous driving conditions. Given such conditions and materials, proper adhesion is important, and therefore pretreatment methods will be discussed. Photo. 1 and Photo. 2 are automotive parts that have been dispersion coated.

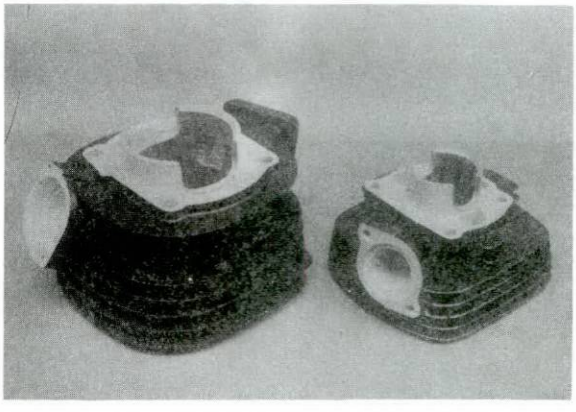


Photo. 1. Ni-P-SiC dispersion coated cylinders.

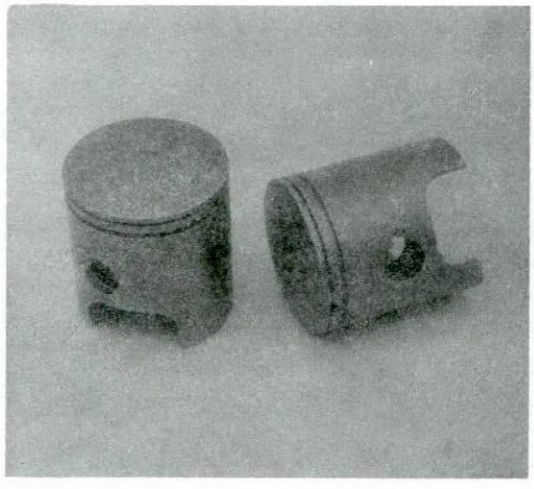


Photo. 2. Ni-P-BN dispersion coated pistons

## 2. Plating with Nickel Sulfamate Bath.

Nickel sulfamate bath is used for electroforming and thick plating. The reason for this is that this bath has the following features:

(1) Plating can be done at higher speeds than with other nickel baths.
(2) Less stress is created within the electrodeposits.
(3) Plating can be done at a higher current density.
(4) The bath has a simple composition and is easy to maintain.
(5) It is comparatively insensitive to impurities.
(6) Very fine and smoothly textured electrodeposits are gained.
(7) Electrodeposits have high malleability and ductility.

Our dispersion coatings are comparatively thick, taking full advantage of the special features of this type of bath. Fig. 1 shows a comparison of the internal stress of coatings gained with both nickel sulfamate and watt baths. As can be clearly seen, plating with nickel sulfamate bath with an added stress relaxation agent produces an ideal coating with almost no internal stress.

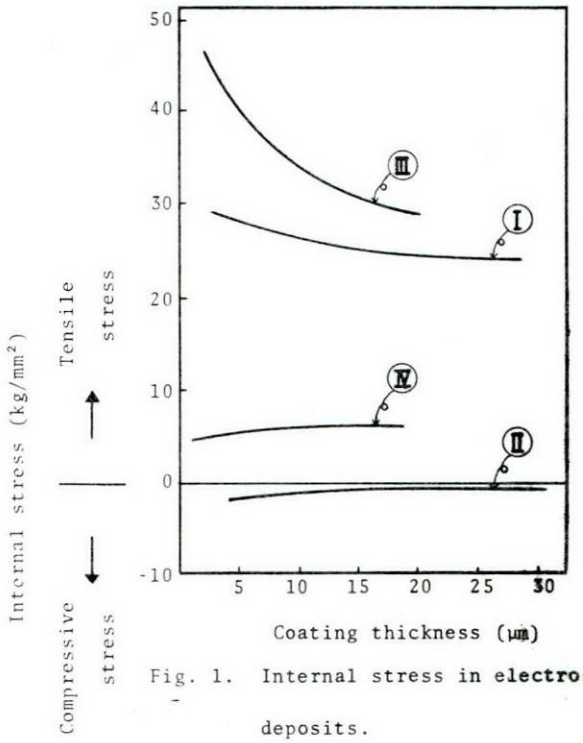



Fig. 1. Internal stress in electrodeposits.

| Mark | Bath | Stress relaxation agent | Current density |
|---|---|---|---|
| I | Nickel sulfamate bath | not added | 20 A/dm² |
| II | ↑ | added | ↑ |
| III | Watt bath | not added | 3 A/dm² |
| IV | ↑ | added | ↑ |

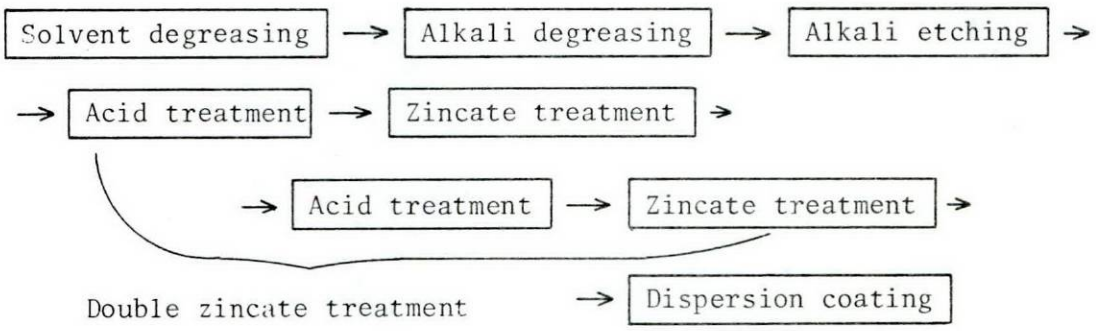
## 3. Pretreatment Method.

The cylinders and pistons which are dispersion coated are aluminum alloy castings made of A356, A514, and sometimes ALSIL (Si content: about 23%). These different types of aluminum and alloys, due to their special characteristics, undergo the following pretreatment:

(1) It is necessary to remove the oxide film formed on the surface of these metals.
(2) Since aluminum itself is an amphoteric metal, if a special pretreatment is not performed, the plating coat will not have good adhesion.

To remove the oxide film mentioned in (1), etching is performed. In the case of alkali etching, and if the part to be plated is a matting part, attention must be paid to the change in the accuracy of dimension. Also, the relationship between aluminum dissolved volume and alkali etching agent life must be taken into consideration. Zincate and bondal treatments are possible for the pretreatment mentioned in (2), but the double zincate treatment is chosen. The diagram below shows the double zincate treatment process.

Table 1. Pretreatment method for aluminium alloy castings.




The object of the alkali etching in the beginning is to remove the oxide film formed on the surface of the aluminum, as well as to roughen the surface of the aluminum enough to prepare it for plating. The alkali etching agent differs according to the processing that is planned for the piece after plating, and according to the use that is planned for the piece; for example:

(1) The dispersion coating is to be thick or there is machining to be done after plating which will change the dimensions of the piece.
(2) The dispersion coating is to be thin, or due to the fact that there will be no machining after plating, the dimensions must be exact, or there is a limit to surface roughness.

The second example is found in the case of Ni-P-BN dispersion coating of pistons which are to be assembled into an engine without any machining after plating is completed. The outside dimension as well as the surface roughness must meet set requirements. In this case the thickness of the dispersion coating and the dissolved volume from the alkali etching process must be closely controlled. Another important requirement is the ability of the alkali etching agent to show little retrogradation even after many pieces have been treated. The following formula is for parts that are to be assembled without any machining: (pre-process dimensions) + (alkali etching dissolved volume) + (dispersion coating thickness) = (required dimensions).

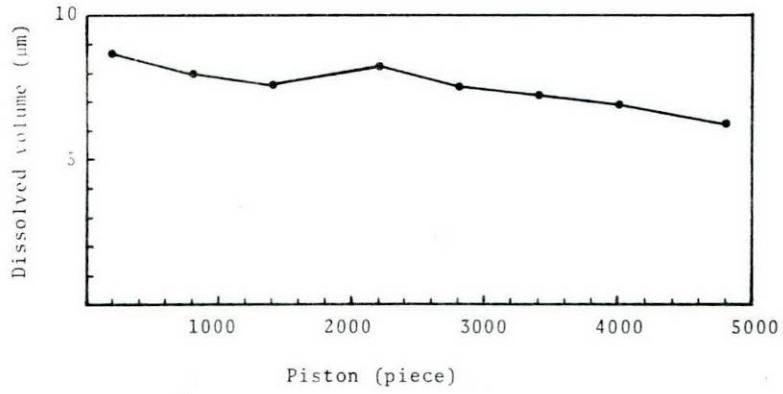



Fig. 2. Relation between number of pistons and dissolved volume in alkali etching. (liquid volume: 500ℓ)

The most important thing about the zincate treatment, is that since the plated parts are aluminum alloy castings, as well as parts that will be used in an engine, there must be good adhesion. For this reason, special attention must be paid to the agents, composition and working conditions of both the acid and zincate treatments.

While the single zincate treatment and the double zincate treatment are similar, the double zincate treatment is better for aluminum alloy castings with a relatively high content of silicon. Also, in the case of zincate treatment, adhesion depends upon its combination with the pre-processing acid treatment. When aluminum alloy castings are treated, the acid treatment bath is contaminated. This is from the dissolution of alloy contents other than the aluminum (Si, Mg, Cu, Fe, etc.). For this reason, the acid treatment is an important process and effects the adhesion of the plating. It is necessary to pay strict attention to the condition of the acid treatment.

The thinner and more uniform the film gained from zincate treatment after acid treatment, the better the adhesion obtained. Here is where the film from the double zincate treatment is much thinner than that gained in the single zincate treatment. Electrical resistance is higher by far, and they are not simple zincate film.

## 4. Giving Special Features to Coatings.

A microscopic view of the structure of Ni-SiC dispersion coating reveals its complex structure of included SiC particles within a matrix. This is what gives excellent abrasion resistance. However, since the matrix is made of pure nickel, when

heated, its hardness is reduced. Also, since the matrix itself is not very hard, under use (driving conditions) the surface tension of the piston-ring may bury the SiC particles which project from the surface layer of the matrix.

Phosphorous is added to the plating solution in an attempt to avoid this problem. The phosphorous is added in the form of phosphorous compounds: phosphorous acid, hypophosphorous acid, sodium hypophosphite; among others. More hardness is gained with the heat-treatment of the Ni-P-SiC dispersion coating from the nickel sulfamate bath which is added the phosphorous; the same as is done with electroless plating. Fig. 3 shows the relationship between the hardness of Ni-P-SiC and Ni-SiC dispersion coatings and the temperature of the heat-treatment.

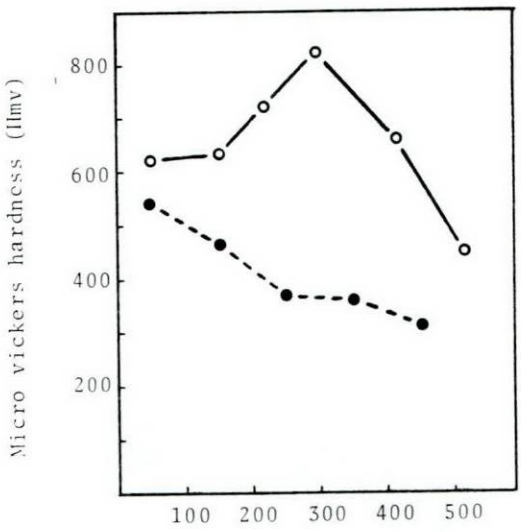



Fig. 3. Hardening through heat-treatment.
○ : Ni-P-SiC dispersion coating.
● : Ni-SiC dispersion coating.

But care must be taken in the amount of phosphorous which is added to the nickel sulfamate bath. Too much can result in a brittle coating; making honing or grinding difficult. On the other hand, if there is too much phosphorous in the plating bath, the electrodeposit stress of the coating increases on the tensile side, and adhesion suffers.

## 5. Ni-P-SiC Dispersion Coating of Cylinders.

Adhesion is most important in the dispersion coating of the cylinder of an aluminum alloy casting. As has already been stated, in order to assure proper adhesion, attention

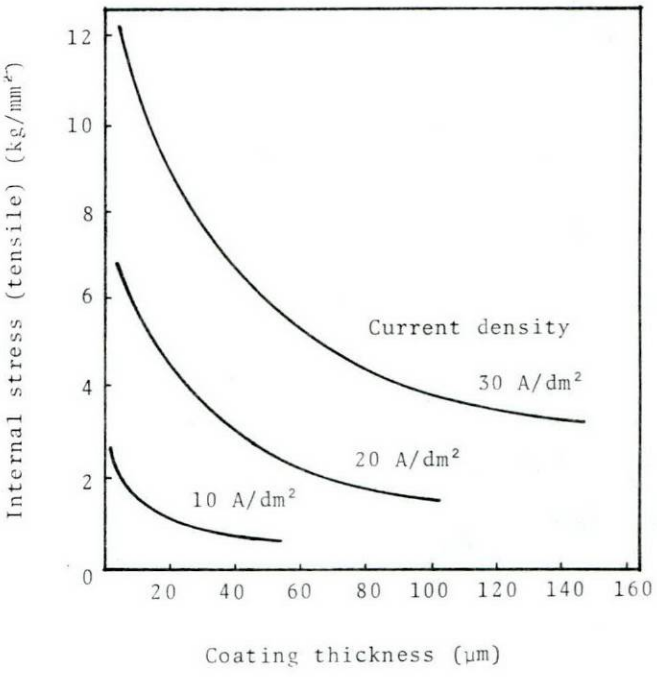



Fig. 4. Relation between current density and internal stress.

must be paid to the pretreatments and the method of the plating process itself. During the plating process, adjustment of the current density is important to achieve proper adhesion. Current density is divided into first and second current density. The first current density is low, while the second current density is the regular 20 $A/dm^2$. Fig. 4 shows the relationship between the stress in the electrodeposits and the current density. As can be clearly seen, the lower the current density, the less the stress in the electrodeposits. Given this formula, if the current density is low in the first phase of the plating, then the coating obtained will have considerably less internal stress with good adhesion. The difference in internal stress shown clearly in this graph can be controlled with the addition of a relaxation agent.

Many things must be taken into consideration when planning the shape and the material of the plating jig: the shape of the piece to be plated (cylinders, etc.); the conduction of the proper electrical current which forms the dispersion coating; the shape of the bath for the plating solution; the rocking apparatus to which the jig will be attached; the structure of cathode contacts; as well as the shape and number of the pieces to be plated. The following are the main points to be taken into consideration regarding plating jigs:

(1) It must be able to conduct the proper amount of electric current.
(2) It must be strong enough to hold the weight of all the pieces placed upon it.
(3) There should be no imperfect contact between piece and jig when the jig is rocked. The pieces, therefore, must be secured fast to the jig, but at the same time, attachment and removal should be easy.
(4) The anode must be located in the center of the cylinder bore; however, the anode jig for the cathode jig must be properly isolated.
(5) The plating solution should drain off the jig quickly and easily in order to avoid loss and spilling when the jig is removed from the bath.
(6) The jig should be constructed so as to avoid disturbing the air agitation, rather, it should help to concentrate the air.
(7) Resistance to chemicals should also be taken into consideration.

Also, if the jig is to be composed of metal only, then the structure of the anode and cathode jigs must be planned so as not to send extra current through the plating jig. And no matter what is done, the jig will receive a coating which will have to be taken off with chemicals. For these reasons, stainless steel and titanium are being used, as both have high chemical resistance rather than good conductivity.

Once the jig has been made to fit the requirements just discussed, cylinders are placed on it and Ni-P-SiC dispersion coated. In the case of cylinders, the resulting coating is more than 100μm thick and is then ground in order to obtain uniform surface roughness and the required dimension. As shown in Fig. 3, it is important to consider what grindstone and under what conditions grinding will be done, as well as rough, second and finish machining, in order to produce uniform surface roughness and because the beginning hardness is more than 650 Hmv.

After machining, electrolytic polishing is performed in order to achieve good SiC particles projection from the surface of the dispersion coating. The electrolytic polishing solution is a phosphoric acid system, electric current density is more than 50 $A/dm^2$, treating time is 1 to 2 minutes, and when electrolytic polishing is performed in these conditions, about 3μm of the nickel matrix is dissolved, and on its surface good projection of SiC particles can be observed. These particles form a hard primary sliding surface, while the nickel matrix with included SiC particles forms a secondary sliding surface.

Also, the 1 to 2μm of space between the projecting SiC particles and the nickel matrix provides an area for lubricating oil to remain, and this oil is supplied for lubrication to the primary sliding surface. Dry-abrasion of coats gained in conventional plating is inferior, and there is a similar tendency with Ni-P-SiC dispersion coating; but after electrolytic polishing, since lubricating oil area is held on the surface of the coating, the part can endure continued periods in an oil-less state. Photo. 3 shows a cross section of a Ni-P-SiC dispersion coating that has undergone the process discussed up to this point.



Photo. 3. Cross section of Ni-P-SiC dispersion coating. ( 50μm )

## 6. Ni-P-BN Dispersion Coating of Pistons.

The coating gained from Ni-P-SiC dispersion coat plating is hard, and therefore has good abrasion resistance. However, since Ni-P-BN dispersion coating has added lubricating characteristics, it stands up to wear even better.

Table 2. Solid lubricants and those properties.

| Property \ Name | | Boron nitride | Graphite | Molybdenum disulfide | PTFE |
|---|---|---|---|---|---|
| Chemical formula | | BN | C | $MoS_2$ | $(CF_2\text{-}CF_2)_n$ |
| Decomposition temperature | °C | 3000 | 3400 | 1098 | 727 |
| Maximum allowable working temperature | normally °C | 700 | 450 | 350 | 260 |
| | instantaneously °C | 900 | 600 | 400 | 350 |
| Thermal conductivity | Kcal/m·hr.·deg | 13 ∿ 25 | 43 ∿ 340 | - | - |
| Friction in vacuum | | low | high | change | low |
| Density | g/cm³ | 2.27 | 2 | 4.85 ∿ 5.0 | 2.1 ∿ 2.25 |
| Hardness | Moh's/shore | 2/33 | 2/- | 2/- | -/55 |

Table 2 and Fig. 5 show the characteristics of various solid lubricants. Boron nitride (BN) is a smooth white powder with a hexagonal layered structure, and is stable both chemically and thermally. In an inert atmosphere it is stable up to about 3000°C. As can be seen in Fig. 5 and table 2, it has a better coefficient of friction than graphite or molybdenum disulfide. At low temperatures it is inferior to teflon, but the maximum allowable working temperature for teflon is 260°C, and for BN it is 700°C. All these characteristics make BN an excellent lubricant at high temperatures.

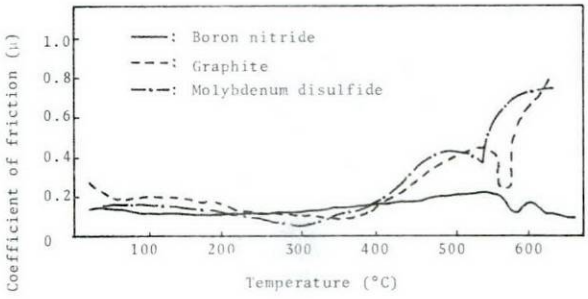



Fig. 5. Change in coefficient of friction of solid lubricants with heat.

If BN is suspended in the plating bath, Ni-P-BN dispersion coating can be made possible. With self lubricating BN particles well dispersed throughout the matrix, the coating is given good lubrication characteristics. In abrasion seizure tests performed with a Faville test machine, Ni-P-BN dispersion coating showed less dry



Photo. 4. Surface of Ni-P-BN dispersion coating. ( 25μm )

abrasion than did other platings. In the case of the pin/block group of aluminium alloy castings, if a pin is dispersion coated, the superiority of the performance of the Ni-P-BN dispersion coating shows clearly. Therefore, lubricating performance is better for the piston of the piston/cylinder group of parts, and the revolving shaft of the bearing related group of parts, when they are Ni-P-BN dispersion coated. Dispersion coating of the surface of the piston helps prevent seizure and scuffing.

The performance of Ni-P-BN dispersion coating proven, the next problem was how to include it into the mass production process. One problem was "wetting," particular to the dispersion particles. When the dispersion particles which are solid, come into contact with a liquid, and the solid/gas interface changes into a solid/liquid interface, we have the condition called "wetting." The degree of freedom that exists regarding the change from the solid/gas interface, to the solid/liquid interface has to do with whether or not the dispersion particles are easy to suspend in the plating solution. It is easy to suspend the BN particles in the plating solution. In this way, the particles change from a solid/gas (air) interface to a solid/liquid one. However, with air agitation, the BN particles change easily from a solid/liquid interface to a solid/gas (air) one, and they are also made to float on the surface of plating solution. This makes proper plating difficult, as it does not leave enough BN particles suspended in the plating solution to be plated in the Ni-P-BN dispersion coating. Measures against this problem include adding a wetting agent to the plating solution, and processing the surface of the solid with a surface activation agent to reduce surface tension. Besides the utilization of a surface activation agent, when the wetting of dispersion particles is a problem, attention must be paid to the preparation of the plating solution.

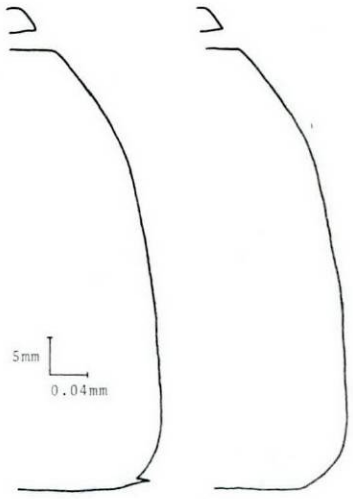
The second problem is that the piston that is dispersion coated must be assembled without any machining. Given this necessity, the following are required of the piece that is to be plated:

(1) Precise dimensions for all areas of the piece.
(2) Uniformity of dimensions of all pieces placed on the plating jig.

To satisfy requirement (1), it is necessary to supply electric current of a constant and uniform density to each and every piece on the plating jig. In the case of a piston, the most important area is the skirt and the edge of the skirt. In order to avoid the concentration of electric current density in these areas, it is necessary to use an auxiliary cathode or to consider its shape. Fig. 6 shows the profile of pistons plated with Ni-P-BN dispersion coating. Also, in order to assure that a uniform current density flows to each piece on

the plating jig, it is necessary to take their vertical and horizontal position into consideration.

In order to satisfy the requirement in (2), that all pieces be plated to uniform dimensions, it is necessary to consider the proper surface area for the anodes and cathodes used, the distance between each other, and their height. Fig. 7 shows the thickness of the pieces plated on our plating jig with respect to their position on the jig. The plating jig holds 24 pistons. As can be seen clearly, accuracy is within 1μm, plus or minus, of the 10μm objective.




(a) Piston not setted auxiliary cathode. (b) Piston setted auxiliary cathode.

Fig. 6. Profile of Ni-P-BN dispersion coated piston.

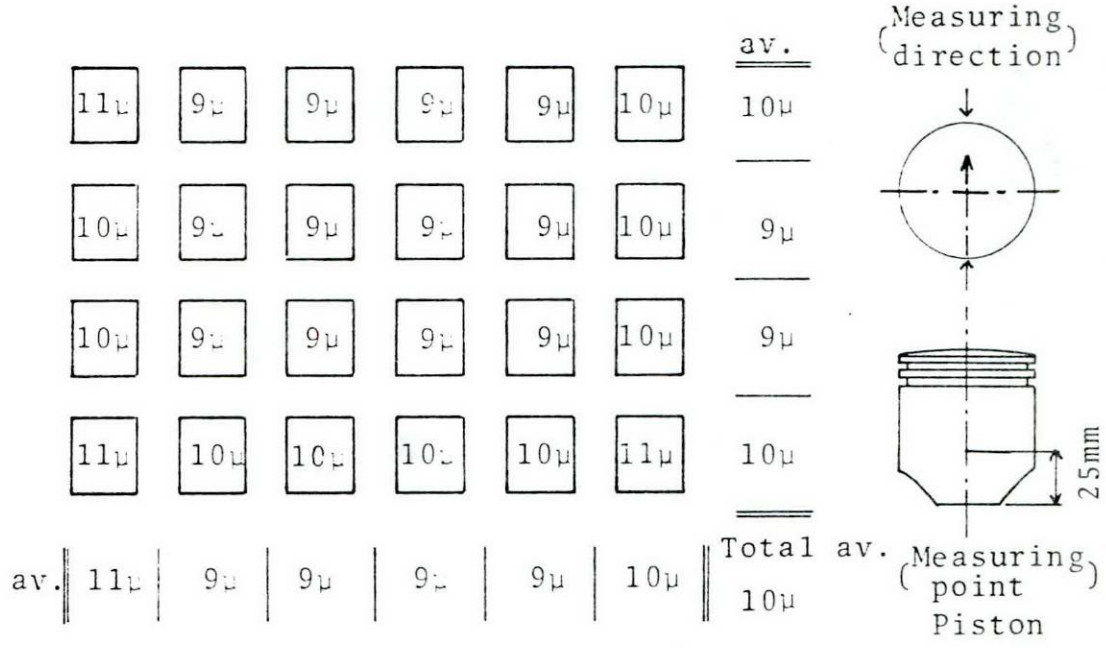



Fig. 7. Distribution of coating thickness for pieces plated on a 24-piston set plating jig.

# 0-6

# Dispersion Coatings I
# Session 0

## Electroless Nickel/P.T.F.E. Composite Plating

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# ELECTROLESS NICKEL/P.T.F.E. COMPOSITE PLATING *

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Godiva Place, Coventry, CV1 5PN,
England.

Although Electroless Nickel/hard particle composite coatings have been available for some time, this process is unique in the market penetration that has been achieved for a composite P.T.F.E. deposit.

This is due to the nature of the product where a consistent volume of P.T.F.E. is distributed throughout the thickness of the coating and not merely applied to the outer surface. In addition, the solution stability and reproduceability is such that control in production is easily maintained.

The development of any composite electroless nickel process depends on two components of the system; the electroless nickel, and the second phase particle dispersion. At Montgomery Plating we have had over thirty years experience with electroless nickel solutions and during that time we have accrued a vast fund of practical know-how and experience, and are thus able to apply this knowledge to the problems of producing electroless composite systems.

As any electroless nickel plater knows, there are solution formulations for baths of varying stability, for different phosphorus levels, for different stress levels, and a wide variety of other deposit and solution parameter variables. In Coventry we have devised a series of simple empirical tests which demonstrate a solution's viability in our particular production environment, and we are able to rapidly determine whether a particular electroless nickel solution is up to our required standards. These tests have been valuable in establishing the required parameters for P.T.F.E. composite plating.

The introduction of extraneous material into an electroless nickel tank obviously has a profound effect on that bath's characteristics. It then becomes of paramount importance that the experience of electroless nickel solution control is applied to this mixture to enable optimum results to be obtained.

In conjunction with the Akzo Corporation of Holland, we have applied their expertise in producing a patented P.T.F.E. dispersion to the problem of tailoring production and technical needs of electroless nickel to obtain a viable system for producing composite coatings.

* The "Niflor" process, marketed under licence by Montgomery Plating Co. Ltd., Coventry, England.

P.T.F.E. differs from many of the second phase particles that have been included in electroless nickel deposits because of its hydrophobic nature. The particles, through virtue of their non-stick tendencies, do not easily wet, which makes them difficult to introduce in a stable fashion to an aqueous environment.

The formulation of a stable electroless nickel compatible dispersion that will withstand the harsh production conditions encountered during the plating cycle is the technological breakthrough. To achieve this the surfactants must be tightly bound to the P.T.F.E. particles and not interfere with the plating solution chemistry, whilst the P.T.F.E. particles themselves must be prevented from coagulating and precipitating at the plating pH and temperature. In addition, the P.T.F.E. particles must be able to incorporate into the growing deposit at a known rate and consistency.

Our tests and trials have isolated electroless nickel solutions with the desired characteristics, which when married to a standard dispersion formulation will produce good results. To produce these superior properties control and operator competence needs to be optimum, at a level which is consistent with a well run plating shop. Given these parameters, the process does not produce a system in which the P.T.F.E. significantly coagulates during use. It is not a system affected by impurities introduced during normal plating operations that any normal electroless nickel solution would tolerate. The system does not require sophisticated control, just good general plating shop practice. In short, if a shop can operate a good quality electroless nickel system, it can operate this composite plating process.

When installing a plant in house for this process, the normal considerations of effluent, services, adjacent processes, etc., have to be taken into consideration. Areas next to chromic acid plants are to be avoided, as are dust laden atmospheres found near to polishing or grit blasting operations. Once again though, these requirements are exactly the same as those dictated by any good quality electroless nickel installation.

One of the plants installed at Montgomery Plating in Coventry, England, has a conventional pre-treatment line of alkaline soak cleaners, electro-cleaners, etches, etc., as for any electroless nickel pre-treatment. We then have 6 tanks of 1,300 litres (343 U.S. gallons) of composite solution, followed by hot and cold rinsing stations.

The composite tanks are standard electroless nickel tanks slightly modified to suit the plating conditions; extraction is not required due to the foam formed on the tank surface during plating, providing both an insulating and steam suppressing cover. Heating can be catered for by any low surface wattage heaters; in our case we have steam heating although electrical heating is used on other plants. Filtration is normally performed in bulk once per shift, together with a tank acid leach and clean. The highly stable nature of the process prevents roughness building up in the tank in the intervening periods.

Jigging considerations for composite plating are the same as for any electroless nickel operation. The inclusion percentage of P.T.F.E. is not affected by the inclination of the plating surface in the vat and so does not require consideration.

Quality assurance of the solution is catered for by the normal three component analysis of nickel, hypophosphite and pH, plus a test of the percentage of P.T.F.E. in solution. The solution P.T.F.E. content will control the amount of P.T.F.E. in the deposit, although large variations in solution content produce only small variations in deposit content.

The P.T.F.E. content of the deposit can be analysed simply from the respective weights of Nickel and P.T.F.E deposited on a stainless steel panel after dissolving the nickel matrix. Experience has shown that control of the included P.T.F.E. level is very easy visually from the appearance of the deposit, but quality assurance provisions of course dictate that this is backed up by substantiated figures.

A nominal figure of 20 volume % is quoted for the standard composite coating, with limits of 15 - 25%. No significant difference in performance in any of the properties has been noted at either end of these inclusion levels.

Physical properties of the coating are obviously a compromise between the electroless nickel matrix and the P.T.F.E. inclusions. The sub micron particles of P.T.F.E. distributed evenly throughout the matrix make hardness evaluations impossible. Even microhardness indentation equipment will pick up the soft particles of P.T.F.E. and so lower the apparent hardness of the nickel matrix to a lower bulk hardness level. There is no reason to suppose, however, that the nickel matrix is at a significantly different hardness from that normally found with electroless nickel deposits, i.e. about 5 - 600 VPN as deposited, rising to 900 - 1,000 VPN on heat treatment.

The conventional heat treating temperature of 400°C. for 1 hour will obviously degrade the P.T.F.E. content of the deposit to some extent, and so a lower temperature of 300°C. for 4 hours is normally specified for maximum hardness. Alternatively, to give the coating its maximum hydrophobicity, 10 minutes at 400°C. will sinter the P.T.F.E. into the coating. This temperature cycle can either replace or be additional to the hardening heat treatment cycle. As deposited, the composite coatings have a bulk hardness of about 250 VPN, rising to about 400 VPN after 4 hours at 300°C.

The heat treatment procedure can give components a considerably enhanced life over components which have not been heat treated, for the same coating thickness. Sometimes it is more economical to substitute a heat treatment cycle than to increase the coating thickness. In addition, there are occasions when loose particles of P.T.F.E. are detrimental to a component's smooth operation, e.g. in the food industry, or in carburettors, when the sintering occurring during heat treatment is doubly beneficial, not only hardening the nickel-phosphorus matrix, but causing the surface P.T.F.E.

particles to become highly adherent. The heat treatment cycle also removes the coatings tendency to "finger mark", which can detract from its normally attractive appearance, similar to that of pewter. Higher temperature heat treatments cause the normally oxidised discoloration found with any coating.

The adhesion of the composite coating to the basis material depends as much on pre-treatment as does any conventional electroless nickel coating. All coatings in the 15 - 30 volume % range will pass the ASTM E290 bend test of 180° without flaking or detachment from the substrate, if the pre-treatment is correct.

Increases in the volume percentage of P.T.F.E. over the 30% mark result in decreasing adhesion due to the smaller area of nickel that is actually contributing to the adhesion process. It is for this reason that 30% is normally set as an upper limit for P.T.F.E. content, although higher apparent surface levels of P.T.F.E. may be catered for, by sintering or utilising the white layer of loosely adherent P.T.F.E. present on a component's surface on removal from the plating bath. This layer then gives enhanced released characteristics in areas that require these properties.

As in all electroless plating systems, the coating will uniformly cover all edges, holes and complex shapes where solution has free access. The inclusion of particles in the coating prevents the usual lustrous, highly reflective appearance by scattering incident light and not just reflecting it. As mentioned previously, this gives rise to the matt grey pewter like surface. However, the quality of finish of the composite coating reflects the quality of finish of the substrate, and the usual care in providing as far as is practicable a blemish-free surface for plating still holds.

One set of results for surface topography changes with thickness on a stainless steel panel were as follows:-

TABLE 1

| | Substrate: | Composite: 10 μm. | Composite: 25 μm. |
|---|---|---|---|
| Talysurf CLA (Centre Line Average) μm. | 0.95 | 2.1 | 4.8 |
| Talysurf $\Delta q$ (Slope) radians | 0.09 | 0.246 | 0.372 |
| Talysurf RPC (Radius of Peak Curvature) $mm^{-1}$ | 35 | 55 | 77 |

The frictional properties of the composite are obviously of great interest as it is in the field of adhesive wear that it has many advantages over rival products. These include the provision of an in-situ, dry lubricating surface, elimination of stick-slip, reductions in friction coefficients and power consumption, and other benefits.

One particular assessment performed by the National Centre of Tribology in England evaluated the coefficient of friction of the composite in comparison with sulphuric anodised, dichromate sealed aluminium, against an 18/8 stainless steel pin. The results illustrated in Table 2 show that the composite gives a lower and more consistent coefficient of friction in comparison with anodising. In addition, stick-slip, which is pronounced in the anodised test specimens after a few cycles, is non-existent in the composite specimens - Figure 1. Also, the superior results of the composite coating continued for an appreciable sliding distance - Table 3.

Table 2 - 100 Cycles

| Composite Specimen No. | Friction Coefficient Start | End | Anodised Specimen No. | Friction Coefficient Start | End |
|---|---|---|---|---|---|
| 1 | 0.11 | 0.12 | 17 | 0.17 | 0.43 |
| 2 | 0.10 | 0.12 | 18 | 0.17 | 0.36 |
| 3 | 0.10 | 0.11 | 19 | 0.12 | 0.21 |
| 4 | 0.10 | 0.12 | 20 | 0.20 | 0.31 |
| 5 | 0.11 | 0.11 | 21 | 0.14 | 0.31 |
| 6 | 0.10 | 0.10 | 22 | 0.12 | 0.24 |
| 7 | 0.10 | 0.13 | 23 | 0.17 | 0.48 |
| 8 | 0.10 | 0.10 | 24 | 0.24 | 0.49 |

Table 3 - 3,000 Cycles

| Specimen | Friction Coefficient (Cycles) Start | 500 | 1,000 | 1,500 | 2,000 | 2,500 | End |
|---|---|---|---|---|---|---|---|
| Composite | 0.11 | 0.12 | 0.12 | 0.13 | 0.14 | 0.17 | 0.19 |
| Anodised (mean) ) | 0.14 | 0.40 | 0.50 | 0.52 | 0.52 | 0.54 | 0.55 |
| ) | | | | | | | |
| Peak values: ) | | 0.67 | 0.65 | 0.71 | 0.69 | 0.70 | 0.71 |

These results, which in the nature of tribological evaluation, may not be representative of another situation involving the same materials do, however, confirm many experiences in the practical application of the composite where the low consistent friction value and long wearing properties have contributed to its successful introduction.

P.T.F.E. is, for all practical considerations, totally corrosion resistant. The electroless nickel matrix is unmodified with respect to its composition, and so will exhibit in bulk the same corrosion resistant properties as those expected from a standard electroless nickel. The combination of P.T.F.E. and electroless nickel does not provide any additional benefit in terms of providing increased corrosion protection, except by providing a hydrophobic surface which sheds water and electrolytes very readily, and this discourages corrosion cells from forming. However, it is a simple matter to provide a duplex coating, the first layer consisting of an ordinary, high quality electroless nickel layer, followed by a top coat of the composite coating. The corrosion resistance of this layer is obviously then superior to a single layer electroless nickel coating. The combined coating is also more economical if a thick layer is required.

In drawing upon case histories to illustrate the existing and potential applications for the composite, it is very difficult to select broad areas of interest. It is not an exaggeration to say that we have not yet entered a manufacturer and have not been able to indicate products and areas where a P.T.F.E. composite coating would considerably improve performance, reliability or economy.

In the U.K. alone we have received over 1,000 hard enquiries about the process. The composite coating has been promoted by a few editorial features, and by the interest of a number of national bodies some of whom have recommended the coating to customers who have had problems. These national bodies have included the Production Engineering Research Association of Great Britain, the Design Council, the National Centre for Tribology, the European Space Tribology Laboratories, and others. Application areas examined have ranged from sub off-shore oil components to parts for solar array deployment mechanisms on satellites.

In this latter application, a coating that will withstand the rigours of a hard space vacuum, be self-lubricating, capable of withstanding high as well as cryogenic temperatures, be dimensionally accurate, as well as satisfying corrosion needs during earth bound storage - are all met by the P.T.F.E. composite coating. Alternative coatings for these applications include ion plated lead, a process that is expensive and not necessarily able to coat large areas or components. Other areas of space application are under consideration, and the U.S. space station project may be an area where a considerable number of components could benefit from the composite coating.

One of the more dramatic successes of the application came in the field of non-lubricated pneumatic cylinders. Conventionally hard anodised or P.T.F.E. coated aluminium cylinder bores gave a life of 10 - 30,000 cycles when subjected to the wearing action of a rubber piston oscillating in the cylinder. 5 microns of the composite under the same conditions gave a life in excess of 8 million cycles. This increase in life into the range normally occupied by lubricated cylinders gives users the option of eliminating costly oil injection equipment, together with the parallel advantage of elimination of oil aerosol release into the working environment. This latter advantage is becoming increasingly interesting as legislation tightens on the control of pollutants in the workplace.

Automotive components, especially carburettor components, have also been extremely successful. In these applications the manufacturer is looking for a dimensionally accurate coating that can be applied with precision to complex parts. This coating must be resistant to sticking and gumming from fuel residues and thus self-lubricating properties are a definite requirement. The inertness of the coating to the fuel environment makes the specification of this type of coating an ideal substitute for the alternative resin based P.T.F.E., hard chrome or electroless nickel coating systems that have been previously used. In certain application areas in the carburettor, the composite coating has out-performed hard chrome by 200%. Precision jigging arrangements are no longer required to hold plating dimensions within tolerance; this is a direct saving over hard chrome plating.

Butterfly valves have sealing surfaces that are subjected to high closure forces to give fluid tight seals. With certain material combinations in metal to metal sealing valves, this can give rise to galling (cold-welding) problems. One customer with a stainless steel disc and nimonic ring has found that 25 microns of heat treated P.T.F.E. composite prevents galling. As additional benefits, a lower leak rate is found, plus an extension of the temperature range of operation into the cryogenic area. Following a Lloyds fire test at highly elevated temperatures, the coating was found to retain its sealing characteristics to the extent of passing the bi-directional sealing requirements for the Lloyds certificate, despite the total degradation of the P.T.F.E. content of the coating.

An interesting area of application has been in the coating of glass bottle moulds. Traditionally, these moulds are coated with a graphite based compound, or dag, which is difficult and dangerous to apply to the operational machine, and which results in bottles being rejected immediately after the swabbing operation. Alternative methods of coating the moulds do not appear widespread; though boron reduced electroless nickels have made some impact on this market they are very expensive and difficult to control.

Theoretically, the temperature of operation of these items of equipment is well in excess of the operating range of P.T.F.E., and so the composite would not appear an obvious candidate as selection for a coating. However,

trials have shown high quality bottle surfaces and release from moulds after continuous operation in excess of 10 days. The mechanism of successful operation here is thought to be via the carbonised remains of the P.T.F.E. particles in the deposit acting as a graphite dispersion in the electroless nickel matrix. Additional release may also be conferred by the gaseous decomposition products forming some kind of boundary lubrication.

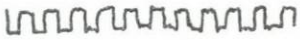
Another unusual application was in the coating of high strength aluminium alloy hubs for Formula One racing cars. The wheel retaining nuts were sticking and jamming on the aluminium during the fast pit stop wheel changes practised at this time. A coating of the composite gave a hard wearing surface with intrinsic lubrication, enabling the hub nuts to be rapidly removed and replaced without any problems. Since this introduction to the racing world, investigations are going on into the composite's application into other areas of this precision engineering, highly stressed industry.

A more mundane application has been in fasteners for computing applications, where low torque assembly is required without flaking of any applied coating which may cause problems with disc memories. The dimensional conformity of the coating allows standard fasteners to be used without making special size allowances for the coating.

Electroless nickel/P.T.F.E. plating has come of age this year, with the properties of the coating continuing to excite those of us who are familiar with it. Installations in the U.S.A., England, Germany, Holland and Switzerland are being expanded and other installation agreements reached as more and more engineers find that electroless nickel/P.T.F.E. composites can help them out of some of the most difficult engineering problems in existence today. The market potential is enormous, with the composite coating being complementary in many areas to existing electroless nickel coated components, as well as opening new markets previously unexplored.

FIGURE 1

Composite, 100 cycles



Anodising, 100 cycles
(same vertical scale)




AMERICAN ELECTROPLATERS' SOCIETY