# APPLICATION OF WEAR RESISTANT COATINGS BY THE BRUSH PLATING TECHNIQUE

by

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A thesis submitted for the degree of Doctor of Philosophy of the University of Aston in Birmingham.

February 1981.

The University of Aston in Birmingham

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DEGREE PhD

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## SUMMARY

The development of cobalt molybdenum and cobalt tungsten brush plating electrolytes is described. Their optimum compositions and operating conditions for commercial applications have been determined. The effects of composition, pH, applied voltage, stylus speed and pressure upon deposit composition and efficiency have been investigated. Transmission and Scanning Electron Microscopy have been employed to study the cobalt alloy deposits produced.

Evaluation of the wear resistant properties of the cobalt alloys developed in this work was carried out in the laboratory using a pin and disc technique and a simulated hot forging test, and by industrial trials involving the "on site" plating of hot forging dies and cold pressing tools.

It was concluded that the electrolytes developed in this work enabled cobalt alloys containing 6% Mo or 8% W to be deposited at 17-20V. Brush plated cobalt deposits possessed a mixed CPH and FCC crystallographic structure at room temperature.

The application of 13μm of either of the cobalt alloys resulted in improved wear performance in both pin and disc and simulated hot forging tests. The results of the industrial trials indicated that by the use of these alloys, the life of hot forging dies may be increased by 20-100%. A commercial forging organisation is using electrolytes developed in this work to coat dies prior to forging nimonic alloys. Reductions in forging temperature and improved forging qualities have been reported. Cold pressing tools coated with the alloys showed a reduced tendency to "pick-up" and scoring of the pressed panels. Reports of a reduced need for lubrication of panels before pressing have also been received.

KEY WORDS ELECTRODEPOSITION
BRUSH
COBALT
WEAR
DIES

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# 1. INTRODUCTION

There are two routes which may be followed in order to improve the life of hot and cold metal working tools. The most obvious is to upgrade the specification of die steel from which these are made, but there are many disadvantages in taking such a course. Increased toughness and wear resistance invariably mean more difficult machining requiring sophisticated equipment with greater operative costs. A further disadvantage is that the new material may well prove inferior to the original die steel with respect to certain properties. For example, although a more sophisticated die steel may have an improved tensile strength, its resistance to thermal fatigue or erosive wear may be poor. However, in most cases this method of increasing die and tool life is not a viable proposition on the grounds of the cost of the more advanced special steels.

The second method by which wear performance can be improved is to employ some form of surface treatment, such that the surface properties are modified with respect to the bulk material. This may take the form of treating the existing surface as for example in nitriding, or the application of a further new layer as in electrodeposition.

With regard to hot forging dies and cold pressing tools, the most commonly used technique is nitriding, but this process suffers from the same disadvantages as many other thermal processes. As it is diffusion controlled, a considerable time is required at nitriding temperatures, with all of the attendant problems of distortion. There are also severe limitations on the size of component to be treated. Thus although carried out on a large scale, nitriding cannot be considered as a complete solution to wear and erosion of metal working tools.

Promising results have been obtained by industrial trials involving the electrodeposition of cobalt-tungsten and cobalt-molybdenum alloys on to hot forging dies. When cobalt alloys were used containing 4% of molybdenum or 8% tungsten, the die lives were increased by up to 100%. However, industrial trials were restricted by the size of component that could be treated, and the reluctance of forge and die shop management to release tools which may be urgently required for production. Hence, a portable plating process capable of "on site" deposition of cobalt alloys coatings appeared to be the answer. Such a technique had existed in "brush plating" for some time, but there were severe limitations due to the lack of satisfactory cobalt-alloy electrolytes. Of the commercially available brush plating electrolytes, the cobalt alloy solutions were amongst the least successful, as deposit thickness was severely restricted due to high internal stressing.

After consideration of the fundamental requirements of a brush plating solution, it was decided to modify the composition of the sodium heptonate complexed cobalt alloy plating baths developed by Still.(51) The cobalt-molybdenum and cobalt-tungsten systems are of the induced codeposition type and their unpredictable behaviour was reflected in some of the experimental results obtained. However brush plating solutions were developed that enabled cobalt alloys containing about 6% Mo or 8% W to be deposited at 17-20V.

Determination of the optimum electrolyte composition was carried out by means of composition trials in which the deposits were examined and the cathode current efficiency for deposition calculated. The effects of voltage, pH, speed and pressure upon deposition characteristics were also investigated.

Evaluation of wear properties of the deposits were carried out by wear testing utilizing a pin and disc machine. In addition, experimental hot forging trials were carried out on the deposits using a standard laboratory scale hot forging rig. Comparisons were made between the results obtained and the wear test results.

A major section of the work involved extensive evaluation of the coatings developed, by means of industrial trials carried out "on site". During this work, a wide variety of hot forging dies and cold pressing tools were electroplated in the forge or tool-room, demonstrating the portable nature of the process. The practices used within manufacturing industry made collection of results extremely difficult, and the results of many trials have yet to be obtained. This was due mainly to the use of treated dies for the production of part-orders and hence tools were still servicable. Throughout the industrial trials, a variety of die and tool steels in various heat treated conditions were plated along with certain cast irons, with few problems. The treated dies were also used to forge a wide variety of component materials, from mild steels, to nimonic and titanium alloys used in the aircraft industry.

# 2. BRUSH PLATING

## 2.1 Introduction to Brush Plating

Brush plating is one of the many names given to the process in which an absorbent pad is wrapped around an anode, soaked with electrolyte and rubbed over the surface to be plated. The process is also known as selective area, tampon, touch up, swab or stylus plating. As far as the small area being plated at any particular instant is concerned, it is a high speed plating process. Current density in the conventional sense has no meaning in relation to this process, and so control is exercised by means of voltage and ampere hour measurement. Components can be electroplated without immersion in a plating vat and selected areas can be plated.

The term "brush plating" is not entirely appropriate since the plating tool is not a flexible brush but consists of an inert electrode covered with a suitable absorbent material to hold the plating or cleaning solution. The inert electrode may be made either the anode or cathode in the circuit depending on the treatment being undertaken. Its polarity would normally be cathodic for cleaning operations and etching and anodic for plating purposes. Usually the total cleaning or plating current employed is only 5-20A at 10-20v D.C. The time required to deposit a particular coating is dependant on the thickness required, the area to be plated and the efficiency of the solution. However, the rectifier capacity necessary is much lower than for conventional vat plating and in consequence the rectifier unit is relatively small and portable. A selected area can be plated with a minimum use of stopping off; the application of adhesive tape around the area to be plated is normally sufficient.

## 2.2. Process Developments

Brush plating originated(4) in the "touching up" of defective deposits applied by conventional vat plating techniques. If a component left the plating bath with a passivated area, it was held against a bus bar, whilst being rubbed with an electrolyte soaked rag covering a wire connected to the other bus bar. Thus a repair was made which enabled the inferior deposit to be corrected without the need for stripping and re-processing. Consequently, the conception of brush plating was originally as a cosmetic aid rather than an electroplating technique in its own right.

Hughes reported(1) a further development into a low voltage technique (6-8V) using solutions

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## 2.3 Advantages of Brush Plating

Many advantages of the technique have been listed and examples of its use illustrated by the protagonists of the process(6). The major points are listed below with particular reference to the relevance of the technique to the work carried out on hot forging dies and cold pressing tools.

### 2.3.1. Touching up of defective electrodeposited components.

Defective areas of an electrodeposit can be readily activated and re-plated by the brush plating technique. This may be immediately after plating; or a considerable period later when the component concerned may be in service and not readily accessible.

### 2.3.2. Plating In-Situ

In many instances, it is possible to save a great deal of time and expense by plating in-situ.
This procedure may be of value where components too large for conventional bath plating are involved, as in the case of the plating of large metal working tools which may weigh several tonnes. It is also

of considerable use in the aircraft industry where the costly dismantling of precision components may be largely avoided.

### 2.3.3. Reduction in cost of stopping off and benefits of plating selective areas.

When operating a conventional vat plating system, considerable expense in incurred in the case of some components in stopping off or masking over areas of a workpiece on which a deposit is not required. This is largely due to the labour intensive nature of such operations. Brush plated deposits, including mechanised techniques have been used(4) to reduce the need for "stopping off". Frequently, as in the case of hot forging dies, wear only occurs in certain regions and so it would be wasteful to plate the complete tool. Repairs of the worn deposit can also be made as and when required.

### 2.3.4. Plating of contaminated components.

Due to the fact that nearly all conventional vat plating solutions are susceptible to both metallic and organic contamination, it is desirable to avoid such problems by selective brush plating of the component rather than by immersing it in a plating solution. Brush plating solutions are normally expendible. Printed circuit boards(6) are sometimes brush plated to avoid solution contamination from other manufacturing stages.

### 2.3.5. Joint application techniques.

In some instances, combined techniques of bath and brush plating can be used. During conventional plating, passivation may occur in low current density regions of complex shaped articles. This is particularly prevalent when alloy plating solutions are used which are subject to poor throwing power. These passivated regions can be activated and re-plated at minimal cost by means of brush plating.

### 2.3.6. Adhesion.

It has been reported by Rubinstein(3) that providing sufficient care is taken in preparation and cleaning, adhesion can be as good or better than that achieved by equivalent bath plating. It has also been suggested that on aluminium, chromium and refractory metals, adhesion may be far superior to that achieved by conventional vat plating due to the high current density used in electrolytic cleaning, followed by immediate deposition of the required metal.

### 2.3.7. Hydrogen embrittlement.

Hydrogen embrittlement can be a serious problem in the plating of high strength materials used, for example, in the aircraft industry. Proprietary solutions are available which are claimed to facilitate the deposition of hydrogen free cadmium metal. Sufficient work(7) has been carried out on the hydrogen embrittlement characteristics of brush plated deposits to make them acceptable to the major American aircraft authorities.

### 2.3.8. Repair of worn or damaged components.

Burring or scuffing caused by a bearing rotating in its housing can sometimes be corrected by selectively brush plating the housing back to size. Dinsdale(8) has reported such an application using a tin deposit, as has Bainbridge(9) on the repair of P.V.C. moulding dies with brush plated nickel, copper, and gold. Selectrons Inc., have reported similar applications(10). Prior to such operations, an anodic dissolution treatment using a similar stylus may be carried out to remove rough damaged surfaces.

## 2.4. Disadvantages of Brush Plating.

### 2.4.1. Labour Intensive Operation.

Considerable expertise needs to be gained in order to achieve good results by brush plating.

The pre-plating cleaning sequence must be thorough, hence reliable operators are necessary to obtain successful results. Manual brush plating is a laborious time consuming operation even though the "effective" current density at the region being plated is high. In certain circumstances, for example the plating of cylindrical components, the system can be mechanised but close supervision is still required. Even after considering the highly labour intensive nature of the process, its costs may be justified when coating expensive components or after consideration of some of the advantages listed above.

### 2.4.2. Expensive Proprietary Solutions.

Solution costs are high due to the high concentrations of metal salts used, the incorporation of relatively expensive complexing agents and development costs. The solution is not normally re-used but fortunately the volume of solution required per unit area is not too great. This is influenced by the shape of the component being plated and the coating thickness specified.

### 2.4.3. Choice of absorbent material for wrapping anode

The traditional material used to wrap the anode has been long fibre cotton wool. This has low strength and particularly on a rough surface is quickly worn away. The fibres break and become incorporated in the deposit. Shorting out of the workpiece and anode may also occur if the cotton wool disintegrates. The material chosen must be resistant to the solution employed which may be acid or alkaline. It must be able to withstand the appropriate solution at elevated temperature which may be as high as the boiling point of the solution and it must not contaminate the plating solution.

## 2.5. Materials and Equipment.

### 2.5.1. Special Electrolytes.

Electrolyes developed for brush plating have a much higher metal content than those used for conventional plating. This is essential if high rates of deposition are to be achieved. Since precise control is difficult when brush plating, the solutions must be capable of producing a sound deposit over a wide range of plating variables:-

Temperature. During plating, the temperature of the electrolyte in the immediate vicinity of the anode may reach its boiling point. In these cases where the boiling point is reached, anode design becomes important, as rapid heat dissipation may prevent such increases in temperature. Constituents which may give rise to toxic fumes under such conditions should be avoided in the make up of brush plating solutions.

Variable Concentration. Due to the high speed of deposition, rapid metal ion depletion of the electrolyte takes place around the anode. The solution should be capable of reasonably uniform deposition over a wide range of metal ion concentrations.

Current Density. High and widely varying current densities are experienced during plating. This is due to the small area of contact with the workpiece and the movement of the anode. The solution must be able to give sound deposits under widely differing conditions of current density.

Purity. The purity of all of the constituents of a brush plating electrolyte must be high as even small amounts of contaminents can reduce cathode efficiency and increase the likelyhood of stressed deposits.

Formulations of brush plating electrolytes which comply with the above requirements are seldom published; however compositions of the simpler single metal electrolytes have been recorded(11). Patents covering the formulation of suitable electrolytes have been granted to Rapids(12) for gold, tin-cadmium, lead-indium(13) copper and brass(14), but these involve the use of soluble anodes as a supply of metal ions. Bride(15) has been granted a patent for a chromium electrolyte as have Nobel-& Ostrow(16) for a gold solution.

### 2.5.2. Anodes.

Early brush plating tools consisted of a metal anode wrapped with a rag, but eventually this technique was superseded by the development of more sophisticated anodes and working tools. Some of the earlier developments resulted in nylon bristle brushes with a soluble anode insert but these gave problems due to intense anode polarisation at the high currents used. Inert anodes appeared to overcome this problem with graphite being most popular as it could be easily machined to a variety of shapes and sizes.

Commercial carbon anodes were used in early work but they did tend to become heavily contaminated with metals such as zinc or copper which resulted in

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For brush plating small or inaccessible areas, the anodes may be ground or further machined to provide access.

The earliest method of retaining the electrolyte was to wrap the anode with an acid resistant cloth or rag. Subsequently, a large number of materials have been tried with the object of providing a chemically inert abrasion resistant absorbent. For most brush plating purposes, long fibre sterile cotton batting is claimed to be most suitable, but may be difficult to obtain. It is also important that any ties used to retain the cotton batting should be of a non contaminating nature.

Other wrappings have also proved successful such as polypropylene which provides much better wear resistance and prevents snagging on rough edges. For particularly arduous conditions, the cotton batting can be covered with a cylindrical sleeve woven from polypropylene or 60% polypropylene 40% cotton.

### 2.5.3. Power Supply

The majority of brush plating operations are carried out within the voltage range 8 to 30v, consequently it is necessary to have a power supply providing variable voltage regulation over this range.

Since in brush plating the current fluctuates rapidly between zero and a given maximum, (due to the anode being removed from and replaced onto the workpiece), ammeters are of relatively little value as a means of control. Initially, this is achieved by noting the voltmeter reading. An ammeter may be provided as a secondary check if problems arise. It should be noted that the time taken to produce a deposit of a given thickness can differ significantly depending on the proportion of time spent passing current as opposed to replenishing the stylus with solution.

In modern equipment there is usually a facility provided for current reversal so that the working tool can also be made the cathode and used for etching and cleaning as well as plating. It is also imperative that some form of safety cut-out should be incorporated so that the current is cut off immediately in the event of a short or break down in rectification. This precaution protects both the operator and the workpiece from damage.

## 3. ELECTROCHEMICAL ASPECTS OF HIGH SPEED PLATING

The theorectical aspects of fast rate deposition must be considered with respect to the brush plating technique, in order to understand the mechanisms concerned. Consequently the electrochemical requirements for high speed plating, together with examples of how these are achieved in practice, are outlined below.

When an electrode process occurs at an electrode, its potential departs from its equilibrium or steady state value, and the electrode is said to be polarised. The term overpotential may be used to describe all effects that result in the departure of the potential of the electrode from its unpolarised value. Hence, a change in potential due to concentration(17) is referred to as "concentration overpotential".

On application of an external e.m.f., a current flows at a finite rate and the potentials of the two electrodes depart from their unpolarised values. The potential of the cathode becomes more negative and that of the anode more positive, and the electrodes are said to be polarised.Fig.1. Thus, the polarised potential of the electrode is due to the overpotential associated with one or more electrode processes that are proceeding at the electrode under consideration. Therefore, polarisation is the departure of the potential of the electrode from its equilibrium or steady state value when a reaction proceeds at a finite rate. The various types of overpotential that result in polarisation of the electrode can be classified as follows:

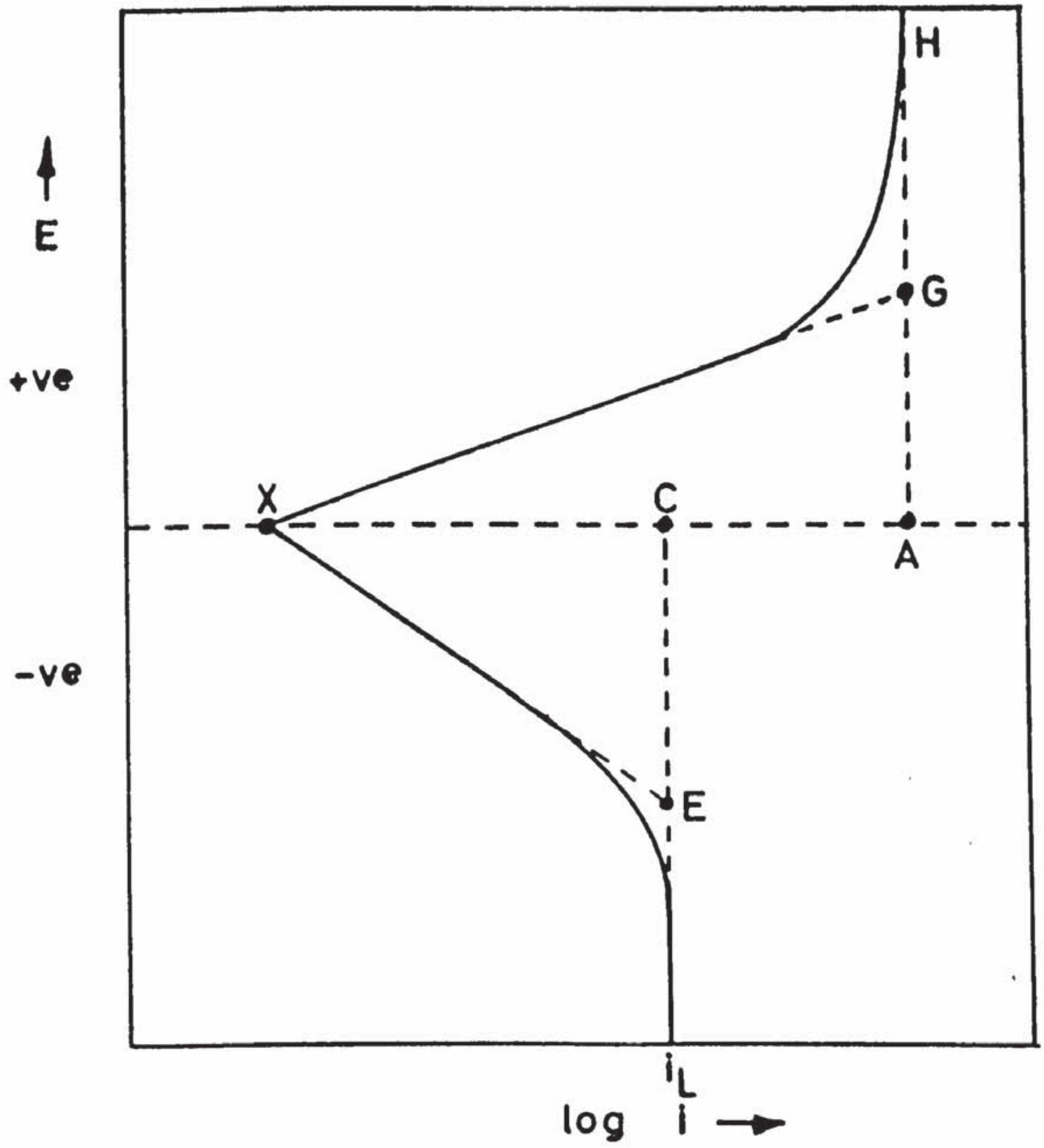
a) Concentration overpotential - due to the change in concentration of metal ions in the vicinity of the electrodes. This accounts for a considerable proportion of polarisation at industrial plating current densities.

b) Activation overpotential - associated with the processes that occur at the electrodes which require activation energy in order to make them proceed. Typical processes involved include hydration or dehydration of ions, discharge of ions at electrodes and the formation of crystals or molecular gases from adsorbed atoms.

c) Ohmic overpotential - additional polarisation effects may be caused by the presence of ionically conducting films, which do not cause changes in reversible equilibrium potentials. These effects may be caused by the oxidation or reduction of organic addition agents.

Fig. 1

Relationship between E and i for a cathodic and anodic electrode process.



d) Resistance overpotential - due to the I-R drop across the main bulk of the solution.

The Nernst equation (i) can be used to demonstrate the effect of concentration on the deposition processes as follows:-

$$E = E^{o}_{M^{z+}/M} + \frac{RT}{zF} \ln a_{M^{z+}} \quad \ldots\ldots\ldots (i)$$

where:- E = Electrode potential at 25°C (V)

$E^{o}$ = Standard electrode potential at 25°C(V)

R = Gas constant = 8.315 J de $C^{-1}mol^{-1}$

F = Faradays constant = 96,486C

z = Valency

$a_{M^{z+}}$ = Activity of charged ions in solution.

Thus, the electrode potential of a metal in a solution of its ions varies logarithmically with the activity of the ions in solution.

As metal is deposited, the concentration of metal ions in the vicinity of the cathode falls, and on increasing current density approaches zero. By reference to equation (i), it can be seen that as the concentration of metal ions approaches zero, the potential becomes more negative, and eventually approaches infinity (Fig.1)(18).

The current density at which this occurs is known as the limiting current density, and it is the raising of this which constitutes the basis for high speed plating. Any increase in current above the limiting current density cannot result in a higher rate of deposition, as metal ions have insufficient time to diffuse through the cathode film. A second process occurs, usually hydrogen evolution.

For a diffusion controlled process(19), it can be shown that

$$i_L = \frac{D_Mz + zFa_Mz+}{(1-t)S} \times 10^{-1} \quad \ldots\ldots\ldots\ldots\ldots(ii)$$

where

$i_L$ = Limiting current density (A/dm$^2$)

$D$ = Diffusion coefficient of $M^{z+}$(cm$^2$/S)

$a_Mz+$ = Bulk activity of $M^{z+}$(g ions/l)

$S$ = Thickness of the diffusion layer (cm)

$t$ = Transport number of $M^{z+}$

$z$ = Valency

From equation (ii) it can be seen that if the limiting current density is to be raised, with a resultant increase in the rate of deposition, there are three possibilities:-

1) Increase diffusion coefficient "D"
2) Increase activity of metal ions "$a_M$"z+
3) Decrease thickness of diffusion layer "S".

"D" - the diffusion coefficient of the metal ions in solution can be raised by increasing the temperature of the electrolyte. In brush plating this is unnecessary as boiling frequently occurs due to the high current densities involved and the relatively small volume of solution in use.

"a" - the activity of the metal ions in solution, may be raised by increasing the metal ion concentration. An example of this is the Ni Speed process developed in the early 1960's by Kendrick and Watson(20,21), where a 600g/l nickel sulphate electrolyte was used to obtain sound nickel deposits at current densities of up to 50A/dm$^2$. High concentrations of metal ions are also used in brush plating solutions as shown in Table I(22), where values are given for both conventional and brush plating electrolytes.

"S" - the thickness of the cathode diffusion layer can be reduced by vigorous agitation. This may take the form of electrode movement, air agitation, ultrasonic vibration, achievement of turbulent flow of electrolyte over the cathode surface, or by mechanical scrubbing of the diffusion layer. In practice, the reduction of the thickness of the cathode diffusion layer is achieved in many ways in conventional plating.

## TABLE I

### Comparison of Metal Concentration of Brush Plated and Conventional Electrolytes.

| Solutions | Approx. Metal Conc g/l | |
|---|---|---|
| | Conventional | Brush |
| Copper (Alkaline) | 20-50 | 60 |
| Gold | 4-12 | 100 |
| Nickel(Acid) | 35-80 | 100 |
| Nickel(Low Stress) | 60-100 | 70 |
| Nickel(Semi bright) | 60-80 | 75 |
| Rhodium | 1.3-2.0 | 20 |
| Silver | 30-95 | 190 |

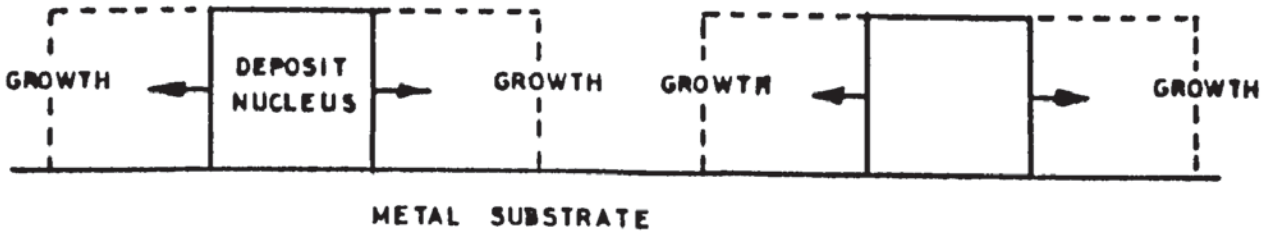
In a process developed by General Motors(23) for the electroplating of car bumpers, an anode-cathode gap of only 12mm was used to raise the speed of a pumped electrolyte and thereby achieve turbulent flow at 4 m/s. Safranek and Layer(24) have demonstrated the importance of turbulent flow, and recommend a minimum solution velocity of 1.25 m/s, below which lamellar flow occured with less effect on the diffusion layer. The Norton abrasives process(25-28) developed by Eisner and Wisdom involved mechanical scrubbing of the cathode surface during deposition by means of a moving abrasive belt or particle impingement. Brush plating can be considered to operate along similar principles, as the surface of the cathode is continually being scrubbed with an absorbent, electrolyte soaked pad, containing the carbon anode.

In a review on the subject of high speed plating, Hart(29) considers the quality of deposits obtained at fast deposition rates. At sufficiently high current densities rough and "treed" deposits may occur, as electrolcrystallisation can take place perpendicular to the substrate (see Fig. 2). This occurs as more energy is available, and the growth of the deposit is not confined to the direction parallel to the substrate surface.

Fig. 2

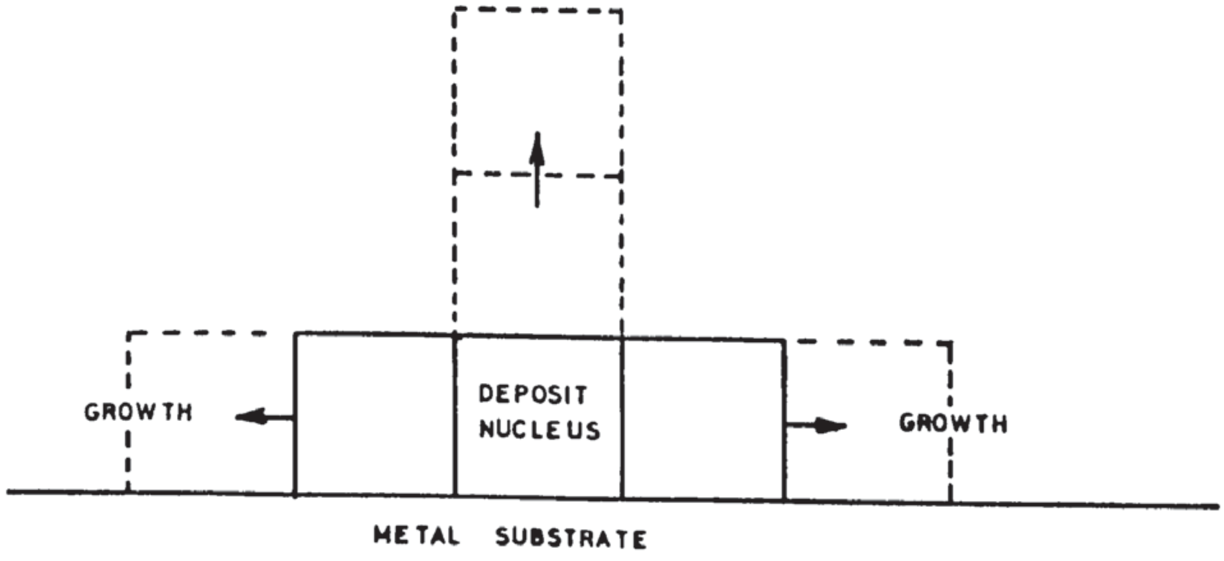
Schematic representation of metal deposition at low and high overpotentials.

LOW OVERPOTENTIALS



2a. Schematic representation of metal deposition at low overpotentials.

HIGH OVERPOTENTIALS



2b Schematic representation of metal deposition at high overpotentials.

Gabe and Robinson(30) have reported this effect when deposition takes place approaching the limiting current density. In processes such as brush plating or the Norton abrasives technique, these surface asperities may be removed during the mechanical scrubbing action of the cathode surface. However in other techniques, employing different methods of diffusion layer reduction, the maximum operating current density may be limited due to deposit roughness.

# 4. REVIEW OF ALLOY PLATING

The development of satisfactory electrolytes for the brush plating of cobalt-molybdenum or cobalt-tungsten alloys required an appreciation of the electrochemical principals involved in alloy deposition. A review of the relevant literature revealed a great deal of information on the conventional vat plating of many alloy systems, but little on brush plating. Hence little is known of the effect of conditions encountered in brush plating on the electrochemical aspects of alloy deposition. The cobalt tungsten and cobalt-molybdenum systems being investigated are of the induced codeposition type, and consequently particular emphasis is given to this classification of co-deposition. Consideration of the possible effects of brush plating these alloys is also included.

## 4.1. Introduction to Alloy Plating

The main reason for producing alloy electrodeposits is to obtain properties superior to those of single metals, e.g. strength, hardness wear resistance or magnetic properties. Replacement of traditional finishes either due to cost, or deposit properties, have been discussed by Krohn et al(31)

Reference is also made to the increasing number of alloy plating systems being investigated.

Lowenheim(32) and Gabe(33) have indicated problems associated with alloy deposition and suggest that only a few of the large number of systems investigated have any commercial potential, as control is difficult even on a "beaker" scale. In some cases, heat treatable alloys can be deposited, but heat treatment may not be possible due to the delaterious effect on the properties of the substrate. A major problem is control of deposit composition. Alloy plating systems are inherently more complex and are susceptible to even small fluctuations in current density, temperature and pH. Commercial control of alloy systems is further complicated by replenishment of the metal content of the bath. For example in binary systems, the two metals must be added to the bath in the same proportion as they are deposited. Some of the techniques used for metal replenishment of plating baths are listed below:-

1) Alloy anodes of the same composition as the deposit. This may not be appropriate as the thermally prepared alloy may not have the same phrase structure as the electrodeposited one, and its anodic behaviour may not be comparable to its cathodic one.

2) Inert anodes with chemical replenishment. This system is seldom used, because of the build up of extraneous ions necessarily added along with the metals.

3) Anodic replenishment of one metal, chemical replenishment of the other. This is the technique used, in the cobalt tungsten and cobalt molybdenum baths developed by Still.

4) Separate anodes of the two metals, hung on the same bus bar. Such systems are seldom practical as unless the metals are very close together in the e.m.f. series it is unlikely they will dissolve at the same potential.

5) Separate anodes of the two metals hung on separate bus bars with separate controls. Close control is possible with such a system but it is somewhat unwieldy.

6) Alternate use of the two metals as an anode. One metal anode is hung on the bar, but after a set period of time removed, to be replaced by an anode of the second metal. Thus the composition of the solution oscillates around a mean. However this technique is seldom used as it requires excessive handling of the anode.

In brush plating, problems associated with metal ion replenishment are avoided, as deposition takes place from a concentrated electrolyte which is then discarded. Recovery of brush plating solutions is seldom practised as the quantities involved in typical brush plating operations are relatively small and hence make replenishment non-viable.

Problems of control increase proportionately with the number of elements in the alloy system, hence binary alloy deposits have received most attention(31) and appear to offer the best prospects for commercial exploitation.

In most cases, the alloys produced by electrodeposition can be considered as true metallurgical alloys as they contain phases which appear on the phrase diagram relevent to their temperature of formation. However two exceptions to this rule concern $^{60/40}$Speculum deposits from the copper-tin system and 63/37 deposits from the nickel-tin system. Work carried out by Rooksby(34) and Raub and Saulter(35) showed a 60/40 Cu-Sn Speculum electro deposit to contain a phase not present on the equilibrium diagram and thermally unstable. Also thermodynamically unstable, an intermetallic phase approaching the formula Ni-Sn was reported by Rooksby(36) and Smart and Robins(37) when investigating 63/37 deposits from the nickel-tin system. Fedot'ev and Vyacheslavov(38) have more recently reported phase structure differences between thermally produced and electroplated binary alloys.

## 4.2. Classification of Co-deposition of Alloys

Brenner(39) split the codeposition of alloys into five types:-

1) Regular codeposition
2) Irregular codeposition
3) Equilibrium codeposition
4) Anomalous codeposition
5) Induced codeposition

Types 1-3 are known as normal codeposition and types 4-5 as abnormal as from elementary considerations it would seem that codeposition of these alloys was not possible.

Regular Codeposition: Deposition is diffusion controlled and as such the effect of plating variables on the metal ion content of the diffusion layer can be predicted from diffusion theory.

Irregular Codeposition: Codeposition is normally controlled by the characteristics of the potentials of the metal against the solution rather than by diffusion. Such solutions contain complex ions, and are markedly affected by the concentration of free complexing agents within the bath.

Equilibrium Codeposition: This is not very common, such solutions are in chemical equilibrium with both parent metals, and the ratio of the metals in the deposit is similar to their ratio in the bath.

Anomalous Codeposition: This type is fairly rare and contains one or more of the iron group metals iron,cobalt and nickel. It is referred to as anomalous as the less noble metal deposits preferentially.

Induced Codeposition: This type is characterised by the deposition of alloys containing molybdenum tungsten and germanium which cannot be deposited alone from aqueous solution. The alloys most readily formed are those with the iron group metals, and the ions present in the bath are termed inducing metal ions (iron group metal ions) and reluctant metal ions (molybdenum, tungsten or germanium metal ions).

## 4.3 Theoretical Aspects of Alloy Plating.

Lowenheim(32) stated two conditions for the useful codeposition of two metals.

1) At least one of the metals must be capable of being independently deposited alone.

2) Their deposition potentials must be fairly close together.

The second condition is of importance as the more noble metal deposits preferentially and this may be to the exclusion of the other metal unless their standard deposition potentials are within about 200mV of each other.

The e.m.f. Series or table of standard electrode potentials is a rough guide for deciding whether two metals can be codeposited from simple salt solutions. It is important to realise that standard potentials represent ideal thermodynamic conditions and do not take kinetic factors into account. Inspection of the table of standard electrode potentials would suggest that no metal more electronegative than hydrogen could be deposited from aqueous solution, because hydrogen would 'deposit' preferentially. But hydrogen actually deposits at a much more negative potential because of hydrogen overpotential, and consequently the potentials of most metals can be reached in aqueous solution without the discharge of hydrogen, or with only partial discharge. Thus the most electronegative metal that can be deposted from aqueous solution is manganese with a standard potential of -1.18v.

Converseley, it may appear from the table of standard potentials that the metals vanadium, molybdenum, germanium and tungsten can be deposited from aqueous solutions as they have electrode potential between -0.253 and -0.09 volts. Especially considering that cobalt with a deposition potential of -0.277v can be readily deposited from similar solutions. Lack of success in the deposition of these refractory group metals is usually attributed to the highly stable metal ion complexes they form in aqueous solution.

If two cathodic processes require about the same potential for their occurence, they may take place simultaneously at about the same rate.
For two different cathodic processes to take place simultaneously;

$$E_1 = E_1^o + \frac{RT}{zF} \ln a_{M_1^{z+}} + P_1 \approx E_2 = E_2^o + \frac{RT}{ZF} \ln a_{M_2^{z+}} + P_2$$

when considering the Nernst equation for each process
Where:-

$E_1$ and $E_2$ = Electrode potentials of metals $M_1$ and $M_2$ at 25°C.

$E_1^o$ and $E_2^o$ = Standard electrode potentials of metals $M_1$ and $M_2$ at 25°C. (V)

R = Gas constant = 8.315 J deg $C^{-1}$ $mol^{-1}$

F = Faradays constant = 96,486 C.

z = Valency

$a_{M_1^{z+}}$ and $a_{M_2^{z+}}$ = Activity of charged ions in solution for metal $M_1$ and $M_2$

$P_1$ and $P_2$ = Terms included for non equilibrium factors (polarisation)

For alloy deposition to occur, the situation breaks down to three possibilities.

1) $E_1^o$ must be about equal to $E_2^o$ so that minor adjustments in the activities of the metals (a) will allow $E_1$ to equal $E_2$

2) If $E_1^o$ does not approach or equal $E_2^o$ large differences in (a) must be provided for.

3) $P_1$ and $P_2$ must be far enough apart to equalise the dynamic deposition potentials.
In most cases in alloy deposition either 1) or 2) provides the mechanism.

There are relatively few cases where the standard electrode potentials are sufficiently close together to allow alloy deposition from simple salt solutions, although tin-lead alloys may be deposited from simple fluoborate solutions and nickel cobalt from sulphate-chloride solutions. In cases where static potentials are far apart, there are two ways in which they can be effectively brought together, only one of which is practical.

First, static potentials can be equalized by lowering the concentration of the more noble metal in the solution. This is not practical as the logarithmic function in the Nernst equation would mean that a very large change in dilution would be needed to alter the deposition potential, by a small amount.

A more practical approach is to equalize static potentials, and thus indirectly the deposition potentials by regulation of the activity of each metal via complex formation. The technique of complex formation is the system adopted in the deposition of many alloys.

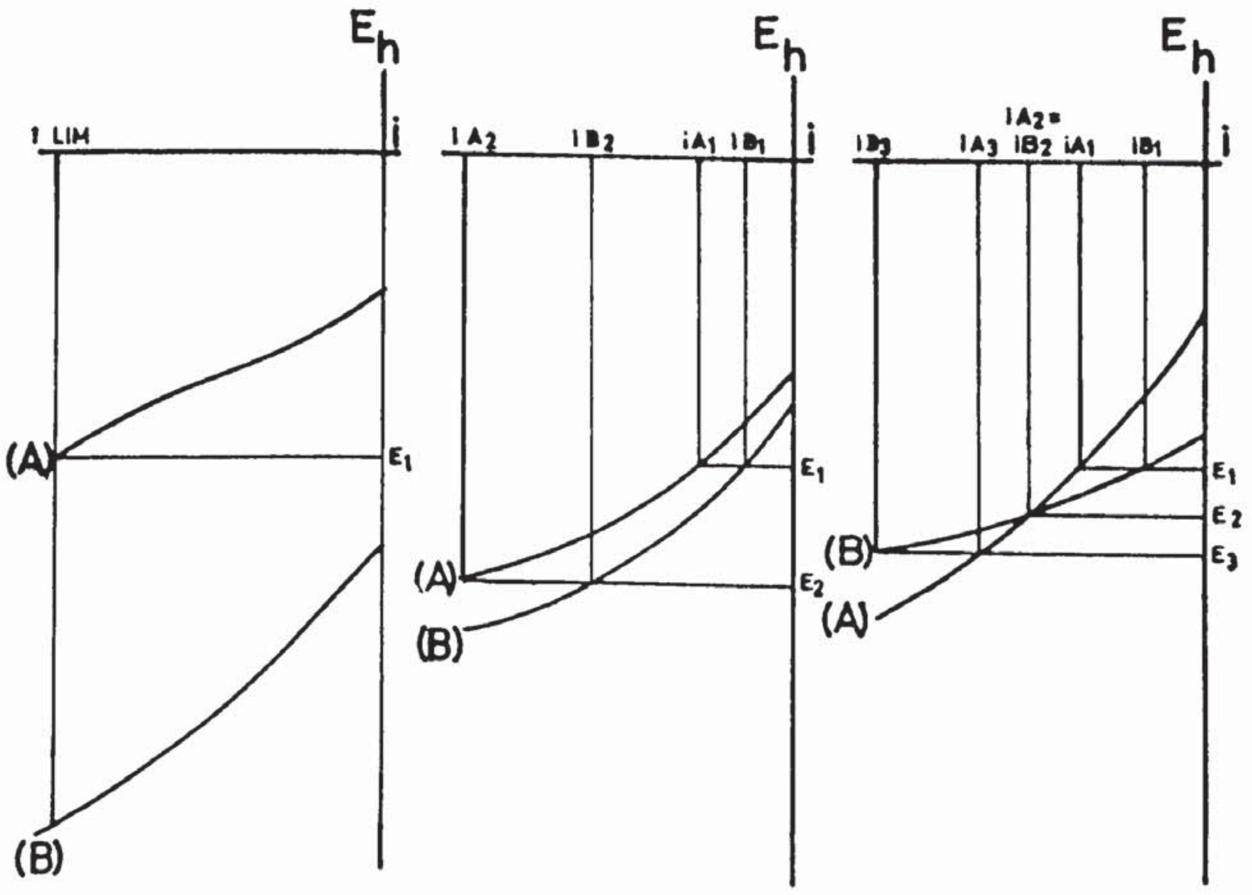
By consideration of each of the cathode potentials - partial current density curves for each component of an alloy system, it may be possible to determine the likely cathode process. Bockris and Reddy(40) Raub(41,42) and Raub and Muller(43) illustrate such curves and explain their evaluation. Three different situations which may be encountered when considering cathode potential - partial current density relations for binary systems are illustrated in fig. 3.

In 3(a) the two curves are far apart, and as such the cathode assumes the discharge potential of the more noble metal. Thus the cathode process consists of the discharge of the cations of metal A; the deposition potential of metal B is not attained. At potential $E_1$ the limiting current density $i_{Lim}$ of the more noble cation is reached and there is no furtherincrease in the rate of discharge of the cations of metal A. Further increases in current density lead to discharge of cation B as the second cathode process. As current density is increased so cation B is increasingly discharged, while deposition of the metal A remains the same on an absolute scale, but decreases on a percentage scale.

In fig. 3(b) the curves are close together and the deposition of the less noble metal is attained at relatively low current densities. Thus co-deposition of metal B is possible before the limiting current density of A is achieved. At the potential $E_1$the partial current densities are $i_{A_1}$ and $i_{B_1}$ and at the potential $E_2 i_{A_2}$ and $i_{B_2}$. The conditions for the simulataneous deposition of two metals are not

Fig 3.

Cathode potential - partial current density curves for the deposition of two cations A and B.



3a 3b 3c

$E_h$ - Cathode Potential

i - Current Density

favourable in such a situation, which is not very common in practice.

Fig 3(c) shows two intersecting cathode potential partial current density curves. At potential $E_1$, the partial current densities are $i_{A_1}$ and $i_{B_1}$ with ($i_{A_1} > i_{B_1}$). At potential $E_2$ the partial current densities are equal ($i_{A_2} = i_{B_2}$), thus the current efficiency for both A and B is 50%. Above potential $E_2$, $E_3$ for example, the partial current density $i_{B_3} > i_{A_3}$. This means that the current efficiency with respect to the cation A decreases. In practice, various values for current efficiency may be found depending on the relative positions of the cathode potential-partial current density curves.

It should be noted that the above considerations apply to the deposition of alloys only when the cathode potential-current density curves of the individual metals do not interact and modify each other as a consequence of simultaneous discharge. However, this is rarely found to be the case. Raub and Muller(43) give many examples of cases where prediction of likely cathode processes by cathode potential-partial current density curves has proved successful.

Thus prediction of alloy deposition behaviour is difficult in the controlled conditions of conventional bath plating. During brush plating, the

the anode and cathode are constantly being separated for solution replenishment and as such there are wide variations in current density. Boiling of the electrolyte is not uncommon and introduces a further complication in a system already difficult to investigate.

## 4.4 The Effects of Plating Variables on Alloy Baths of the Anomalous and Induced Codeposition Type.

As there is little published literature available on the process of brush plating from alloy solutions, it is difficult to predict the effect of plating variables on the systems under consideration. The following discussion of behaviour in conventional vat plating may serve as a rough guide when attempting to make such predictions, but it should be noted that the unfamilar conditions encountered in brush plating may lead to erroneous suppositions.

### Effect of metal ratio

The effect of the metal ratio of the bath on the alloy content of the deposit from the anomalous codeposition of cobalt-nickel has been investigated by numerous workers but the results obtained were similar. Piontelli et al(44,45) using a sulphamate bath and Glasstone et al(46,47) using a sulphate bath found the small percentage of cobalt present in the bath resulted in a high percentage of cobalt in the deposit.

Such an effect is to be expected due to the anomalous nature of codeposition (ie the less noble cobalt deposits preferentially). The concentration of alloying elements in induced codeposition deposits indicate that initially the baths behave in a similar manner to the anomalous type in that low metal ion concentration of the reluctant metal in the bath produces higher concentrations of reluctant metal in the deposit. Typical examples of this are the iron-tungsten, cobalt-tungsten and nickel-molybdenum alloys from acid solutions by Holt and Black(48), Holt et al(49) and Seim and Holt(50) respectively. Cobalt-tungsten and cobalt-molybdenum systems investigated by Still(51) show that increases of concentrations of reluctant metal ions in solution, initially result in almost linear increases in deposit concentrations. However in both cases a limit is reached where a further increase in the concentration of molybdate or tungstate in solution does not result in greater concentrations of alloying element in the deposit. This is of particular significance, as the solutions used in this investigation utilize similar basic components to those used in Still's work.

## Effect of Total Metal Content

The total metal content of the bath has little effect on the composition of alloys of the anomalous codeposition type. The work of Glasstone and Speakman(46) and Fink and Lah(52) show that in a simple sulphate bath for the deposition of cobalt-nickel alloys an increase in total metal content of approximately seven times produces only a slight increase in cobalt content of the deposit. Although there appears to be no such data on cobalt molybdenum and cobalt tungsten from acid baths, it would be reasonable to assume that the high speed plating conditions during brush plating would necessitate high metal concentrations in order to give high speed and efficiency.

## Effect of complexing agents.

Although it is possible to produce cobalt-nickel alloys from complex baths there is little point in doing so as simple salt baths produce adequate results. Consequently work in this field is almost limited to that carried out by Sree and Rama Char(53,54) on the deposition of the alloys from a pyrophosphate bath containing ammonium citrate. The effect of the complexing agents on the bath was found to inhibit the deposition of cobalt with the result that the metal ratio of cobalt-nickel in the deposit was almost the same as in the bath over a wide range of current density.

The effects of complexing agents on induced codeposition have only been studied with respect to neutral or alkaline baths and are a doubtful guide as to the effects of complexing agents on the Co-Mo and Co-W, acid electrolytes. Also, due to the very high temperatures and current densities involved in brush plating it is likely that comparison with bath plating solution would be misleading.

## The effect of pH

The effect of pH on the anomalous deposition of cobalt-nickel is that the cobalt content of the deposit increases slightly at low pH value. This has been reported by Glasstone and Speakman(46,47) when investigating the sulphate bath.

The general effect of raising the pH in cobalt molybdenum and cobalt-tungsten acid baths was to increase the cathode efficiency. Still(51) demonstrated this, with a sharper increase in efficiency with pH being noted for cobalt-tungsten baths than for cobalt-molybdenum. The overall level of efficiency for cobalt-molybdenum baths was reported to be higher than for cobalt-tungsten. In brush plating, it is possible that due to the high current densities and temperatures encountered, a reduction in pH would lead to the low cathode efficiencies and low levels of molybdenum or tungsten in the deposit.

### The effect of current density on the composition of the deposit

In general the cobalt content of the nickel cobalt alloys deposited from simple salt baths is found to decrease with increasing current density. However, due to the anomalous nature of this system the effect of current density on the deposit may be divided into various current density levels. At low current density levels, Glasstone and Speakman(47) and Piontelli and Patuzzi(44) found that the alloy deposited normally (ie nickel deposited preferentially being more noble). Then at a higher current density (approximately 1-3 A/dm$^2$) the cobalt content in the deposit reached a maximum. This maximum was reached at approximately 1A/dm$^2$ in the case of the sulphate bath of Glasstone and Speakman(47) and at approximately 3A/dm$^2$ in the case of the sulphamate bath of Piontelli and Patuzzi(44). Higher current densities were investigated by Young and Struyk(55) (chloride bath) and Young and Egerman(56) (sulphate bath). These results showed that the deposition of the alloy is initially normal and that anomalous deposition is only fully achieved at higher current densities.

The relationship between current density and the composition of the deposit for the induced codeposition of tungsten and molybdenum varies with the type of bath employed. In general an increase in current density will reduce the percentage of the reluctant metal present in the deposit. This is true of all the alloys deposited from acid type baths as reported by Holt and co-workers(48,49,50,59) when depositing tungsten and molybdenum with iron, cobalt and nickel, and most of those obtained from alkaline baths.

In brush plating, it is extremely difficult to predict the effect of the large variations in current density which occur due to the removal and replacement of the stylus on the workpiece. Rubinstein(27) gives an indication of the order of magnitude of current densities involved in brush plating as compared with those in bath plating (Table II).

## TABLE II

## A Comparison of Current Densities in Brush and Conventional Plating.

| Solutions | Current Density A/dm$^2$ | |
|---|---|---|
| | Conventional | Brush |
| Copper (Alkaline) | 1.0 - 7.5 | 150.0 |
| Gold | 0.5 - 5.5 | 40.0 |
| Nickel (Acid) | 1.0 -10.0 | 100.0 |
| Nickel (Low Stress) | 1.0 -10.0 | 100.0 |
| Nickel (Semi-bright) | 1.0 -10.0 | 150.0 |
| Rhodium | 1.0 - 8.0 | 150.0 |
| Silver | 5.0 - 1.0 | 1250.0 |

Insufficient work has been carried out with alloy deposition at such high current densities in order to predict the effect.

Due to the nature of the brush plating technique the current density cannot be controlled, even within "reasonable" limits and thus in brush plating, current density is not a practical means of control.

## Effect of Bath Temperature on Composition of Deposit.

The relationship of bath temperature and alloy content for induced codeposition is surprisingly consistent in view of the inconsistencies normally associated with these systems. In general a rise in temperature leads to a slight increase in alloy content of the deposit as would be expected from diffusion theory. This effect has been reported by Holt and Black(48) when depositing cobalt-iron alloys from an acid bath. In addition to the slight increase in alloy content a rise in temperature also improves the quality of cobalt-tungsten electrodeposits as reported by Golts and Kharlarnov(58), but had no noticeable effect on the quality of cobalt molybdenum deposits obtained by Ernst et al(59).

As with current density, temperature cannot be considered as a useful means of control whilst brush plating.

It is conceivable that the thermal properties of the work piece may have a considerable effect on the properties and composition of the deposit produced. For example, when depositing on to thin brass sheet, higher temperatures could be expected at the surface, as compared with plating a large forging die where the greater metal mass would act as a heat-sink and lower the temperature of deposition. In brush plating, two further variables exist which also may effect the composition and quality of deposit. Firstly, the speed of stylus movement may be of particular importance due to the interuption of surface layers which exist in conventional bath plating. Also the pressure applied to the stylus when plating would appear to have some effect on the process.

Thus, the mechanisms involved in the conventional bath deposition of alloys are not fully understood. With regard to the process of brush plating, little information has been published with respect to deposition of a single metal. Work carried out on the brush plating of alloys has always been highly commercially orientated and as such is seldom published. However, even if such information were generally available, it is doubtful if it would be of much use in the understanding of alloy deposition by brush plating.

# 5. ASPECTS OF WEAR

The process of wear can be considered as one of the most wasteful aspects of modern industrial society. In every system of engineered components, wear takes place with the inevitable cost of replacing or refurbishing worn parts. Such operations are expensive, but when the lost production is taken into account wear becomes of paramount importance. As labour costs have risen sharply in recent years, the cost of "down time" caused by the effects of wear have also increased; consequently many branches of manufacturing industry are investigating methods of alleviating such problems.

Wear can also be considered as one of the most complex subjects to investigate, as all engineering systems are different and consequently many mechanisms and combinations of mechanisms exist. For example, in hot forging, severe wear takes place due to metal movement over the die, mechanical fatigue and plastic deformation occur due to the element of impact involved and thermal fatigue occurs due to the temperature cycle encountered by the dies. Such a combination of factors make the assessment of die life and wear performance extremely difficult.

## 5.1. Types of Wear

As most wear systems are complex multiwear mechanism processes, investigators have considered simple systems with the object of gaining basic information about the various types of wear which take place. The main types of wear which occur are presented in the following discussion, along with their relevance to the process of hot forging and cold pressing.

## 5.2. Adhesive Wear

When two surfaces come into contact with each other, they meet at their asperities. Wear by adhesion occurs when such surfaces slide against each other, and the pressure between the contacting surface asperities is high enough to cause local plastic deformation and adhesion. Asperity deformation occurs until such time that the real area of contact has increased enough to support the load, thus causing an increase in the area over which adhesion can take place as sliding continues. Eventually the adhesively formed junctions rupture at their weakest points, usually resulting in metal transfer from one surface to the other. However, if particles remain undislodged from their adhesive junctions they can act as agents for subsequent abrasive wear.

Adhesive wear has been the subject of many investigations(60,61,62), but the process of wear particle formation has not clearly been established, although investigated by Bowden and Tabor(63), Tabor(64) and Tabor and Landheer and Zaat(65). The effect of load and speed variations has been demonstrated by Welch(66) who defined mild wear (oxidation) and severe wear (oxidation and metal removal). Welch reported the sharp transition between these two modes of wear to be directly dependant on load and speed. Archard(67) and Rabinowicz(68) have commented on the inability of Welch's work to take account of variations in microstructure.

Due to the pressures and temperatures involved in hot forging, the wear which takes place can almost certainly be classed as severe, with oxidation processes occuring at the die surface together with metal removal.

### 5.3. Abrasive Wear

Typified by the example of a metal surface being scratched by a conical indenter, abrasive wear has also been the subject of many investigations. Kruschov(69) and Kruschov and Babischev(70) attempted to investigate abrasive wear by testing Commercially pure metals (Fe, Cu, Pb, Ni, W, Mo, Al) in their annealed conditions. They found that their wear resistance (reciprocal of wear volume) decreased linearly with load and sliding speed, but increased with bulk hardness.

Serpick and Kantor(71) and Popov(72) demonstrated the effects of volume fraction of carbides and microstructure in steels. Two important implications of this early work are as follows:-

1) At a given hardness, the wear resistance of a heat treated steel is less than that of a pure metal treated to the same hardness.

2) Steels of different compositions heat treated to the same hardness do not show the same wear resistance.

Therefore, it can be concluded that abrasive wear resistance is not solely a function of hardness or microstructure, but a complex function of both.

The "scales" produced during hot forging lead to a certain amount of abrasive wear. It is important to note that Still(51) found that in most cases of die coatings exhibiting low wear rates, scale adhesion was poor or non existant.

## 5.4. Deformation and Erosive Wear

In commercial sand blasting operations, the interior of the machines used for such processes undergo severe erosive wear by the impingement of the sand particles. Erosive wear is usually characterised by the impingement of a fluid; or a continuous stream of high velocity low mass particles. When low angles of impact are concerned, a situation occurs similar to abrasive wear, but high angle impact can lead to surface deformation. Fatigue effects, crack initiation and crack propagation all play important parts in erosive wear, depending on the system under consideration.

In forging, scale and wear debris can strike the die surface, and depending on angle of impact can lead to resultant abrasive type wear or sub-surface deformation. Erosion is one of the many important die failure mechanisms in hot forging.

## 5.5. Delamination theory of Wear

Suh(73) proposed a mathematical treatment of wear based on dislocation theory, plastic deformation and fracture of metals near a surface. Predictions based on the mathematical model so formed have been confirmed both analytically and experimentally. The most significant features are as follows:-

1) The wear rate (or volumetric wear) depends on or is influenced by the surface topographical features of the metals in contact.

2) Wear rate is proportional to the normal load.

3) Wear rate does not depend directly on hardness.

4) Above all, wear rate depends on material structure and properties.

This would appear to be the most complete analysis of the theoretical aspects of wear to date and is largely confirmed by consideration of practical wear systems.

With respect to hot forging, die life can be improved by improving the finish of the surface of the forging dies. In general, forging at lower loads leads to less wear and less cracking. Although Still(51) demonstrated some correlation between deposit hardness and wear resistance for cobalt-alloy coatings, this was by no means complete or predictable. It is suspected that structural changes in the deposits had a great bearing on the improvement in wear performance.

## 5.6. Wear Testing

Conventional wear tests (Falex, pin and disc, block and disc, or Amsler) have severe limitations when used to predict wear behaviour in actual industrial conditions. Such tests are useful when comparing a number of materials with each other, but their value is doubtful in absolute terms. This is mainly due to the fact that operating variables such as temperature cycles, repeated impact, and effect of scale cannot be sucessfully reproduced.

When considering hot forging, a far more satisfactory method of wear testing is to reproduce as near as possible the conditions encountered, by using a small scale hammer or press(74,75,76). A far more representative wear test may be carried out with such a system, the results of which tend to bear far more correlation with industrial practice.

By far the best technique of evaluation of coatings systems is by an actual industrial trial, as even the most proficiently set up laboratory experiments cannot accurately reproduce service conditions. In industry, different forge operators use different techniques and it is not unknown for workers to forge "cold" billets. Dennis, Lodge(77) and the present author have carried out such trials and in spite of many of the practical difficulties involved have gained meaningful results. Extremely careful interpretation of such results is needed, as by definition, industrial trials cannot be carefully controlled and labour relations and industrial politics can sometimes mask a "good" or "bad" result.

## 5.7. Wear of Hot Forging Dies

Hot forging dies encounter some of the most arduous service conditions found in industrial practice. Wear takes place due to the effects of elevated temperature, fatigue, scale, thermal and mechanical shock. Consequently dies are known to wear out or fail in service as a result of any combinations of the following:-

1) General erosion of the die leading to out of tolerance forgings.

2) Stress cracking on sections of the die containing stress raisers.

3) Thermal fatigue cracking.

4) Sticking of the forging within the die cavity is due to cracking caused by mechanisms 2 and/or 3. Subsequent additional damage to the die may be caused by the use of excessive force when removing the forging.

5) Excesssive use of lubricants.

6) Erosion of the 'flash lands' leading to a thick forging "flash" which cannot be removed easily.

7) Malpractice in the forging shop, ie. forging of cold billets etc.

Improvements in die materials and coating processes will be to no avail if good forging practice is not adopted ( see points 4,5 and 7). Die design is also an important consideration as stress raisers can be avoided (point 2). Thus points 1, 3 and 6 are left and it is those that most readily respond to improved materials/surface treatment. Isakpobeje(78) investigated the failure mechanisms experienced by forging dies after a variety of surface treatments had been evaluated. These results were obtained after evaluation of coatings and treatments on the laboratory scale hot forging test (section 14.2). In this work one of the most significant factors leading to a reduction in useful life was the quality of surface finish of the machined die. It was also concluded that the application of a cobalt molybdenum deposit on to B.H 13 and No.5 die steels delayed thermal fatigue cracking at working temperatures below 750°C.

# 6. IMPROVEMENT OF DIE LIFE IN HOT FORGING AND COLD PRESSING.

There are two routes by which the useful life of dies may be increased. Firstly, the choice of die steel can be directed toward the more highly alloyed sophisticated steels, which, because of their improved toughness and wear resistance, are better able to withstand forging processes. However, with the majority of the more highly alloyed die steels, increased toughness invariably means difficult machining and higher labour costs for the manufactured dies. Under certain circumstances the increase in cost is justified by selection of a more satisfactory 'bulk' die material, but in most cases the highly alloyed steels do not prove to be commercially viable.

The second route by which die life may be extended is by some form of surface modification. In many cases, this proves to be the preferable option as existing dies can be treated, whilst new dies can still be manufactured from the cheaper die steels. Extension of die life in such a way can also prove considerably more convenient as it does not require the expensive machining of materials which are difficult to machine.

## 6.1. Coating Requirements for Hot Forging Dies.

It is important to consider requirements of the adopted surface treating system as well as the properties needed to extend die life. Ideally, the system should be cheap, and require little capital expenditure. It should be quick and preferably be a continuous rather than a batch process. The system should also not be restricted as to the size shape or composition of the component to be coated. Adhesion should also be of a high order. Consequently there are few processes which can claim to posses all the aforementioned attributes, and hence the research into new techniques and systems.

If the properties of the coatings are considered with respect to their ability to improve die life, even fewer commercially available processes appear suitable. The coating could be hard to reduce erosion or soft to act as a solid lubricant. In either case they can be coherent or microdiscontinuous, the latter helping to hold die lubricants on the die surface if they are used. Adhesion of the coating is particularly important in hot forging as is a high fatigue limit and a coefficient of thermal expansion compatible with the substrate. Low internal stress is also important as cracks initiated in the coating may propagate into the bulk material.

## 6.2. Coating Requirements for Cold Pressing.

The loading on a cold working tool is much less than that of a hot forging die, with no thermal cycling and little erosive wear, so that failure is unlikely to be from mechanical breakdown of the die. Instead, dies fail due to pick-up of metal on the die and subsequent scoring of the workpiece. The coating is therefore required to have a low mutual solubility with the material of the workpiece in order to reduce the cold welding. In addition, a natural lubricity, with a low shear strength would be a great asset.

## 6.3. Review of the Available Treatments and Coatings.

Although there is an extensive range of coating systems marketed for wear resistant applications, it is intended to consider only those coatings which may be useful for metal working tools and to comment briefly on their advantages and disadvantages.

6.4. Thermochemical Treatments - such as carburising, nitriding carbonitriding and nitrocarburising, all rely on the production of an alloy or intermetallic layer followed by the diffusion of the layer into the substrate. Heating of the component is inevitable, with the attendant risks of distortion and/or tempering back the die steel.

In carburising, the component is held in the austenitic region at about 900°C for several hours in a carbon rich environment, followed by quenching or controlled cooling. The more modern techniques(79,80) of gas carburising claim close control of tolerance and case profile(81), but the main drawback of such systems is a lack of hardenability of the case when large components are treated with slow effective quenching rates.

Components treated by nitriding have less chance of distortion as nitriding takes place at only 510-530°C in a nitrogen rich gaseous atmosphere. using low alloy steels, hardnesses of 650Hv can be obtained whilst special alloy nitriding steels can give surface hardnesses over 1000Hv(82). This hardness is due to the formation of alloy nitrides on the surface and is not the result of a quenching operation. The surface layer is harder when produced at lower temperatures, but this gives rise to long treatment times of up to 96 hours for conventional gas nitriding(83). Ion or plasma nitriding, in which the nitrogen ions are accelerated electrically into the surface of the workpiece, is much faster and is claimed to produce a better quality coating.(84)

Carbonitriding is similar to carburising with respect to the temperature of operation, but involves the incorporation of nitrogen in the carbon rich case. It is said to overcome hardenability problems with large sections, but is not popular due to the relatively high temperature of operation.

Nitrocarburising is more popular, as it involves holding the component to be treated at 540-600°C over a period of 1-3 hours(83). However treatment takes place in a cyanide salt bath and as such is discouraged on environmental grounds.

In addition to the more usual carbon and nitrogen diffusion techniques, other elements are also diffused into the surface of the substrates. Lodge(77) has reviewed many such treatments which can diffuse aluminium, boron, chromium vanadium titanium niobium, silicon and manganese. These, as with all thermochemical treatments suffer from distortion problems and/or long treatment times.

6.5. Hybrid Processes may be regarded as two stage systems where a coating is applied and diffused into the surface.

Diffusion of an electrodeposited coating is typified by the Stanal process, where a tin alloy is diffused into treated surfaces with resultant surface hardnesses up to 900Hv. Although it has good wear resistance, it is thought that it would have poor cracking resistance if used on a hot forging die or for similar applications. Similarly the Foreg process utilising a copper/tin alloy is unlikely to withstand the severe conditions encountered by forging dies(83). Sprayed and diffused coatings claim to overcome the adhesion problems frequently encountered with conventionally sprayed coatings(85), although very little information has been published on this system.

## 6.6 Chemical and Physical Vapour Deposition Techniques.

In Chemical Vapour Deposition (CVD) the coating is formed by a chemical reaction between gaseous reactants introduced into a chamber containing the heated components. The process is capable of depositing a wide range of coatings which may be metals, carbides, nitrides, oxides and bromides up to a thickness of 50 µm. Such coatings can be very hard, up to 4000Hv and their chemical inertness gives some measure of corrosion protection(86,87) Adhesion is good, due to the diffusion of the coating into the substrate, and the system has excellent throwing power. It is essentially a "soft" vacuum technique, being carried out at 5-500 torr. However, in certain cases(88) substrates can be heated to 2000°C; a factor which limits the process to certain substrates and can create distortion problems on others. High alloy steels are invariably used as a substrate for this process.

There are also a number of Physical Vapour Deposition processes which generally operate at a much higher vacuum (with all the attendent costs and problems). The most popular PVD system is that of ion-plating, where the coating vapour encounters an electrical plasma around the substrate, and is accelerated toward the surface to be coated. The coating rate is rapid, and excellent adhesion is claimed(89). Although there are many other vacuum techniques for application of coatings, few have been developed to a stage sufficiently useful for commercial viability.

6.7. <u>Electroless</u> deposition involves the immersion of the article to be plated in a solution of the appropriate metal ions. An external emf is not applied; deposition occuring due to a chemical reduction reaction catalysed by the presence of freshly deposited metal. Thus the coating is built up provided that there is an ample supply of metal ions in solution, and the catalysis of the reduction process continues. The range of coatings which can be deposited is more limited than by electrodeposition, the most noticeable omission being chromium. Most of the electroless nickel alloy deposits suffer the same limitations with regard to galling as the pure metal, however nickel/phosphorous deposits have been produced from electroless(96) baths with plated hardness of up to 500Hv. Simple heat treatment improves this to over 1000 Hv, but the hot hardness of these alloys limits their maximum operating temperature to below 300°C(96). It is claimed that electroless nickel-boron alloys have similar properties to the nickel phosphorus alloys, but with improved hot hardness.(97)

6.8 <u>Electrodeposition.</u> Coherent coatings of most metals, many alloys and some composites(90,91) can be obtained by electrodeposition. Although a wide variety of electrodeposits are used to improve wear resistance in various environments, the ones potentially useful for the coating of hot forging dies are chromium, nickel and cobalt, their alloys and composites.

Chromium is the most widely used electrodeposit despite its many apparent disadvantages. The solutions have low cathode current efficiency resulting in the danger of hydrogen embrittlement and the need for high plating current densities to produce worthwhile coating thicknesses. The deposit has poor throwing power, and is highly stressed and cracked, although in some situations(90), cracking helps to retain surface lubricants. In non reducing conditions, the oxide skin has a low coefficient of friction(92) and can be considered a useful wear resistant coating in areas where abrasive wear is the dominating wear mechanism. However, it may be suspect in situations where shock, fatigue, impace or chloride attack may be encountered.

Few alloys of electrodeposited chromium have been developed because of its electrochemical characteristics and no commercially significant composites of chromium are known. One process which may be of use for low temperature working is a P.T.F.E./chromium composite in which the P.T.F.E. is cryogenically fixed into the enlarged microcracks in the chromium deposit.(93)

Nickel can be electrodeposited from various baths under controlled conditions, but its use is limited for use on hot forging dies, due to its tendency to form a low melting point slag with iron oxides above 300°C(94) and to gall when in contact with steel iron or nickel surfaces(91). Consideration of the previous use of electrodeposited cobalt alloys is included in section 7.

A considerable amount of work has been carried out recently on composites based on either electrolytic nickel or electroless nickel/phosphorus alloys. A variety of codeposited particles have been tried ranging from diamonds(98) and hard ceramics(94,99,100) to metals(99) and plastics(100). The properties of the composite vary with the metal/alloy/particle combination chosen, but most are hard and can be plated to a reasonable thickness. The electrolytic nickel composites appear to be too soft for abrasive or rolling wear conditions, but the electroless composites can be heat treated to hardness in excess of 1,400Hv. Little is known about their hot hardness or their resistance to hot iron oxides.

## 7. PREVIOUS USE OF ELECTRODEPOSITED DIE COATINGS

Chromium plating of carbon steel forging dies is used in the Sheffield cutlery industry, where shallow simple die impressions are treated. However, there is a limitation on the configuration of die which can be chromium plated due to the inherent properties of the chromium plating system,particularly poor throwing power. There have also been some reports of catastrophic cracking of chromium plated hot forging dies.

The cobalt-tungsten and cobalt-molybdenum systems appear to offer the best possibilities for improving die life as a number of investigations have been made into their use. A patent was granted to Prosser(102) in 1971 for the deposition of a cobalt-tungsten alloy used for the extension in life of dies made from 5% Chromium steel. Still(51) carried out further work on both systems, and found that considerable improvements in die life could be obtained when cobalt alloys containing either 4% molybdenum or 8% tungsten were used. More recent work by Dennis and Lodge(77) has shown improvements in die life of up to 100% were possible when using deposits from solutions based on those of Still.

With regard to the use of electrodeposited coatings for use on cold pressing tools, there appears to be little recorded literature. In the automobile industry, the cold pressing dies used for producing car body panels are seldom treated, but a number of materials and heat treatment conditions are used. Electrodeposition on such substrates is complicated by the ingress of drawing lubricants into the surfaces to be treated with resultant plating problems. However, Dennis(77) and Lodge have bath plated a number of die segments using cobalt molybdenum alloys; with limited success.

## 8. PREPARATION OF BRUSH PLATING EQUIPMENT

### 8.1. Selection of Stylus Handle

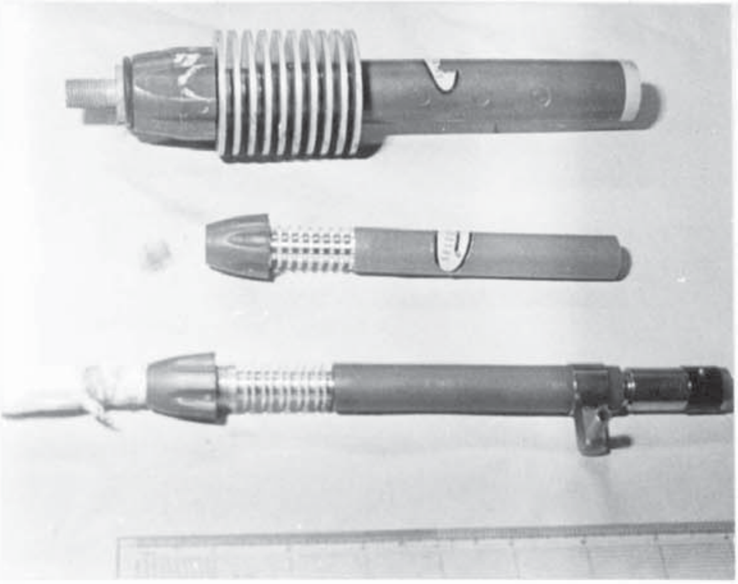
The styli handles chosen for this work were selected from a range of commercially produced brush plating equipment. Fig. 4(a) illustrates some of the various sizes and types of handle available. A large stylus may be selected when there is a need to plate a great area at high speed. Also illustrated is a "rotating head" stylus which may be turned by means of a flexible drive; for use in confined areas where physical movement of the entire stylus is difficult. For the majority of experimental work carried out in this project a medium size stylus handle was chosen as this was found suitable for both laboratory scale plating trials, and the plating of hot forging dies and tools.

### 8.2 Anodes

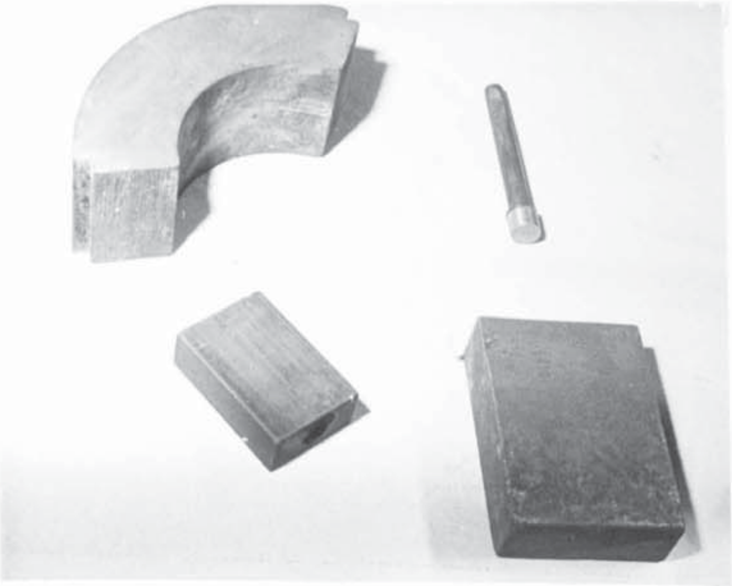
There are a great number of commercially produced carbon anodes available for brush plating. They are often shaped to various forms and sizes in order to carry out specific brush plating operations. Fig. 4(b) shows a typical selection which may be used for a wide range of industrial applications. The smaller "rod" anodes are attached to the stylus handle by means of a locking collar, whilst the larger anodes

Fig 4.

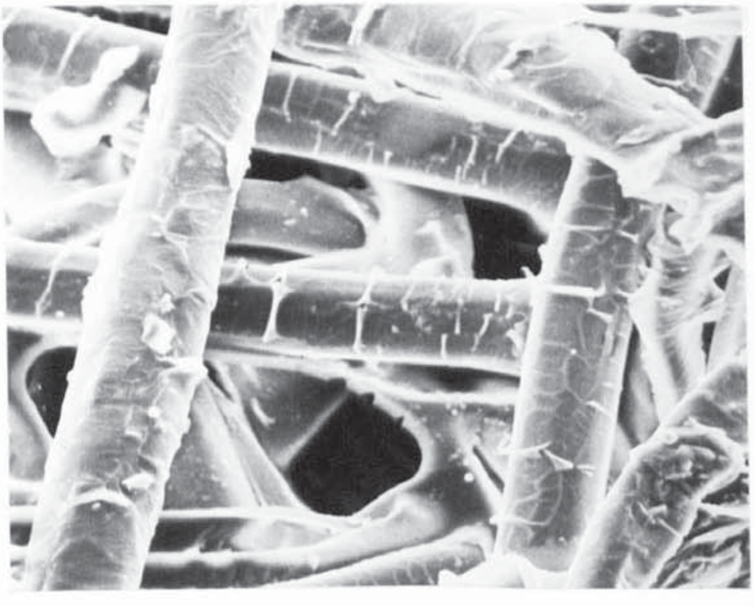
Brush Plating Equipment



4a
A selection of stylus handles.



4b
Carbon anodes.



4c
Scanning electron micrograph of felt used to wrap anode x 300.

are drilled and threaded to take a retaining bolt. For the majority of the work carried out, a "rod" anode 80 mm x 8 mm diameter was used, which was found suitable for most plating operations. Occasionally, these rod anodes were machined to a smaller size in order to allow confined areas to be plated. In cases where very small areas had to be plated, a platinum/ iridium alloy stylus was used 80 mm x 3 mm x 1mm.

## 8.3. Stylus Preparation

After the anode was attached to the stylus handle the assembly was "wrapped" ready for use. Long fibre cotton wool was wrapped around the anode, and held in place with cotton "tube" gauze. A convenient way of performing this operation involved sliding the cotton gauze over the wrapped anode by means of a proprietary finger bandage applicator. Although this is considered suitable for many purposes, in the present work, a further covering was used in order to prevent snagging of the cotton gauze, particularly on machined surfaces. Selection of such a covering proved difficult, as it must tolerate acids and alkali's at high temperature without degredation. Ideally, it must also have some abrasive action to provide a scrubbing effect. After experimentint with many such coverings, the one adapted for use consisted of a nylon-polypropylene felt mixture. An SEM photograph Fig. 4(c) shows the open nature of the felt with its consequent ability to retain electrolyte. This covering was held in place by means of rubber bands. Fig 5. illustrates an "exploded" view of a made up stylus ready for brush plating. The component parts are shown, namely the anode, handle, long fibre cotton wool, cotton gauge and felt cover.

When brush plating on steel substrates a number of cleaning and etching operations are carried out, consequently a stylus is prepared for each stage of cleaning as well as for the actual plating operation. Thus, up to six styli may be required to perform a single brush plating sequence.

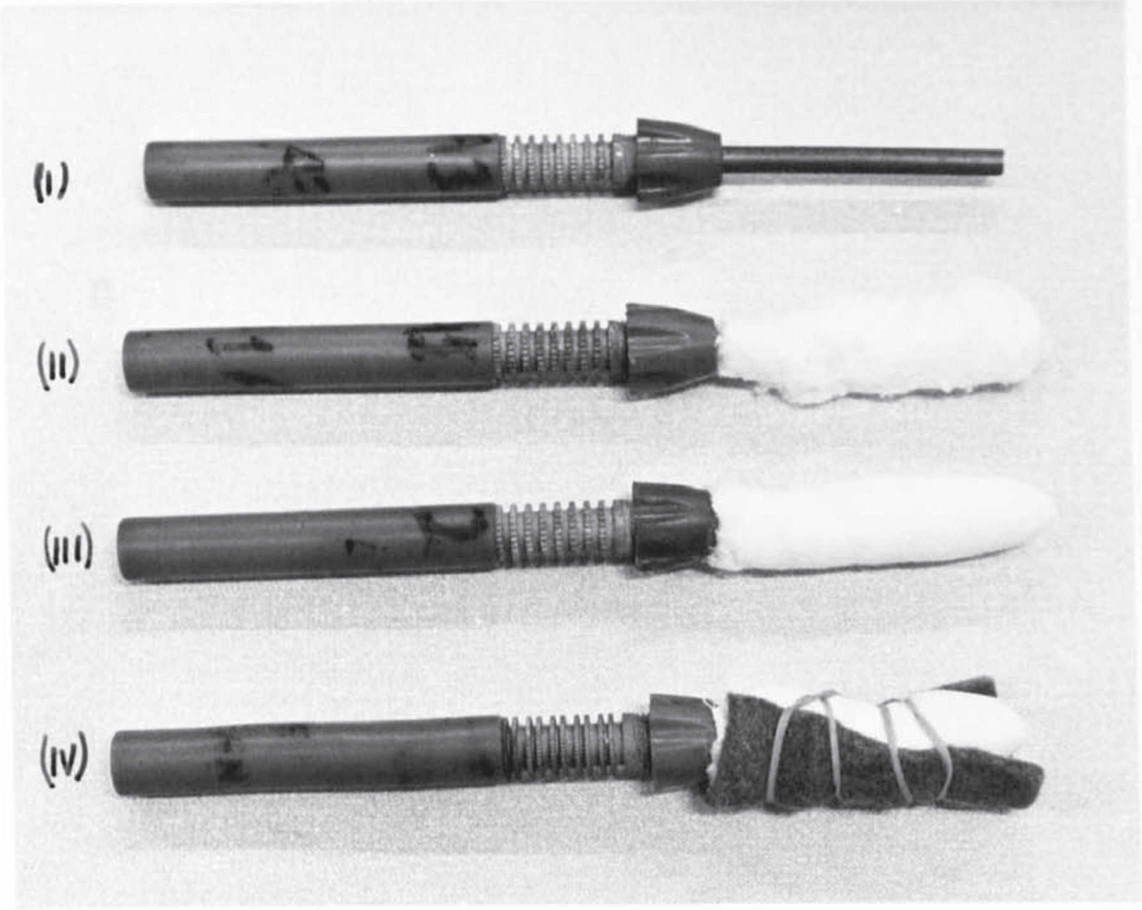
## 8.4. Power Supply

The power supply used in this investigation was a commercially produced unit specifically designed for brush plating (Fig 6). Output voltage can be continuously varied up to 50v whilst the maximum current that it is capable of providing is 35A. Safety cut outs are incorporated, as is a facility for reversing the polarity of the output, and an accurate ampere-hour meter.

In brush plating, the use of the ampere-hour meter is extremely important, as the weight of metal

Fig 5.

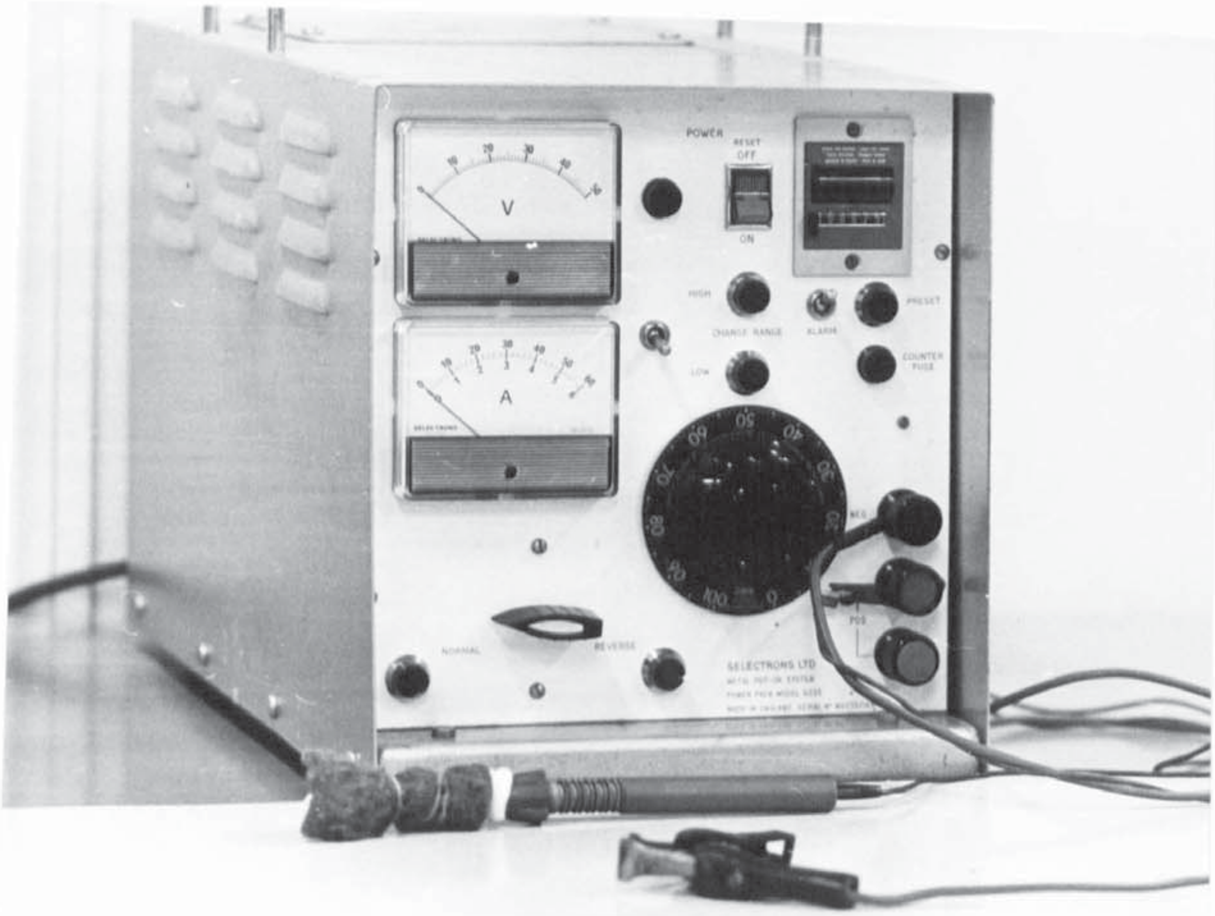
Component parts of brush plating stylus



(1) Carbon anode + stylus handle.
(11) Anode wrapped with cotton wool.
(111) Cotton wool covered with cotton gauge.
(1v) Stylus ready for use; gauze covered with felt.

Fig 6.

Brush plating power supply.



deposited is proportional to the charge passed through the system. Providing the operator is competent, it is reasonable to assume an even deposit thickness; consequently the ampere hour meter may be used to estimate the thickness of the deposit. Thus it was considered of the utmost importance to check the accuracy of the ampere hour meter on the power supply. This was carried out using a standard copper coulombmeter to estimate the true charge passed.

Coulombmeter Composition per litre distilled water

150g $CuSO_4.5H_2O$

50g $H_2SO_4$

50ml ethanol.

Recorded charge passed on power supply meter 4.558 Ah

Wt deposited at 4.5 amps in 1 hour = 5.3460g

96,500 coulombs deposit 31.7g (assuming 100% cathode efficiency)

$\therefore$ Coulombs required to deposit 5.3460g =

$$\frac{96,500}{31.7} \times 5.3460 = 16274.1$$

$$= \frac{16274.1}{3600} = 4.520 \text{ Ah}$$

$$\% \text{ Error} = \frac{\text{Meter reading - true reading}}{\text{true reading}} \times 100 =$$

$$\frac{(4.558 - 4.520)100}{4.520} = \underline{\underline{0.84\%}}$$

For the purpose of this investigation, this level of error was considered satisfactory, as comparative and not absolute values of charge passed were of more importance.

# 9. PREPARATION OF BRUSH PLATING SOLUTIONS

## 9.1. Purification of Sodium Heptonate

Sodium heptonate, the sugar like organic compound used as a complexing agent in these alloy plating solutions, cannot be obtained in a pure enough condition for immediate use. Consequently, before making up the brush plating solutions, sodium heptonate had to be purified. This was carried out by re-crystallisation of a super saturated sodium heptonate solution after treatment with activated carbon at 70°C. In practice, sodium heptonate was dissolved in distilled water held at 70°C. When a super saturated solution had been obtained (approximately 1000 g/l) 50 g/l of activated carbon was added and thoroughly mixed by means of air agitation. After approximately two hours, the carbon was filtered off and the super saturated solution of sodium heptonate allowed to slowly crystallize out. The resultant crystals were washed dried and bottled ready for use.

## 9.2. Preparation of Single Metal Electrolytes.

Electrolytes for depositing cobalt were formulated from a combination of the following:- sodium heptonate, cobalt sulphate and glacial acetic acid. As commercially pure cobalt sulphate was used, it had to be carbon treated in a similar way to the sodium heptonate. When electrolytes containing both sodium heptonate and cobalt sulphate were required both components were dissolved in distilled water at 70°C, treated with activated carbon, held at temperature and subsequently filtered. 50 g/l of activated carbon were used, and the solution was held at temperature for two hours. The purified electrolyte was allowed to cool to room temperature and losses due to evaporation were made up with distilled water. A calibrated digital pH meter was used to measure pH, which was normally adjusted to the required value with dilute sulphuric acid, or sodium hydroxide. When preparing a conventional electroplating bath further "plating out" would be required to remove metallic contaminents, but earlier work had shown this to be unnecessary when preparing brush plating solutions.

Trials with certain single metal electrolytes necessitated the addition of glacial acetic acid to the brush plating solution. In these cases, the required amount was added prior to pH adjustment.

## 9.3. Preparation of Cobalt Molybdenum and Cobalt Tungsten Electrolytes.

In the preparation of these electrolytes, sodium heptonate was always included in the solution make-up in order to complex the second metal ion. Molybdenum or tungsten were added in the form of sodium molybdate or sodium tungstate.

Initial preparation of the alloy solutions was similar to that for single metals, namely, the cobalt sulphate and sodium heptonate was dissolved in distilled water at 70°C and purified by means of activated carbon. However, whilst still warm, the pH of the solution was adjusted to approximately 1.5 to avoid the formation of stable insoluble cobalt complexes,when the alloying elements were added. Sodium tungstate or molybdate were dissolved in distilled water, and gradually added to the still warm electrolyte. Whilst this procedure was being carried out, a careful watch was kept on the pH of the electrolyte, and dilute sulphuric acid was added to bring the pH back down to 1.5. On cooling, evaporation losses were made up and the pH checked after the addition of any glacial acetic acid that may be required. The brush plating solutions produced were tightly bottled for subsequent use.

## 10. MANUFACTURE AND PLATING OF TEST PANELS.

### 10.1. Test Panels for Solution and Deposit Evaluation

Initial trials were attempted by brush plating mild steel panels with the appropriate solution, but because of the colour of the substrate, the deposit could not easily be seen. This proved a great problem, as the effects of "burning" and "stressing" could not be detected. Consequently brass sheet 0.125 mm thick was used after being guillotined to suitable sized panels. The rolled sheet was cut into 5cm x 5cm panels, as this was found to be convenient with respect to the time spent plating each individual panel.

### 10.2. Pre-treatment of Brass Substrates.

All panels were degreased thoroughly in iso-propyl alcohol prior to further processing. If appropriate, they were then weighed accurately and their weights carefully recorded. A cathodic electrocleaning operation was then carried out using the brush cleaning technique, with a conventional alkali electrocleaning solution. This involved lightly swabbing the surface of the brass panel with a stylus soaked in the cleaning solution, and adjusting the polarity of the power supply output such that the panel was cathodic with respect to the stylus. The voltage used for this operation was in the range of 10-15v, and the procedure was carried out over 2-3 minutes (sufficient time to clean a panel 5cm x 5cm). On completion of this cleaning stage, the panel was thoroughly swilled using a jet of water; as total immersion is inappropriate due to the electrical contact required in this form of plating.

## 10.3. Plating Procedure for Test Panels

After the relevant cleaning procedure had been carried out, the panel was then ready for brush plating. The ampere hour meter on the power supply was set to zero and the stylus was made anodic with respect to the panel. It was found advantageous at this point to swabb the surface of the test panel with electrolyte before switching on the power supply, as this helped to prevent "burning". The current was then switched on, and the voltage gradually increased to the "working" voltage (usually 10-20v). During this time, the surface of the panel was gently rubbed using the electrolyte soaked stylus, and it was not allowed to become stationary at any time. Occasionally the stylus was removed from the workpiece and recharged with electrolyte from a beaker close at hand. Uniform movement over the entire workpiece was also important, as concentration on one specific area would lead to uneven deposit distribution. Throughout plating, electrical continuity was checked using the ammeter, and progess monitored using the ampere-hour meter. After initial trials, deposit thickness could be predicted when the area of the panel, and the number of ampere hours recorded during deposition were known. When the required ampere-hour reading had been reached plating was complete, and the panel was thoroughly washed dried and reweighed

## 11. MANUFACTURE AND PLATING OF EXPERIMENTAL HOT FORGING DIES.

### 11.1 Die Manufacture

Assessment of the wear resistant properties of some of the coatings was carried out on a laboratory scale hot forging rig. Consequently, the dies used for this were manufactured from Electem No 5 die steel, a material in common use in the hot forging industry. The composition of No 5 steel is recorded in table III.

## TABLE III

Chemical Composition of Electem No 5 die steel

| Element | % | Element | % |
|---|---|---|---|
| C | 0.5-0.6 | Ni | 1.25-1.75 |
| Si | 0.3 max | Cr | 0.5-0.8 |
| Mn | 0.5-0.8 | Mo | 0.25-0.3 |
| S | 0.04 | | |
| P | 0.04 | | |

Forged bar in the annealed condition was turned to 5cm diameter, and discs approximately 1.25cm thick were sliced from this stock. Heat treatment was carried out by soaking in a salt bath maintained at 840°C for 50 minutes, followed by oil quench and temper for 20 minutes at 600°C. This heat treatment operation produced a tempered martensite structure having a hardness between 388-411 Hv. At this point, hardness was checked prior to further machining to "size", the final finish being attained by surface grinding. A Vickers hardness was then determined on the working face of each die before plating to ensure that the hardness was within specification.

## 11.2. Pretreatment and plating of No 5 die steel

The finished dies were degreased in iso-propyl alcohol, and grit blasted to provide a better surface for deposition. Measurements were taken to enable the surface area to be calculated and an etching and cleaning sequence followed. Proprietary surface activators were available but expensive; alternative formulations are given in table IV.

## TABLE IV

| ACTIVATOR | COMPOSITION |
|---|---|
| 1 | 150g/l Ammonium Sulphate solution, adjusted to pH2.0 with dilute sulphuric acid. |
| 2 | 110g/l Sodium Chloride solution, adjusted to pH2.0 with dilute hydrochloric acid. |
| 3 | 180g/l Tartaric Acid solution adjusted to pH5.0 with concentrated sodium hydroxide solution. |

The pre-plating cleaning sequence used was as follows:-

1) Electroclean with proprietary conventional alkaline cleaning solution 10-15 volts. Stylus made cathodic with respect to the die. Water swill.

2) Anodic etch using activator 2 gives an even dark surface to the die. 8-15 volts used. Water swill.

3) Remove black smut by electrocleaning with activator 3, with the stylus still cathodic with respect to the workpiece. This procedure is carried out at 15-20 volts until an even light grey etched surface is visible. Water swill.

4) Reverse current; ie. stylus is now anodic with respect to the die, and using activator 1 at 10-15 volts briefly electroclean the surface. It is extremely important at this stage <u>not to swill</u> with water, but to leave the activator 1 on the surface of the die before plating.

5) Leaving the stylus anodic with respect to the die, the surface of the workpiece is then swabbed with electrolyte, the ampere hour meter set to zero,

and plating carried out, to the required ampere-hour measurement.

For the simulated hot forging test approximately 12µm of the cobalt alloy was used and this was obtained after the application 1 ampere-hour per square decimeter of surface area.

On completion of the operation, the die was thoroughly swilled in water and dried ready for testing .

## 12. DEVELOPMENT OF COBALT MOLYBDENUM AND COBALT TUNGSTEN BRUSH PLATING SOLUTIONS.

The starting point for the development of successful cobalt alloy brush plating solutions were the bath plating electolytes described by Still(51). These were cobalt-tungsten and cobalt-molybdenum alloy plating solutions complexed by sodium heptonate. Later work by Dennis(77) et al indicated the potential of these deposits for wear resistant applications, but there were severe limitations due to the limited size of die that could be treated by conventional vat plating. The composition of these baths is recorded in table V.

## TABLE V

**Composition of Cobalt Tungsten and Cobalt Molybdenum Plating Baths.**

g/1

Cobalt Sulphate - 150.0

Sodium Heptonate - 100-200

Sodium Tungstate - 15.7-47.3 For Co W solution

Sodium Molybdate - 3.2-12.6 For CoMo solution

Sodium chloride - 28.0

Boric Acid - 40.0

Operating current Density - $4 A/dm^2$

pH - 1.5-2.0

Temperature - 55°C

Using baths of this composition, cobalt alloy deposits were obtained containing up to 19.5% Mo or 22.5% W.

In order to develop brush plating solutions from the bath compositions, it was thought necessary to increase the metal concentrations of the electrolyte, and remove additions that were not required. Sodium chloride was not used due to its possible decomposition during electrodeposition, whilst the buffer, boric acid, was unnecessary as brush plating solutions are seldom reused.

Development of the cobalt alloy brush plating solutions was started by investigating the effect of sodium heptonate on the plating properties of cobalt sulphate based single metal electrolytes.

## 12.1. Effect of Composition on Cobalt Brush Plating Solutions.

Two concentrations of cobalt sulphate solution were used in these initial trials in an attempt to optimise the concentration and composition of single metal electrolytes. Solutions were formulated containing 500 g/l or 250 g/l of cobalt sulphate such that five concentrations of sodium heptonate could be introduced to each level of cobalt sulphate. Thus in all, ten solutions were made up containing either 250 g/l or 500 g/l of cobalt sulphate, and 0, 100, 200, 300 or 400 g/l sodium heptonate. All solutions so produced were purified with activated carbon, and their pH was adjusted to 1.5 by means of dilute sulphuric acid and a calibrated digital pH meter. This value was used as it represented the lower "safe" range of pH used for the vat solutions. Brass panels 5cm x 5cm were plated at 17 volts to 0.3 A/hr as recorded on the power supply ampere hour meter, and the weights deposited were recorded. The results of these experiments were recorded in the appropriate table, together with calculated cathode current efficiency for deposition.

A further investigation was carried out into the effect of glacial acetic acid on the deposition characteristics of the higher concentration of cobalt sulphate solution. This addition of glacial acetic acid was thought to reduce the tendency for "burning" when deposits were first laid down. Two solutions were formulated, one containing 500 g/l of cobalt sulphate, the other also containing 500 g/l of cobalt sulphate, but in addition 200 g/l of sodium heptonate. Glacial acetic acid was added to both of these solutions at 0, 10.5, 21.0, 42.0, and 84.0 g/l, making a total of ten solutions in all. Again, all were purified with activated carbon, and adjusted to pH 1.5. Panels of brass 5cm x 5cm were weighed, plated at 17 volts for 0.3 A/hr and reweighed; the results were used to calculate cathode current efficiency for deposition.

## 12. 2. Composition Trials for Cobalt Tungsten and Cobalt Molybdenum Electrolytes.

Work with simple single metal electrolytes indicated that the higher concentration of 500 g/l cobalt sulphate solution should be used as a basis for the proposed alloy brush plating solutions. Two separate trials were required; one each for the cobalt molybdenum and cobalt tungsten systems. The sodium heptonate complexing agent was used at levels of 100,200,300 and 400 g/l and sodium tunstate or molybdate was added at 0,12.6,25.2,50.4, and 70.0 g/l. Glacial acetic acid was also added at 0,10.5,21.0, 42.0, and 84.0 g/l, and the resultant solutions were purified by carbon treatment as previously described. Prior to carrying out the plating trials, each solution was adjusted to pH 1.5 as in section 12.1. Brass sheets, 5cm x 5cm were used as test panels and were thoroughly degreased, and weighed before plating. The panels were plated at 17 volts for 0.3 A/hr, one each for the sixty four solutions under investigation.

From these trials, it was found that electrolytes of the following composition gave sound deposits containing a reasonable level of alloying element, and having satisfactory cathode current efficiency.

| | |
|---|---|
| Cobalt Sulphate | 500 g/l |
| Sodium Heptonate | 200 g/l |
| Sodium Molybdate or Tungstate | 50.4 g/l |
| Glacial Acetic Acid | 42.0 g/l |

Having obtained solutions capable of giving sound deposits, it was decided to investigate the effect of various operating parameters on the "base" solution.

## 12. 3. Effect of Voltage on deposition characteristics for CoMo and CoW alloys.

The base solutions developed in section 12.2 were used for investigation into the effects of voltage. Sufficient solution was prepared to allow a number of 5cm x 5cm brass panels to be plated at differing voltages. As in previous trials, the panels were degreased and weighed before plating. Voltages of 10,15,20,25 and 30 were used, and panels were plated to 0.3 A/hr as in section 12.1. After plating, the panels were washed, dried and reweighed such that cathode efficiencies could be calculated. For this trial, voltages over 30 volts could not be used as heat evolution and solution boiling took place, possibly severely reducing the "life" of the wrapped anode. Also, voltages below 10 volts were impractical as a considerable length of time was required to attain the 0.3A/hr required for a valid assessment of deposit quality.

## 12.4. Effect of pH on deposition characteristics for CoMo and CoW alloys.

Initial brush plating trials with cobalt molybdenum and cobalt-tungsten electrolytes showed that a pH of 1.5 appeared to give sound deposits with satisfactory cathode current efficiency. However, it was considered necessary to determine over what range of pH these alloys could be deposited; and the subsequent effect of pH variations on deposit composition and cathode current efficiency. Sufficient electrolyte of the composition recorded in section 12.2 was prepared to enable variations in pH to be made to the same batch of solution. Using dilute sulphuric acid, and calibrated pH meter, various samples of solution from the same bath were adjusted to pH values in the range pH 1.0 to pH 3.0.

As in previous trials, brass panels 5cm x 5cm were plated to 0.3 A/hr at 17 volts, the weight of the panel before and after deposition being recorded. In order to prevent solutions being tested at an unknown pH, great care was taken to change the anode wrapping material between each test to prevent cross contamination.

The range of pH 1.0 to pH 3.0 was chosen, as above pH 3.0, the electrolytes became unstable, with the possibility of precipitation of insoluble metal ion complexes; and the more highly acidic solutions were avoided on the grounds of operator safety.

## 12.5. Effect of Speed and Pressure.

The degree of stylus movement required during the brush plating operation raises the question of what is the optimum speed of movement of the stylus with respect to the workpiece? Further to this, it was considered of importance to note the effect that applied pressure of stylus on workpiece had on deposit characteristics.

In order to carry out these investigations on speed and pressure, a brush plating system had to be developed in which the speed of stylus relative to workpiece could be accurately measured, along with the applied pressure. The machine developed for this work is shown in Fig. 7. Essentially, it consists of a metallurgical polishing machine modified to take a brass disc on which the cobalt alloy is deposited, and a stylus held vertically Fig. 8.

The gearing of a low speed motor was altered such that the speed of the driven rotating table was 5½ rpm. A rhestat was also used to allow speeds below this to be achieved. These speeds were slow enough to be accurately determined by means of timing the rotation of the table using a stopwatch. A special stylus assembly was also developed, such that it could be held vertically with respect to the rotating brass disc to be plated. In this arrangement, a small circular pad of felt was held in place by means of plastic tubing, adjacent to the shaped carbon anode (see Fig. 9). The electrolyte was drip fed on to the rotating brass cathode at a controlled rate. A brass disc 20cm dia x 2mm thick was used as a test piece, which was held in place on the rotating turntable by a centre bolt. The brass discs used, were degreased thoroughly in iso propyl alcohol and weighed before adhesive tape was applied for "stopping off" unplated areas.

Fig 7.

Metallurgical polishing machine converted to investigate the effect of speed and pressure in brush plating.

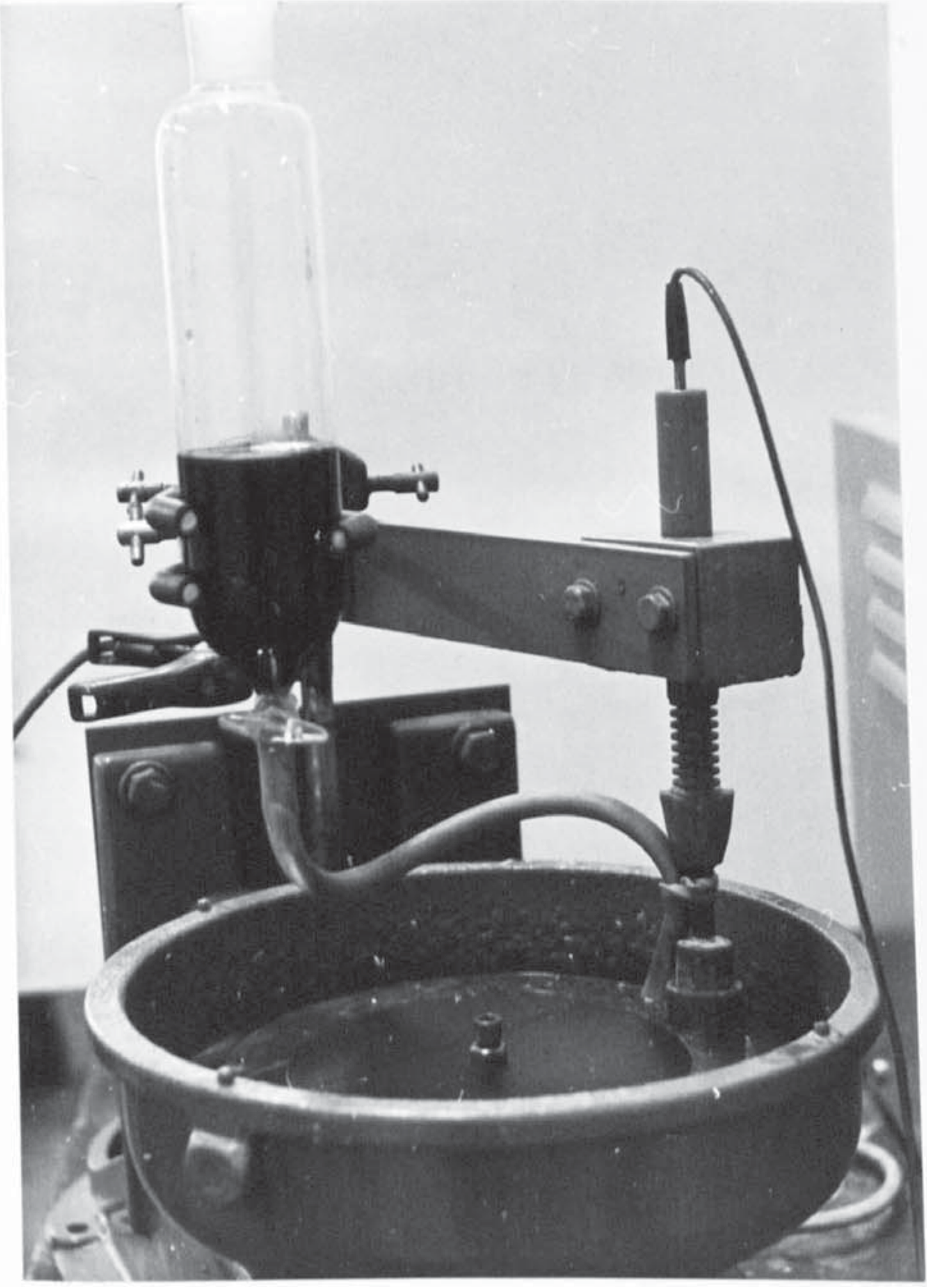


Fig 8.

Diagramatic representation of speed and pressure apparatus.

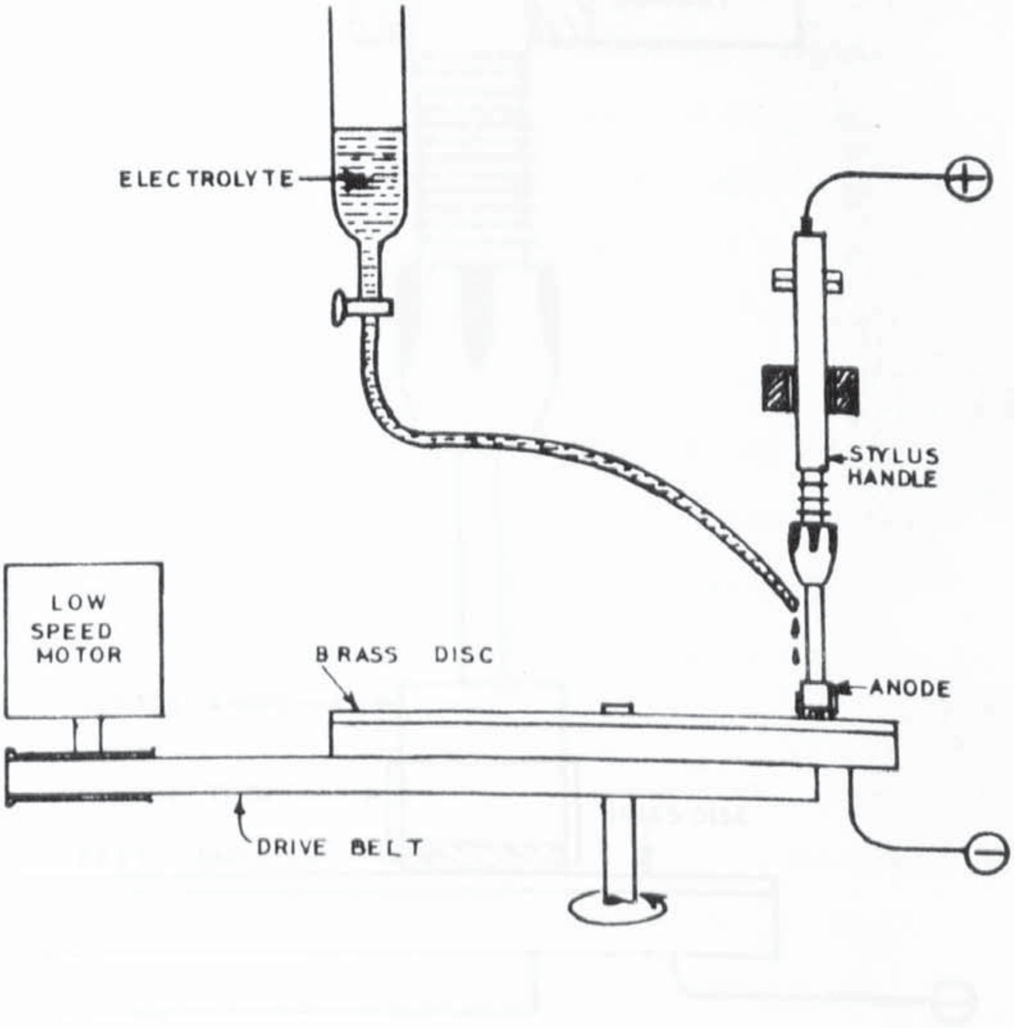
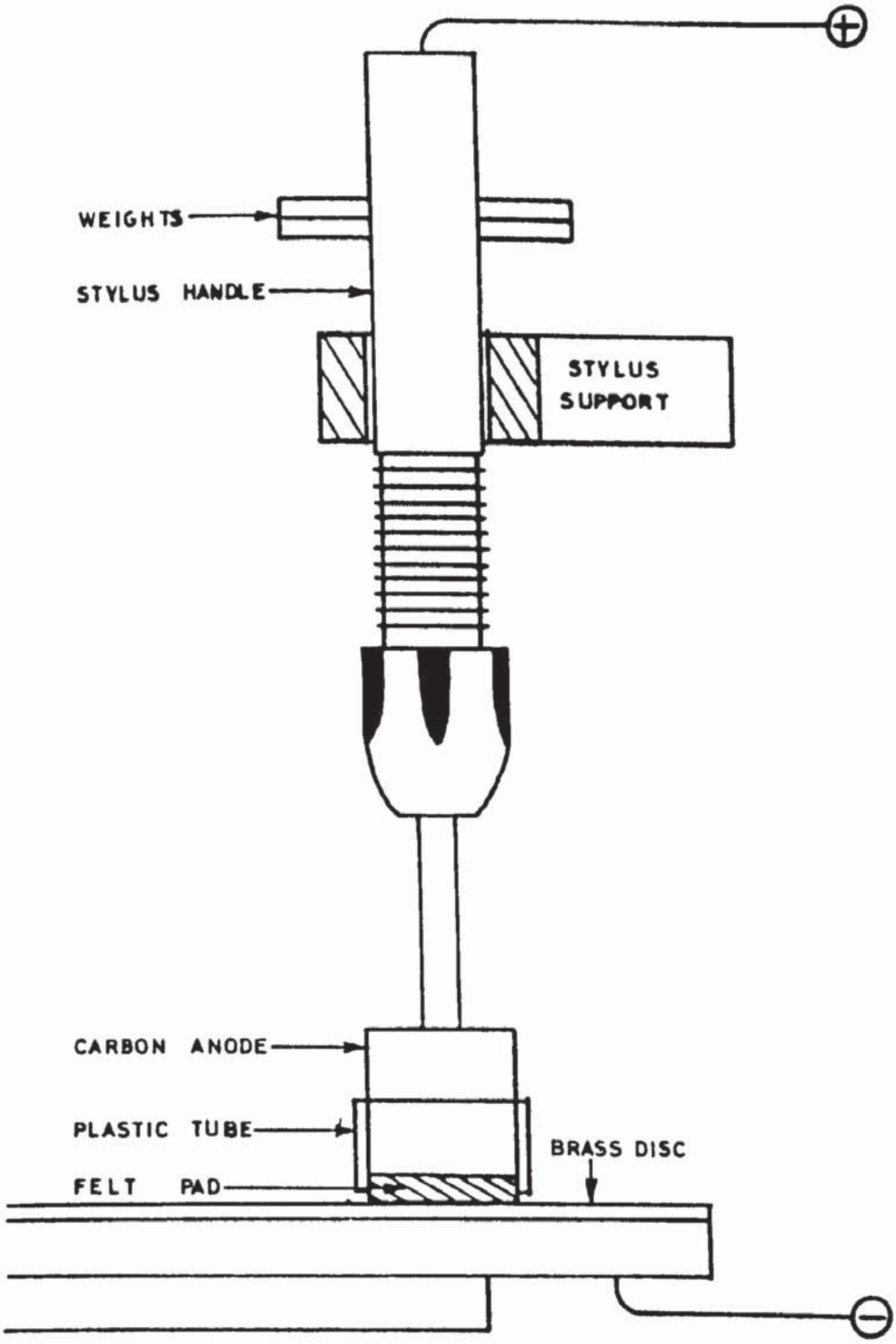


Fig 9.



Anode arrangement for speed and pressure apparatus.

An anular ring of tape was removed, the width of the plated area produced by the stylus; and the disc was electrocleaned and swilled before fitting to the rotating table. The stylus was moved into place and allowed to rest on the surface of the substrate, the motor switched on, and the brass disc rotated beneath the anode. As in conventional brush plating by hand, it was found advantageous to cover the surface of the substrate with solution before the current was switched on. Due to the speed, range chosen, and the geometry of the system the maximum voltage used had to be limited to 15 volts, otherwise burning of the deposit occured. The speed of the plated area with respect to the stylus was calculated by considering the mean perimeter of the plated anulus; and multiplying this by the number of revolutions per minute at which the disc rotated. Thus the effective speed of movement could be altered by moving the stylus nearer to, or further away from the centre of the disc. However, as this operation was carried out, so the total plated area of the anulus changed, necessitating the calculation of the proposed plated area prior to carrying out a trial. In an effort to maintain a consistent deposit thickness, an equivalent number of ampere hours per square decimeter of area were applied at each trial. Thus, a higher number of ampere hours were used when plating a large diameter anulus.

After completion of a trial, the brass disc was removed washed dried and reweighed. This information was used to calculate the cathode current efficiency of deposition.

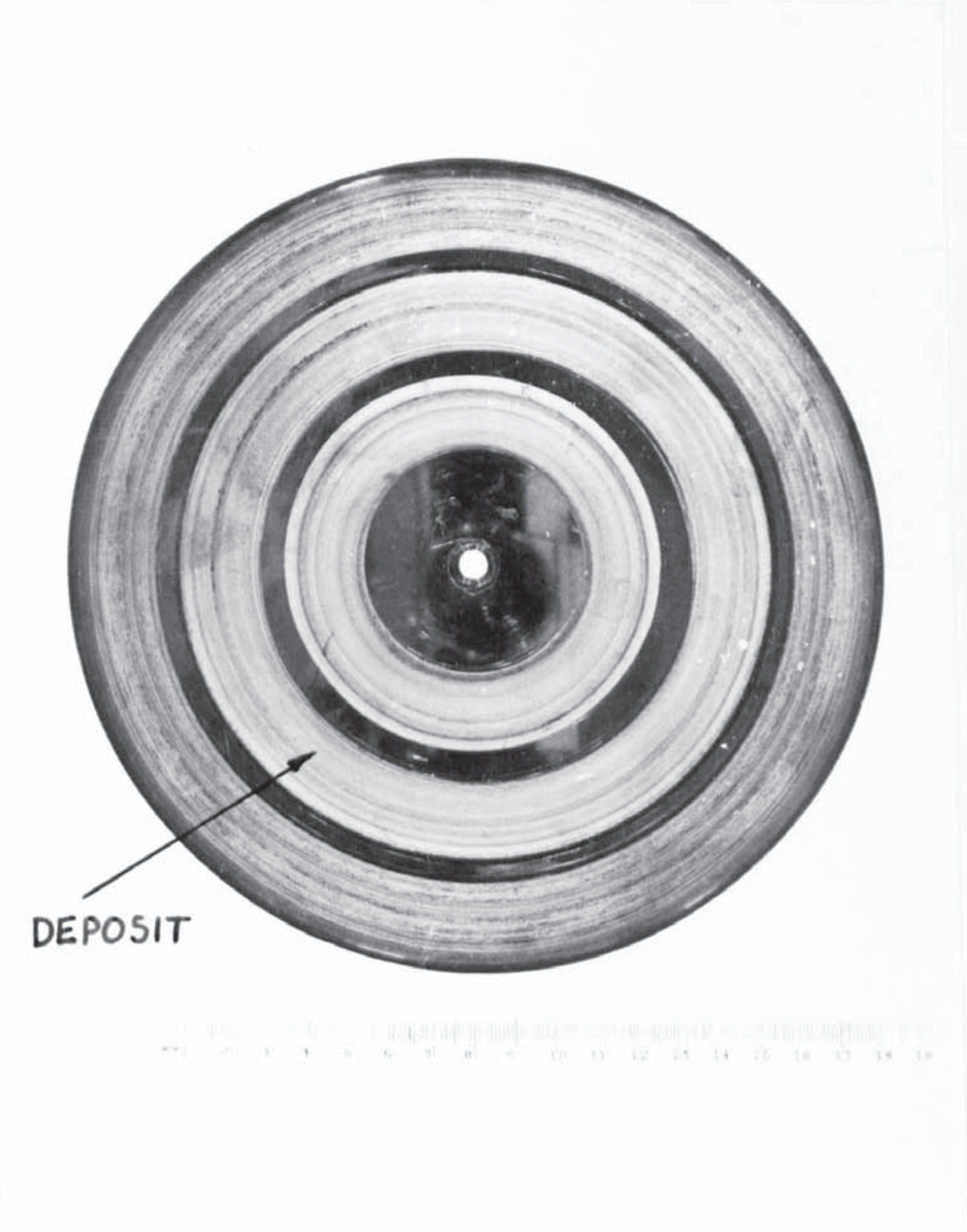
A similar trial was also carried out to determine the effect of pressure on the brush plating system. Circular weights were firmly attached to the stylus handle such that pressures in the range 45-125 g/cm$^2$ could be attained at the anode. With similar preparations to those of the "speed" trial, a number of brass discs were plated at 15 volts for the equivalent of 0.3 A/h /dm$^2$ (taking the anulus area into account). Fig. 10 shows a typical brass disc after plating. For reasons of economy two or even three concentric rings of deposit could be produced on a single disc.

### 12.6. Comparison of Cobalt Tungsten Electrolyte with Proprietary Solution and determination of Experimental Variability.

It was considered of great importance to determine the extent of experimental error when carrying out brush plating trials. Furthermore, an indication of

Fig 10.

Brass disc after plating on the speed and pressure apparatus.



the effect of different substrates on deposit characteristics was necessary. A comparison of performance with commercially produced brush plating cobalt tungsten solution was also carried out. There appeared to be no proprietary cobalt-molybdenum electrolytes available for comparison, consequently these trials were limited to the cobalt-tungsten system. The solution used for this trial was the same composition as the cobalt-tungsten "base" solution refered to in section 12.2. Using this solution, six brass panels were plated under identical conditions; each 5 x 5cm panel being treated at 17 volts for 0.3 Ah . The weight of the deposits obtained was determined, and the cathode current efficiency calculated. In addition to this, six panels of No 5 die steel and six of mild steel were also plated under similar conditions. As with the brass panels, the cathode current efficiency was evaluated and presented in the same table. To provide some measure of comparison with a commercially available electrolyte, a "Selectron" Cobalt Tungsten solution was also used to plate six brass panels. As in the case of the previous trials, cathode current efficiency was determined and presented with other results. However, the suppliers of the proprietary solution suggested that it be used at a maximum of 11 volts, as stressing and burning could occur above this level. In practice, this proved to be a major disadvantage, as approximately double the time was required to attain the 0.3 Ah necessary for the test.

The results of these trials were used to calculate the mean and standard deviation of cathode current efficiency and deposit composition, thereby a representation of experimental reproducability was gained.

## 13. EVALUATION OF PLATING SOLUTIONS AND DEPOSITS

### 13.1. Determination of deposit composition.

The electron probe microanalyser was employed to determine the analysis of the cobalt-tungsten and cobalt-molybdenum coatings produced by brush plating. Samples for this purpose were taken from the central area of the 5cm x 5cm brass panels used for the plating trials. Each panel was cut in half using metal shears, and a sample approximately 20mm x 5mm was prepared from the central region. Considerable time was saved by mounting a number of such specimens side by side in a single mount, so that a batch of analysis could be completed at one time; without the need to "pump down" the vacuum system for each individual analysis. Great care was taken when carrying out this procedure to ensure that the correct order of analysis was maintained and that the samples were mounted in the order intended.

After mounting and polishing, analysis was carried out on the cross section of the deposits, the results obtained being subjected to the usual corrections for this form of analysis. This procedure was carried out for all trials involving the cobalt alloy plating solutions, as the percentage of alloying element in the deposit was required to calculate the cathode current efficiency of deposition. Analysis results were recorded in the appropriate table.

## 13.2. Calculation of Cathode Current Efficiency of Brush Plating Solutions.

### 1) Simple Cobalt Solutions

Calculation of cathode current efficiency for cobalt brush plating solutions was carried out on the basis that 1 Faraday deposits the gram equivalent weight of cobalt which is:-

$$\frac{58.94}{2} = 29.97\text{g cobalt}$$

$\therefore$ 1.0 Faraday = 96,500 coulomb deposits 29.97g cobalt. But in these trials, 0.3 Ah were used to plate a panel.

0.3 Ah = 1080 coulombs

$\therefore$ At 100% cathode efficiency theoretical weight deposited after 0.3A/hr = $\frac{29.97}{96,500} \times \frac{1080}{1} = 0.3354$g

$\therefore$ In a trial where cobalt only is being deposited, and 0.3 Ah has been passed, then the % cathode current efficiency = $\frac{\text{wt deposited}}{0.3354} \times \frac{100}{1}$

Example if 0.2238g of cobalt were deposited in 0.3Ah

$\therefore$ Cathode current efficiency = $\frac{0.2238}{0.3354} \times \frac{100}{1}$ = %66.73

The above calculations assume that all of the current used either deposits cobalt or represents the wasted energy in the liberation of hydrogen.

## 2) Cobalt alloy Brush Plating Solutions.

As in the case of the determination of cathode current efficiency of cobalt deposition, the equivalent calculation for cobalt-molydenum or cobalt-tungsten also involves consideration of the amount of each element deposited by 1 Faraday. Thus, the gram equivalent weight deposited by 1 Faraday for each of the elements is:-

$\frac{58.94}{2}$ = 29.97g cobalt

$\frac{95.95}{6}$ = 15.97g molybdenum

$\frac{183.86}{6}$ = 30.64g tungsten.

A valency of 6 was used for the molybdenum and tungsten as this was the valency state of the ions present in sodium molybdate and sodium tungstate. The cathode current efficiency for alloy deposition was calculated on the basis of comparing the theoretical number of gram equivalents deposited, with the actual number.

For example, in a brush plating trial:-

0.2195g of a cobalt-molybdenum alloy containing 5.3% molybdenum was deposited after passing 0.3 Ah.

1 Faraday (96,500 C) deposits 1 g equivalent.

$\therefore$ 0.3A/hr (1080 C) deposits $\frac{1080}{96,500}$ g equivalent

$$= 0.01119$$

Wt of alloy = 0.2195g;% Mo = 5.3

$\therefore$ wt of Mo in deposit = 0.01163g

$\therefore$ wt of Co = 0.2079g

No of g equivalents of cobalt = $\frac{0.2079}{29.97} = 0.006937$

No of g equivalents of molybdenum = $\frac{0.01163}{15.97} = 0.0007282$

Total g equivalents deposited = 0.007665

$$\% \text{ Efficiency} = \frac{\text{g equivalents deposited}}{\text{Theoretical g equivalents deposited}} \times 100$$

$$= \frac{0.007665}{0.01119} \times \frac{100}{1} = 68.5\%$$

In the case of cobalt-tungsten alloys, similar calculations were carried out to determine cathode efficiency, the only difference being the use of 30.64g for the gram equivalent weight of tungsten.

As in the calculations for a single metal, it was assumed that all of the current used either deposited the alloy, or liberated hydrogen.
Using the analysis obtained from E.P.M.A the cathode current efficiencies were calculated for each alloy plating trial, and the results presented in the appropriate table.

## 13.3. Structure of Cobalt and Cobalt Alloy Brush Plated Deposits

Attempts were made to determine the structure of the brush plated electrodeposits by using X-ray Diffraction. Samples were selected from the complete range of electrodeposits produced in order to gain as much information as possible about factors affecting structure.
The samples selected were as follows:-

|  | Electrolyte | Deposit Composition |
|---|---|---|
| a) | 500g/l Cobalt Sulphate Solution | Co |
| b) | 500g/l Cobalt Sulphate + 100g/l Sodium Heptonate | Co |
| c) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate | Co |
| d) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 12.6 g/l Sodium Molybdate | Co-10.3% Mo |
| e) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 50.4 g/l Sodium Molybdate | Co-5.3%Mo |
| f) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 12.6g/l Sodium Tungstate | Co-15.6%W |
| g) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 50.4g/l Sodium Tungstate | Co-19.5%W |
| h) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 50.4 g/l Sodium Molybdate + 10.5 g/l Acetic Acid | Co-8.15%Mo |
| i) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 50.4g/l Sodium Molybdate + 42.0g/l Acetic Acid | Co-6.35%Mo |
| j) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 50.4g/l Sodium Tungstate + 10.5g/l Acetic Acid | Co-10.8%W |
| k) | 500g/l Cobalt Sulphate + 200g/l Sodium Heptonate + 50.4g/l Sodium Tungstate + 42.0g/l Acetic Acid | Co-10.3%W |

All the above samples (on their brass substrates) were cut to 1½cm x1½cm such that they would fit into the diffractometer. Certain problems were envisaged with reflections being obtained from the brass in addition to the deposit, consequently in addition to obtaining traces for all the above samples, a further trace was carried out using a piece of the brass substrate. Thus the peaks from this could be eliminated from those obtained for the deposits.

Original traces were carried out using a Co $K\alpha$ source, but the diffraction peaks from the brass substrate confused the result. Greatly improved traces were obtained using a Mo $K\alpha$ source, where the brass peaks could barely be resolved.

Where the most intense peaks occured, the $2\theta$ angles were noted and using $n = 2d \sin\theta$ the "d spacings" were calculated. These lattice spacings were subsequently used in an attempt to index the traces using the X-ray Diffraction Powder File.

## 13.4. Transmission Electron Microscopy

Considerable practical difficulty was experienced in preparing samples for T.E.M examination. By the very nature of the process of brush plating, adhesion is high and the preparation of foils made difficult.

Attempts were made to brush plate on to stainless steel substrates as when preparing foils from conventional plating baths, but in the case of brush plating, the brittle foils could not be removed, as the low pH electrolyte caused adhesion. Furthermore, the maximum thickness at which the brush plated deposits were reasonably sound was approximately 25μ, consequently the foils once obtained would be delicate. However, a few foils were eventually prepared by brush plating on to an unclean stainless steel substrate.

Once obtained, it was found that the more usual practical techniques of "thinning" resulted in break up of the foil. The technique of ion beam thinning was used on the prepared foils, and proved successful for only two samples; a cobalt only deposit, and a cobalt-molybdenum sample containing approximately 2.8% Molybdenum.

## 13.5. Scanning Electron Microscope Studies.

The surface topography of a selection of the brush plated deposits was examined using the Scanning Electron Microscope. Samples 1cm x 1cm were cut from the 5cm x 5cm brass panels used for the "composition trials", mounted on stubs and viewed directly.

## 13.6. Hardness of Brush Plated Deposits.

As most of the deposits produced were 10μ-15μm thick, the Vickers Microhardnesses were determined on cross sections of the deposits. The samples used for analysis were mounted and polished such that micro hardness determination could be carried out. Four impressions were made for each deposit at an applied load of 10g. The mean of these results was recorded in the appropriate table. However, micro hardness determination of these relatively thin deposits was not easy, as placement of the diamond in the exact centre of the deposit proved difficult. To gain some indication of the degree of scatter of the hardness results, microhardness tests were carried out on the cobalt tungsten samples used for the trial concerning experimental error, and comparison with a proprietary brush plating solution.

## 13.7. Levelling Properties of Cobalt Molybdenum Brush Plated Deposits.

A steel panel was specially prepared to determine the extent of surface levelling imparted by the brush plating operation. After stopping off, each section of the panel was abraded to varying degrees in order to provide a substrate graduating in surface roughness.

One section of this panel was left unplated, a further section brush plated to a 'silky feel' and the last section was plated to 1 Ah/dm$^2$ (the amount normally put on hot forging dies). By measuring the centre line average roughness values of the plated and unplated areas, it was possible to determine the effect of brush plating on surface roughness.

## 14. WEAR PERFORMANCE OF COATINGS

In addition to extensive industrial trials, two laboratory based techniques were used to assess the wear performance of the cobalt molybdenum and cobalt tungsten alloy coatings. A "pin and disc" machine was used to wear test the coatings, whilst a laboratory scale hot forging rig was used to simulate the conditions experienced in industrial hot forging. This "hot forging test" was considered necessary, as it allowed a measure of control to be exercised which was impossible under typical industrial conditions. It was also thought to more accurately reproduce the arduous forging operation than the conventional pin and disc technique.

### 14.1. Pin and Disc Wear Testing.

In order to compare the wear properties of the cobalt-tungsten and cobalt-molybdenum alloys with other wear resistant coatings, conventional pin and disc wear testing was carried out. The arrangement used for this test is shown in Fig 11 and a diagrammatic representation in Fig. 12. A rigid arm which holds the pin under test is pivoted at one end in the horizontal and vertical planes. At the opposite end, a load is applied as shown in the diagram (the actual load at the pin being calculated by knowing the distances between the load and the pin, and the pin and pivot centre). A stop was incorporated in the assembly to prevent the arm skidding off the disc and two tranduces were used to determine the loss in length of pin and the horizontal displacement.

The pins used for this test were rough turned from 8mm diameter bars of BH13 tool steel; the required heat treatment was carried out and then they were finished to 50.mm long by 6.0mm diameter. Table VI gives the chemical composition of BH.13 and the heat treatment requirements to obtain resultant hardness values of 528-562 VPN. It was considered of great importance that the end of the pins were finished perpendicular with respect to their lengths to ensure complete contact of the disc. Using specially made jigs, the end of the pins were surface ground such that

Fig 11.

Pin and disc wear testing apparatus.

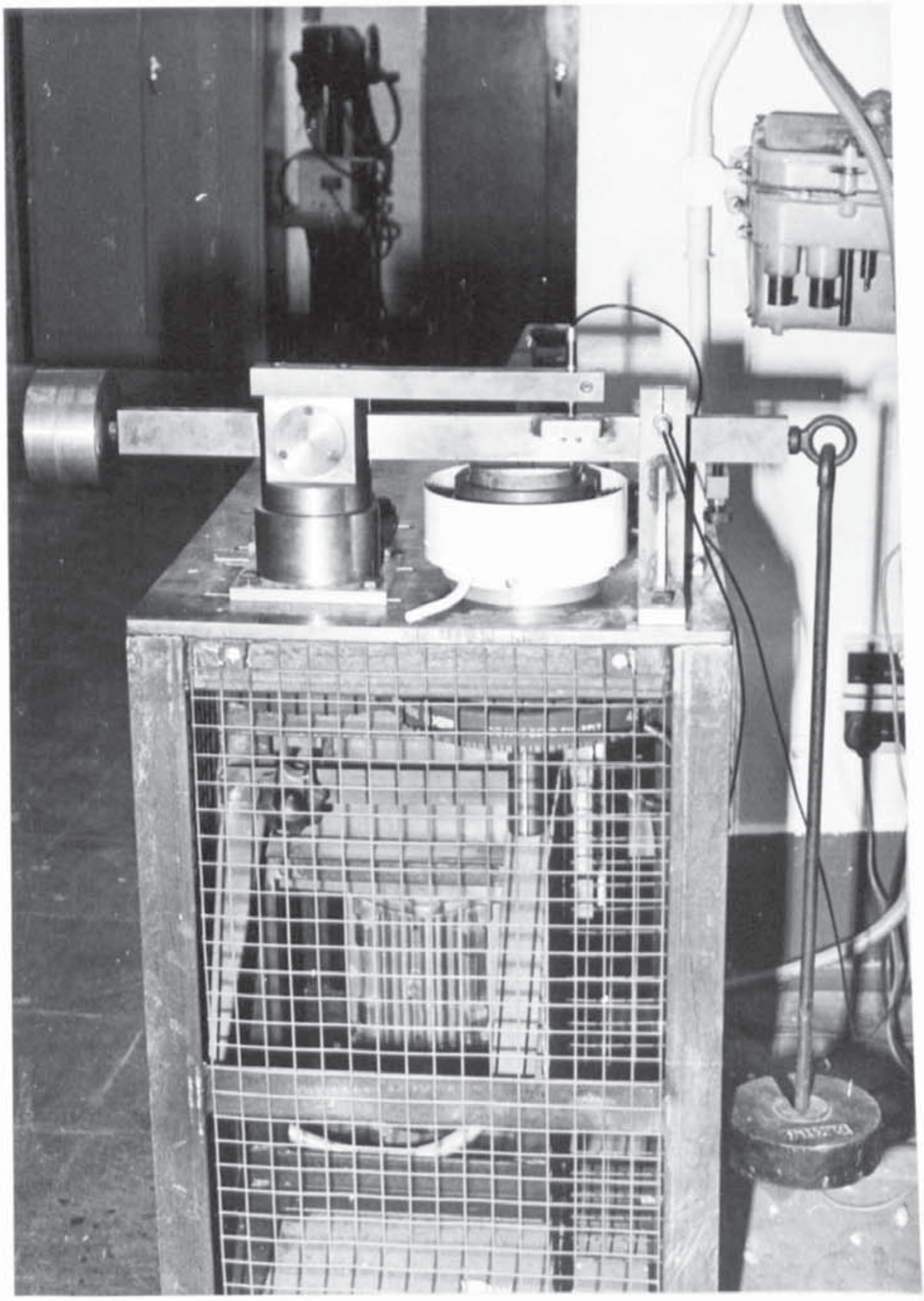
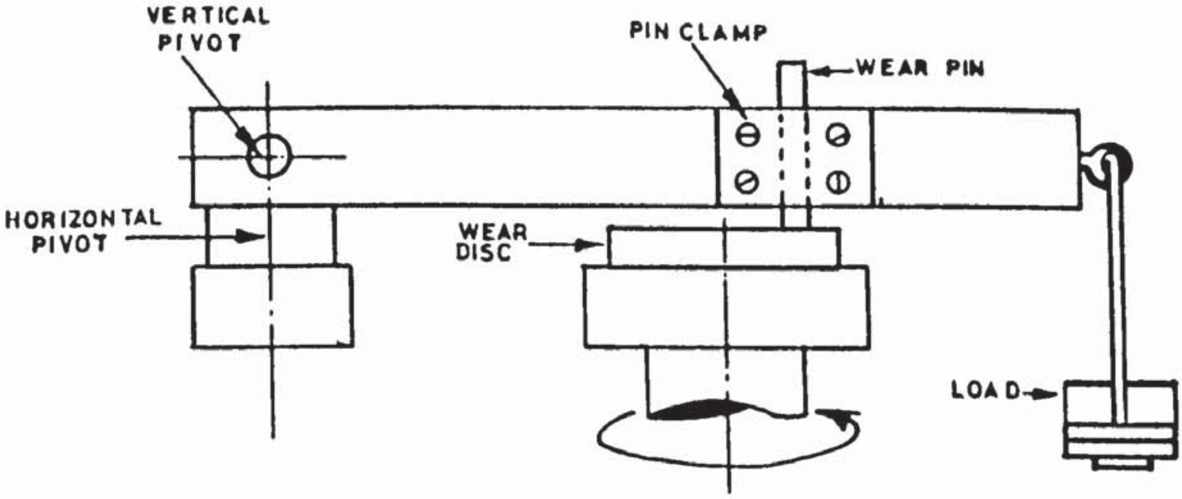


Fig 12.

Diagramatic representation of pin and disc arrangement



## TABLE VI

## Chemical Composition and Heat Treatment requirements of B.H. 13

Tool Steel. (Wear Test Pin Material)

| Element | % |
|---|---|
| C | 0.40 |
| Si | 1.2 |
| Mn | 0.4 |
| Cr | 5.3 |
| Mo | 1.4 |
| V | 1.0 |

Heat Treatment of wear pins:- Austenatise at 1010°C (vacuum) nitrogen gas quench. Temper 550°C furnace cool.

Heat treated hardness in range 528-562 VPN.

## TABLE VII

Chemical Composition and Heat Treatment
of EN31.
(Wear Test Disc Material)

| Element | % |
|---|---|
| C | 0.9-1.2 |
| Si | 0.1-0.35 |
| S | 0.05 |
| P | 0.05 |
| Mn | 0.30-0.75 |
| Cr | 1.00-1.6 |

Heat Treatment of wear discs:- Austenatize in salt bath at 820°C.
Oil quench and temper at 150°C furnace cool. - Final Hardness 716-763 VPN

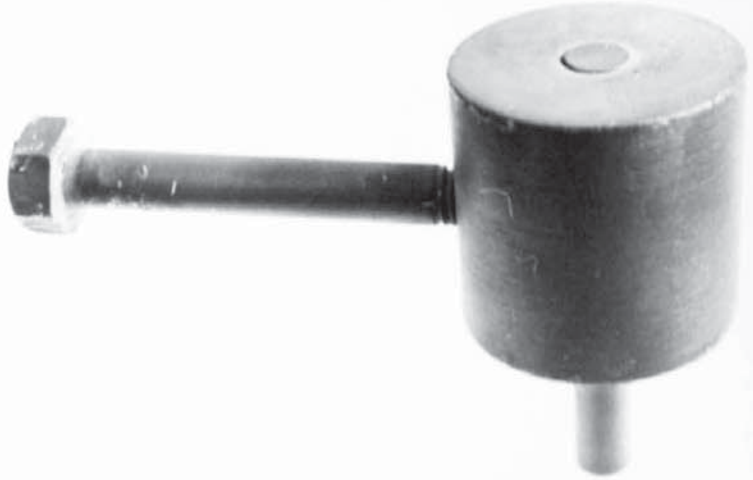
this could be achieved.

The discs used in these trials were rough turned from suitably sized stock of EN 31, the composition and heat treatment requirements of which can be found in table VII. After heat treatment and finishing to size (12.5cm diameter x 1.5cm thick), their hardness was checked to ensure they were in the range of 716-763 VPN. This particular choice of pin and disc material was made on the basis that a considerable amount of earlier work had been carried out using this combination to wear test a large number of surface finishes and treatments.

With regard to the testing of brush plated electrodeposits, it was decided to plate the pins rather than the discs. The main reasons for this was that considerable time would have been required to plate an entire disc, and the loss in weight of the disc would be small compared to its mass; thereby giving an inaccurate measurement. However, a satisfactory technique was required to hold the pin in order to deposit a uniform coat on its end. A small jig was manufactured as shown in Fig 13 to allow the pins to be plated by holding them rigidly by means of a retaining bolt. Thus, the area to be plated was greatly enlarged, and "edge effects" were avoided; with sufficient current being passed to allow approximately 12μm to be deposited on to

Fig 13.

Jig used to plate wear test pins.



the end of the pin and jig. With the cobalt tungsten and cobalt-molybdenum alloys so developed 1.0 $Ah/dm^2$ was used.

After preliminary trials, it was found that an applied load of 10Kg at the pin gave a wear rate which could be recorded within a reasonable time. Results were recorded by determining the reduction in length of the pin, and dividing into this the distance the pin travelled relative to the revolving disc and recorded in mm $cm^{-1}$. The total distance travelled relative to the pin was calculated by measuring the diameter of the wear track on the disc, calculating its circumference and multiplying this by the rotational speed in r.p.m. Thus by knowing the total time of the test, and the speed of the disc, the distance travelled could easily be calculated. A tachometer was used to determine accurately the speed of rotation of the disc, and this was adjusted to 240 r.p.m. and maintained at this level for each test.

To perform a test, a pin was pre treated as for No 5 die steel and plated with the appropriate alloy. It was then washed dried and its length recorded. On clamping the pin to the arm, it was of utmost importance that the arm was maintained in a horizontal position whilst the clamps were tightened such that the entire face of the pin was in contact with the disc. Before the test was begun, careful degreasing of the disc was carried out to prevent a lubrication effect. The time was recorded, and the disc set in motion with the 10Kg load applied to the pin. A chart recorder was used to display the output of the two transducers, such that an appreciable change in length of the pin could be measured. After sufficient time (approximately 3 hours), the test was stopped and the pin removed and re-measured. The results were calculated as previously described, along with a determination of the coefficient of friction during each test. Torque was measured by transducer measurement of a fixed stop, and knowing the applied vertical load of 10Kg, a value of dynamic coefficient of friction could be calculated.

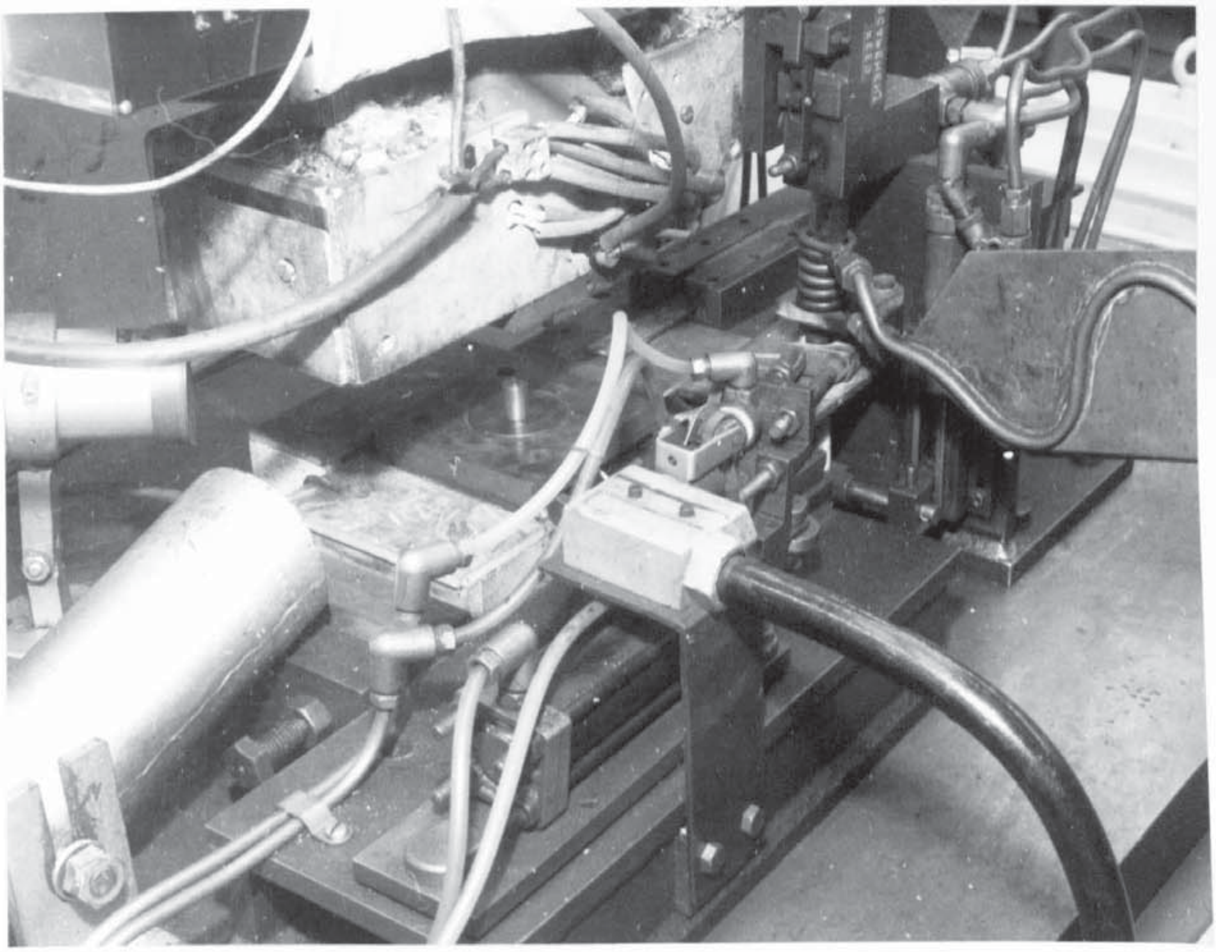
## 14.2. The Simulated Hot Forging Test

The laboratory scale hot forging test used to evaluate wear and erosion of die steels specially treated in order to improve their wear resistance has been described previously.(75)

The test was essentially an upset forging operation carried out between two flat dies coated with the cobalt system under examination. A mechanical press, which had been modified, supplied an automatic feed of hot billets and ejection of forgings (see Fig.14). The complete forging cycle occupied only 10 seconds thus enabling a large number of forging operations to be carried out in a relatively short time. A billet of EN 3B steel 1.2cm diameter x 1.8cm long was fed into an H.F coil and heated to approximately 1200°C. It was then transferred to the forging dies by tongs where an optical pyrometer was used to determine its temperature. The forging stroke was not activated until the billet temperature lay in the range 1110-1140°C. During forging, the billet height was reduced from 1.8cm to 0.6cm, and subsequently ejected. A counter mechanism operated by the forging stroke determined the number of forging operations. A standard test of a thousand forging operations was employed as this was comparable with earlier work. The dies were held in the press in bolsters which were electrically heated to 130°C. Heating of the die bolsters was necessary as without auxiliary heating the bulk die temperature only rose to about 60°C due to the small billet/bolster mass ratio. Such a low temperature rise during forging was not consistent with industrial experience where the billet/bolster mass ratio is higher leading to a much greater heat imput to the

Fig 14.

Mechanical press used for laboratory scale hot forging trials.



die. After forging, the surface of the die was descaled electrolytically. The back and sides of the die were coated with a suitable lacquer and using a carbon rod as an anode, the surface of the die was cleaned cathodically in a solution of 5% V/V $H_2SO_4$ containing 0.1% by weight O-tolylthiourea as an inhibitor. The solution temperature was $75^{o}C$ and the applied current $18\text{-}30A/dm^2$. The maximum time permitted for descaling was 1.5 minutes; this was divided into 30 second periods, each being followed by vigorous brushing of the die surface with a hard brush.

After descaling the surface, four wear traces were taken at $45^{o}$ to each other, as shown in Fig. 15. It was possible to alter the sensitivity of the apparatus so that varying degrees of wear could be evaluated. The length of the trace obtained could also be expanded by X2, x5, and x10 (ie when set at X10, for each 1cm traversed by the stylus, 10cm of trace were produced). Typical traces are shown in Fig. 16. The central plateau region was of approximately the same size as the billet diameter ie. 1.25cm. This represented the area of sticking friction associated with the upset forging operation; it was therefore an area of almost zero metal flow and remained virtually unworn on completion of the forging test. The "wear ring" extended outwards from the edge of the central plateau almost to the diameter of the

Fig 15.

Positions at which wear traces were obtained on the experimental die surface.

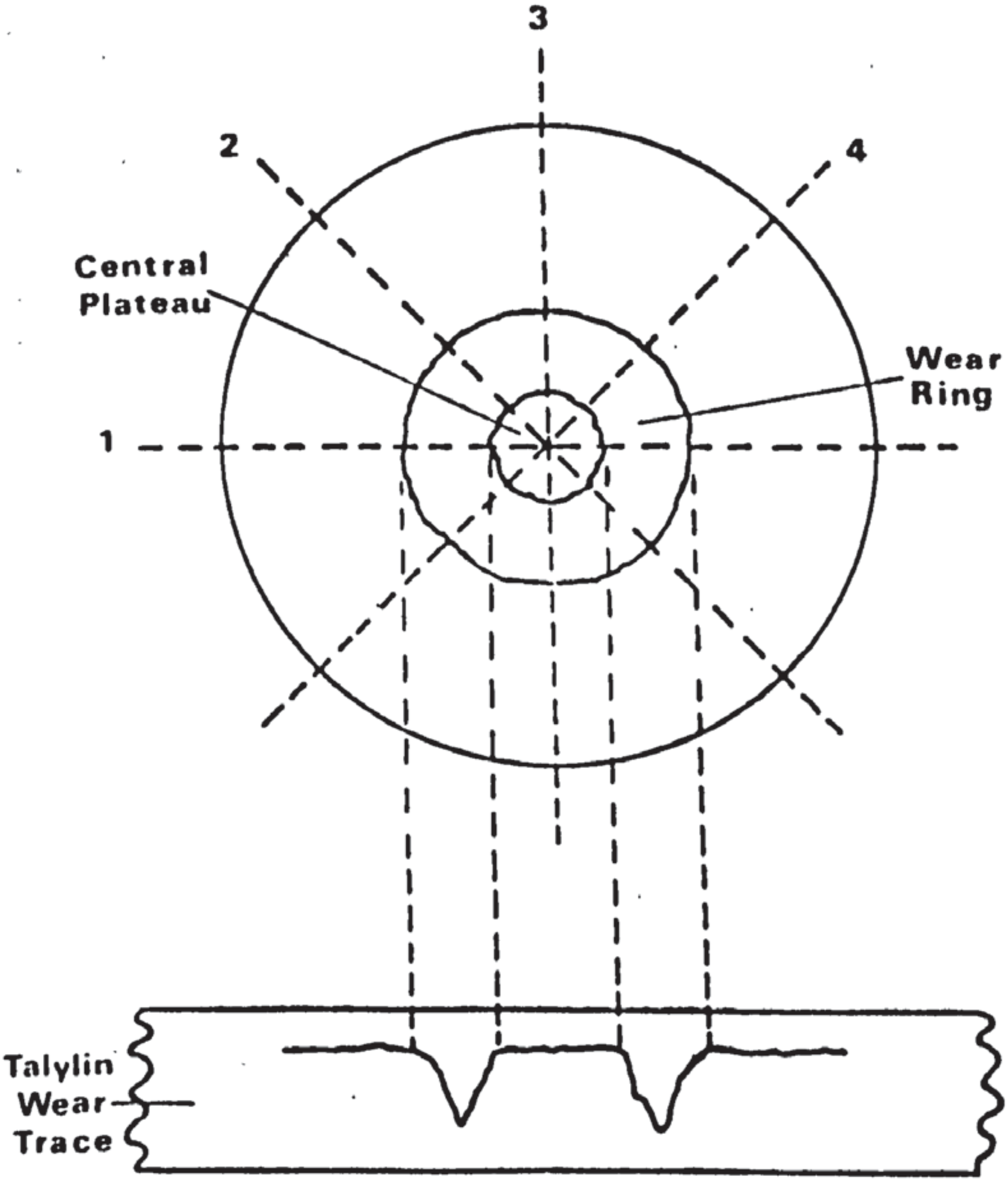
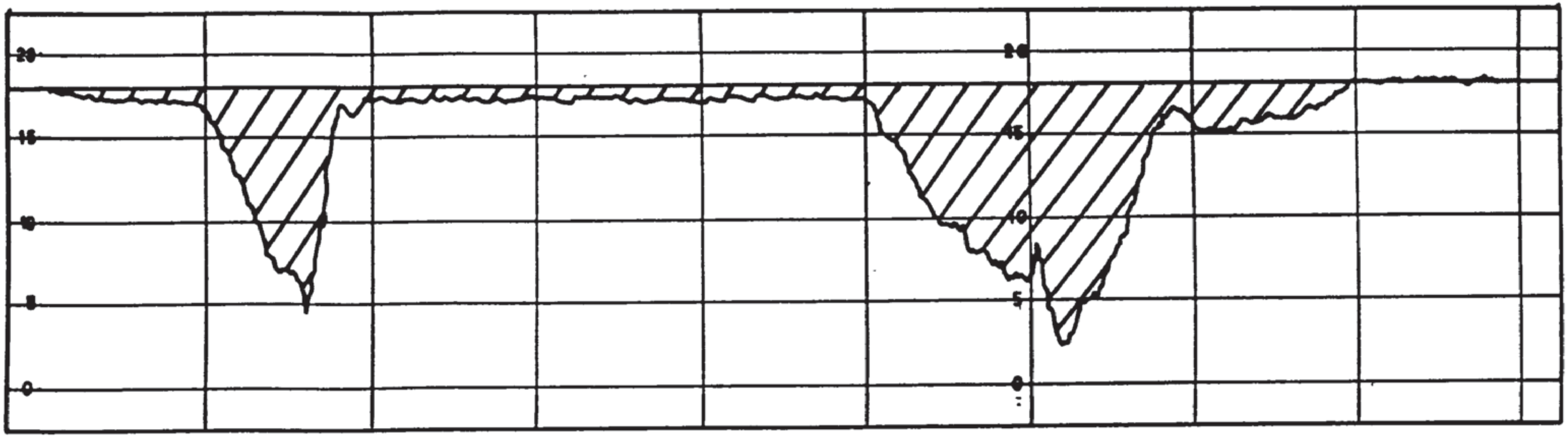


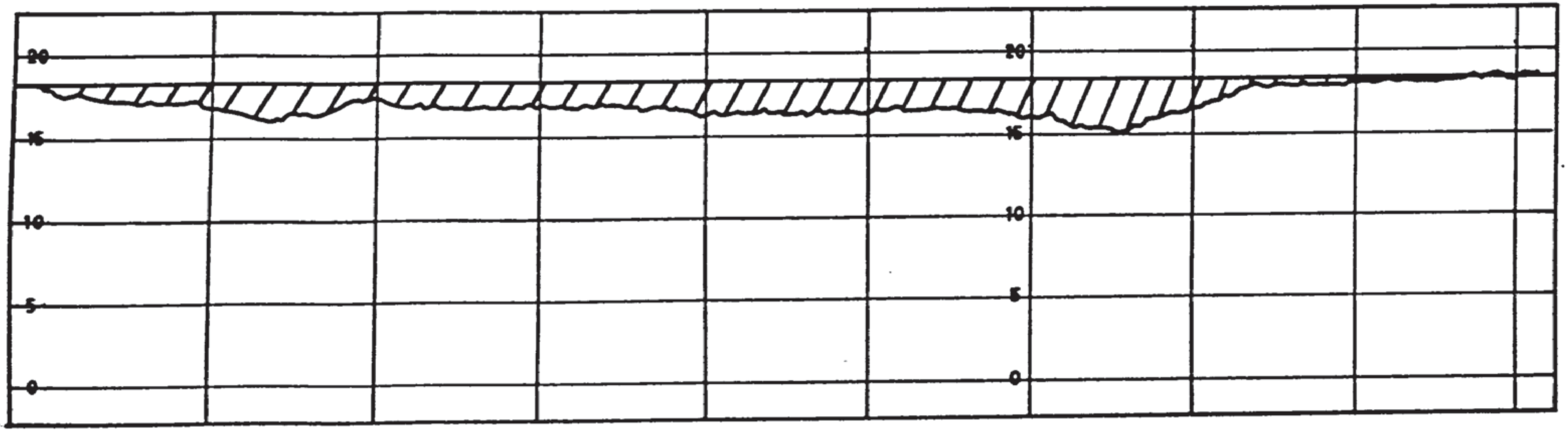
Fig. 16

Fig 16.

Typical wear traces obtained on flat dies after the hot forging test.



16a. Trace obtained from an unplated Electem No 5 die after the hot forging test. Shaded region shows the eroded areas.



16b. Trace obtained from a Cobalt-Molybdenum plated die after hot forging test.

forged billet, approximately 2.5cm. This area was one of metal flow during the forging operation and consequently severe wear of the die surface occured. The extent of wear as assessed in terms of the mean wear volume was evaluated as described below:-

In order to calculate the amount of wear a line was drawn across the wear trace connecting the two original surfaces, (Fig 16a). The outer and inner extremities of the wear ring were then marked and the diameters measured. From these measurements the mean wear diameter was calculated using the expression:-

$$\text{mean wear diameter} = \text{inner diameter} + \left(\frac{\text{outer dia} - \text{inner dia}}{2}\right)$$

The area bounded by the wear trace and the original surface line (shown cross hatched in Fig 16a) was then determined using a planimeter. This gave the apparent wear area, in $\text{cm}^2$ which was dependent upon the magnification employed in producing the trace. The wear volume, in $\text{cm}^3$, (ie the quantity of metal lost during the forging operation) was then found by rotating half the wear area about the mean wear circle ie

$$\text{wear volume} = \frac{\text{Wear area}}{2} \times \text{mean wear diameter} \times \pi$$

The mean of the four wear volumes calculated in this way was then found.

For each forging trial, the wear volumes of top and bottom dies were calculated, and their mean calculated. This technique was used to evaluate the wear properties of cobalt tungsten and cobalt molybdenum deposits on dies plated as in section (11.1). Also presented in the appropriate table are similar wear results obtained from alternative brush plated coatings.

## 14.3 Industrial Trials.

In addition to the assessment of wear by the two laboratory scale techniques, it was considered of great importance to evaluate the cobalt alloy coatings on hot forging dies and cold pressing tools. Consequently, having developed solutions capable of depositing sound cobalt alloy coatings (see section 12.2), it was decided to investigate "on site" application in a number of tool rooms and forges. This would enable the possibility of "on site" electrodeposition to be studied along with the effectiveness of the wear resistant coatings.

The problems involved in carrying out industrial trials were considerable, as managers actions and decisions, were governed by finance and production targets. Mutual cooperation between the author and the relevent management was essential if meaningful results were to be obtained. In many cases this involved plating metal working tools at short notice, or being prevented from doing so due to an immediate requirement for the die.

The selection of hot forging dies for treatment was also of great relevence. Dies which fail prematurely due to poor design were avoided if possible, as it was considered that any amount of surface treatment would not alleviate inherent design weakness. However invariably it was the "problem" dies that die shop managers wanted treating as "if it works on this, it will work on anything!" In fact, a number of such dies were treated, but preference was given to dies having a known predictable life with least scatter. It was considered that selection of such dies would best indicate any advantages incurred by the application of the deposit. In the case of hot forging dies, the improvement in performance sought after plating were as follows:-

1) Improvement in number of forgings before die was out of tolerance and had to be re-sunk.

2) Improvement in quality of forgings - surface finish, tolerances, due to lack of scale build up.

3) The lowering of forging loads, ie use of smaller forging presses.

4) The lowering of forging temperatures.

5) Prevention of forgings "sticking" in die impressions.

6) Speed of production:- would the coating mean less "down time" for press, due to reduced "dressing of the impression".

In the case of cold pressing tools, evaluation in coating performance could not be assessed in such a simple manner. Many of the cold pressing tools plated in this work were used in the automobile industry engaged in car body panel production. In this instance, the improvement of die "life" has little meaning, as the tools are used throughout the production of a particular model of car, and may produce many thousands of pressings. Cold pressing tools are far more complex in construction than the hot forging dies, and present a considerable challenge for brush plating. This was mainly due to the variety of die materials encountered and the frequency with which welded assemblies had to be plated. Improvements in performance after plating the cold pressing tools were sought as follows:-

1) Reduction in "pick up" ie limiting the degree of scoring of the pressed panel and tool, caused by welding of the pressing to the forming tool.

2) Reduction in "down time" (and hence operating costs) due to reducing "pick up".

3) Removal of the need to lubricate panels prior to pressing into difficult shapes.

Although the brush plating of metal working tools "on site" involved the same pre treatment and plating techniques as used on the laboratory scale dies (see sections 11.1), thorough degreasing was essential. In most cases, the cold pressing tools treated had been in production for a considerable period and had become heavily contaminated with drawing lubricants and grease. It was imperative to remove as much of this as possible, and an extremely effective proprietary degreasing agent "Inhibisol" was used for this purpose. In the case of hot forging dies, the entire working area was plated, but only certain sections of cold pressing tools were treated, where it was considered that "pick up" or scoring may be a problem.

After an estimation of the area to be plated had been made, the required number of Ampere-hours was determined for the application of 12µm of deposit. This calculation was made on the basis that the passage of 1Ah when brush plating an area of 1 $dm^2$ resulted in a deposit of approximately 12µm thick (assuming even coverage of the surface). When plating tools of a complex nature, burning of the deposit was likely due to an increase in effective current density on sharp corners, consequently the deposit in such areas was constantly visually monitored. Plating in these areas was immediately suspended on the suspicion of burning or stressing. On completion of the plating operation great care was taken to remove excess electrolyte and any water remaining after washing down the treated area, in order to prevent seepage into the die assembly unit.

Perhaps the most difficult aspect of industrial trials was the monitoring of the dies after treatment. During these trials, there were instances of the coating being ground off before putting into production, or "cold" billets being forged and ruining the dies. Hence monitoring of coating effectiveness had to be sufficient to prevent the aforementioned happening without being so great as to render special attention to the die and give "false" results. The frequency with which results were obtained was dependent entirely on the scheduling of orders and hence out of the author's control. Consequently many of the dies plated during this investigation have as yet to be tested. Similarly a number of treated dies have been scrapped due to unforeseen modifications. The results of all of the industrial trials are presented in the appropriate section, together with the available information on performance.

# 15. RESULTS OF ELECTROLYTE DEVELOPMENT

## 15.1. Composition Trials on Cobalt Brush Plating Solutions.

The results of the composition trials carried out on cobalt sulphate based electrolytes are presented in tables VIII and IX.

Table VIII is concerned with the effect of the concentration of sodium heptonate on efficiency for electrolytes containing 500 g/l and 250 g/l cobalt sulphate. These results are illustrated in fig.17, where it can be seen that at all levels of sodium heptonate used, the efficiency of solutions containing 500 g/l of cobalt sulphate was greater. The addition of 400 g/l of sodium heptonate to solutions containing either level of cobalt sulphate resulted in an equivalent fall in cathode efficiency of 25%. All deposits produced in this trial were examined visually for evidence of stressing or burning, however the majority of the coatings used were sound.

Table IX indicates the effect of sodium heptonate and glacial acetic acid upon the cathode efficiency of a 500 g/l cobalt sulphate based brush plating solution. Line (a) in fig.18 illustrates the effect of the concentration of acetic acid only

## TABLE VIII

## Effect of the concentration of Sodium Heptonate on Cathode Efficiency for Electrolytes containing two levels of Cobalt Sulphate.

| Cobalt Sulphate g/l | Sodium Heptonate g/l | Weight Deposited(g) after 0.3A/h | Cathode Current Effic.% | Deposit Quality |
|---|---|---|---|---|
| 500 | 0 | 0.3020 | 83.20 | Sound |
| " | 100 | 0.2490 | 73.36 | " |
| " | 200 | 0.2270 | 67.70 | " |
| " | 300 | 0.1908 | 58.88 | " |
| " | 400 | 0.1954 | 58.25 | " |
| 250 | 0 | 0.2476 | 73.90 | Slight Stress |
| " | 100 | 0.2108 | 62.90 | Sound |
| " | 200 | 0.1683 | 50.24 | " |
| " | 300 | 0.1902 | 56.77 | " |
| " | 400 | 0.1615 | 48.21 | " |

Operating Conditions:-

Brush Plated at 17.0V

pH 1.5

# TABLE IX

## Effect of the Concentration of Glacial Acetic Acid on Cathode Efficiency for Cobalt Sulphate Eelectrolytes

| Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Acetic Acid g/1 | Weight deposited(g) after 0.3A/H | Cathode Current Effic.% | Deposit Quality |
|---|---|---|---|---|---|
| 500 | 0 | 0 | 0.3020 | 83.20 | Sound |
| " | " | 10.5 | 0.2698 | 80.53 | " |
| " | " | 21.0 | 0.2660 | 79.40 | " |
| " | " | 42.0 | 0.2576 | 76.89 | " |
| " | " | 84.0 | 0.2432 | 72.59 | " |
| 500 | 200 | 0 | 0.2308 | 68.90 | " |
| " | " | 10.5 | 0.2369 | 70.71 | " |
| " | " | 21.0 | 0.2356 | 70.32 | " |
| " | " | 42.0 | 0.2168 | 64.71 | " |
| " | " | 84.0 | 0.1983 | 59.19 | " |

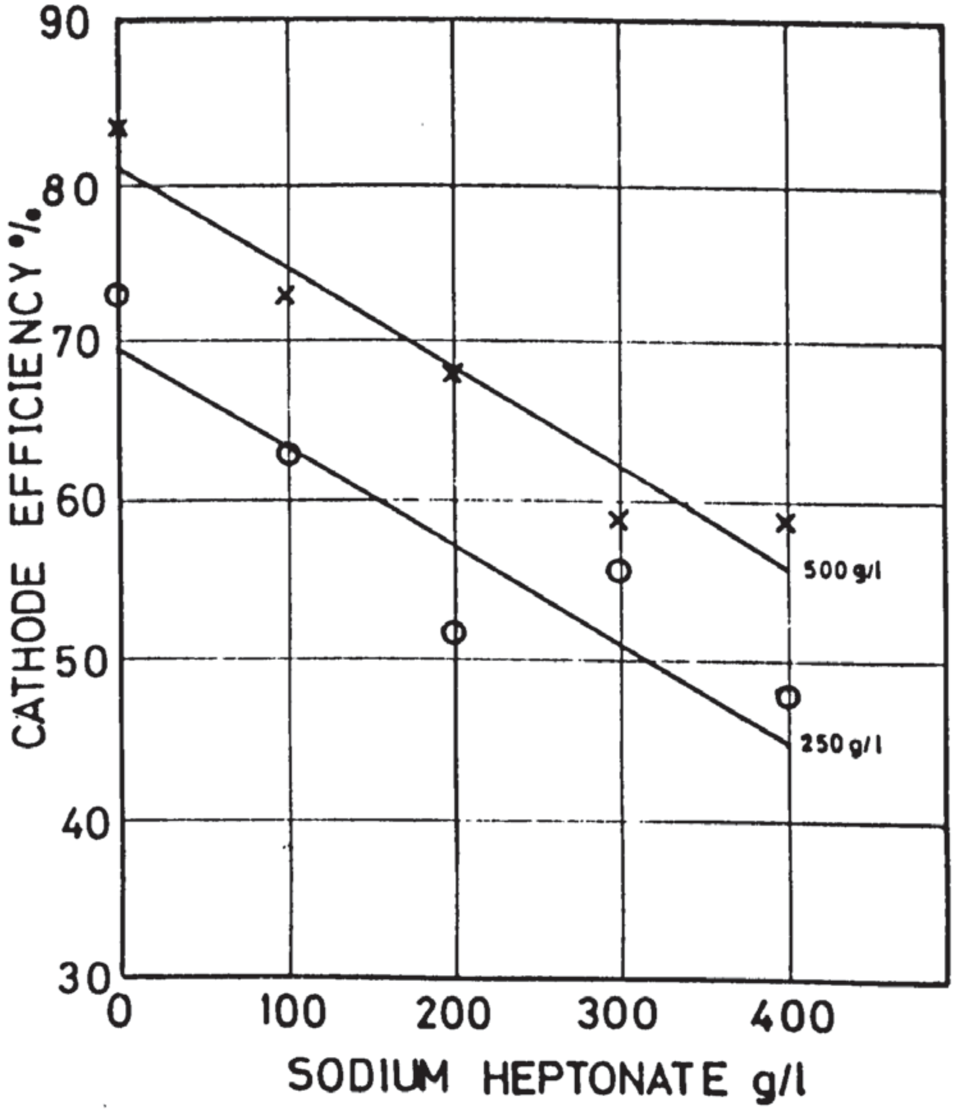
Operating Conditions:-

Brush plated at 17.0V

pH 1.5

Fig 17.

Effect of the Concentration of Sodium Heptonate on Cathode Efficiency for Electrolytes Containing two levels of Cobalt Sulphate.

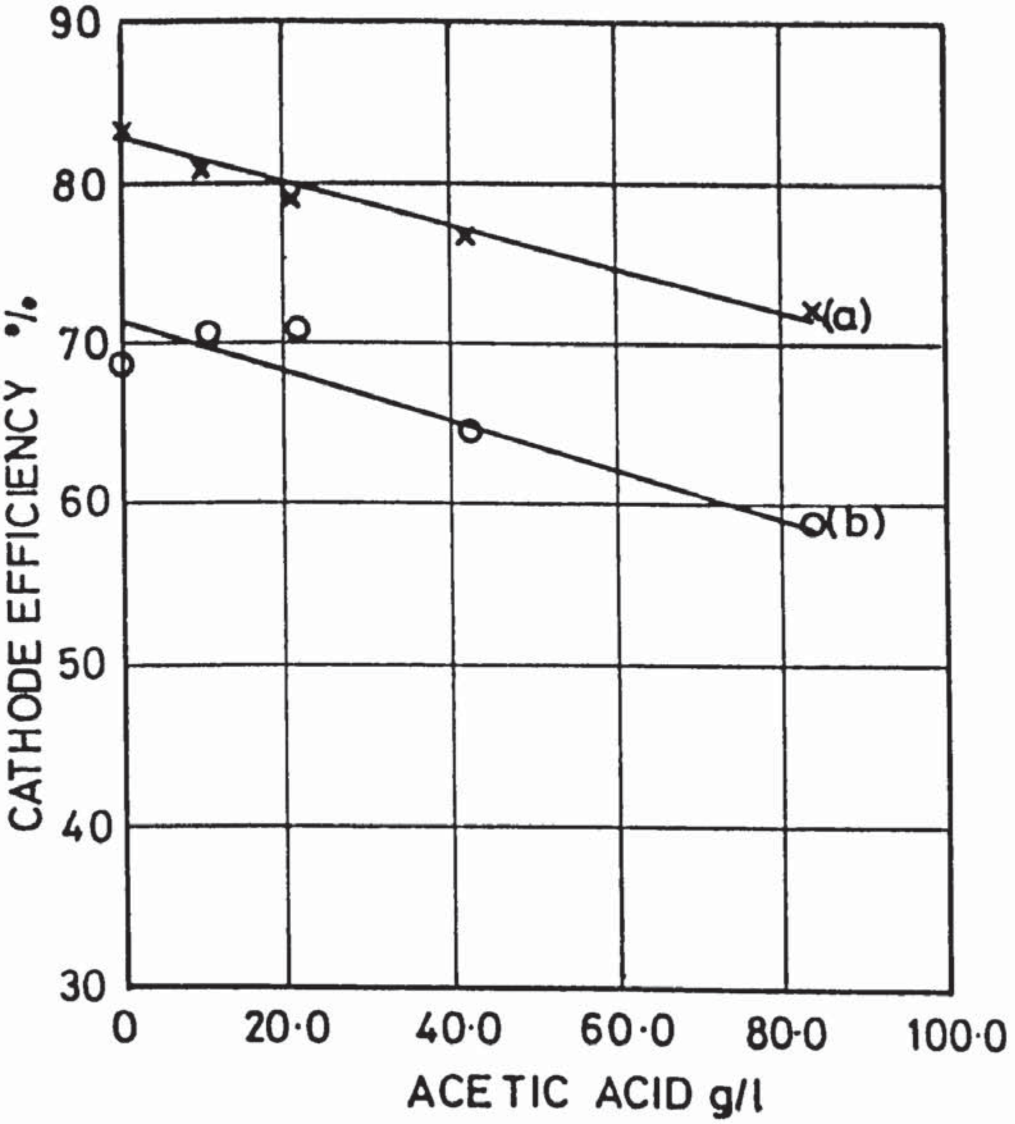


Operating Conditions:-
Brush plated at 17V on to
5 x 5cm brass panels for
0.3Ah pH 1.5

Composition:-
500g/l or 250 g/l
Cobalt Sulphate
0-400 g/l Sodium
Heptonate.

Fig 18.

Effect of the Concentration of Glacial Acetic Acid on Cathode Efficiency for Cobalt Sulphate Electrolytes.



Operating Conditions:-
Brush plated at 17V on to
5 x 5cm brass panels for
0.3Ah pH 1.5.

Composition:-
500g/l Cobalt Sulphate
0-84g/l Acetic Acid
(a) No Sodium Heptonate
(b) 200g/l Sodium Heptonate

on efficiency, whilst line (b) shows the combined effects of acetic acid with the addition of 200 g/l sodium heptonate. In both cases, it can be seen that progressive additions of acetic acid result in a lowering of cathode efficiency, but solutions containing 200 g/l of sodium heptonate were less efficient overall. However, when plating with solutions containing acetic acid at the operating voltage (17v) burning of the deposit appeared less likely on a change in the direction of stylus movement. Furthermore the addition of acetic acid to the solutions permitted slower stylus movement with less evidence of deposit burning.

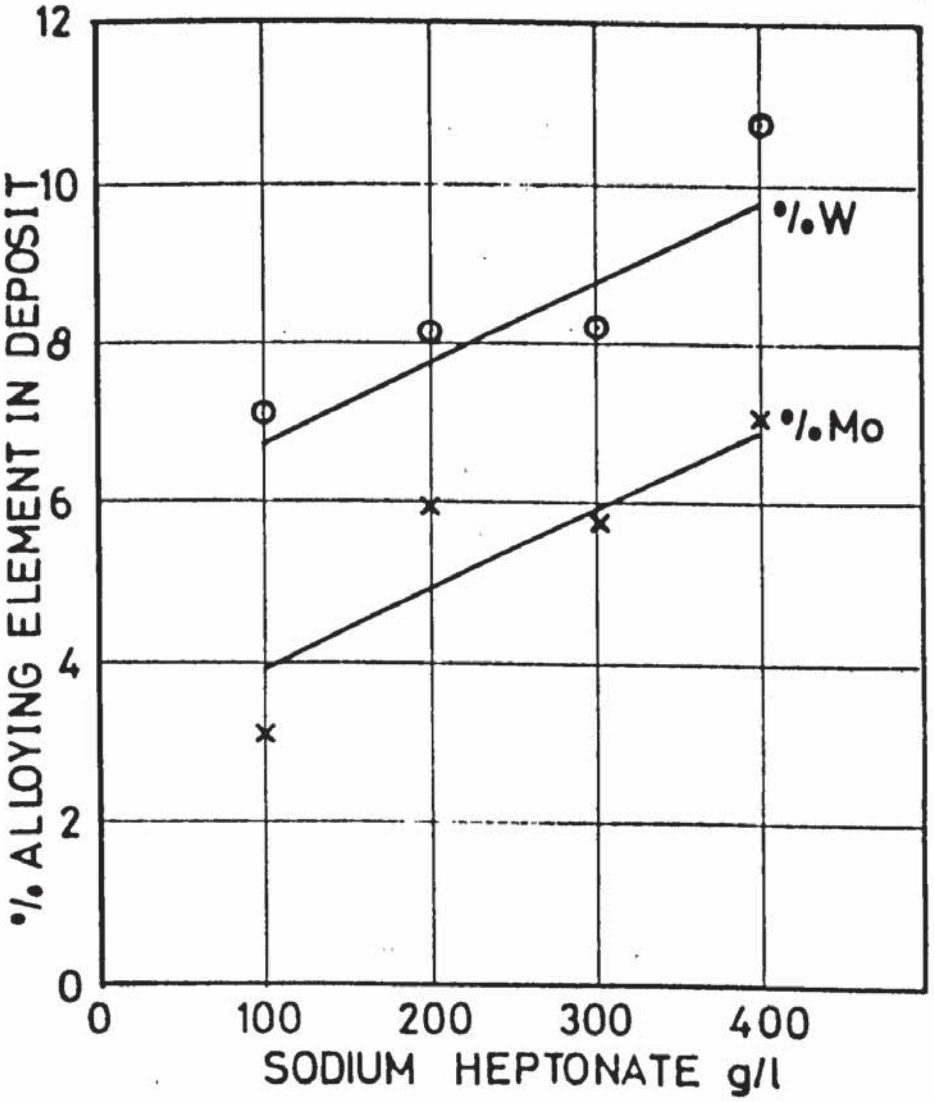
## 15.2. Composition Trials on Cobalt Tungsten and Cobalt Molybdenum Electrolytes.

The results of the composition trials on cobalt molybdenum and cobalt tungsten electrolytes are shown in tables X and XI respectively. For each electrolyte composition tested, the cathode efficiency was calculated and presented along with an assessment of deposit quality. The trends exhibited by these results are best illustrated by reference to Fig. 19-22.

Fig 19 demonstrates the effect of the concentration of sodium heptonate on the composition of the deposit. These graphs are for electrolytes containing 42.0 g/l of acetic acid and either 50.4 g/l Sodium tungstate or 50.4 g/l sodium molybdate. Over the range 100-400 g/l of sodium heptonate, the cobalt tungsten deposits contained the highest concentration of alloying element. Increasing the concentration of sodium heptonate within this range resulted in higher concentrations of alloying element being incorporated into the deposit for both systems. As the concentration of sodium heptonate was increased from 100 to 400 g/l, the amount of molybdenum in the deposit rose from 3.1% to 7.3%. Over the same range of sodium heptonate concentration, the level of tungsten in the cobalt tungsten deposits rose from 7.3% to 10.5%.

Fig 19.

Effect of Concentration of Sodium Heptonate on the Composition of the Deposit.



Operating Conditions:-
Brush plated at 17V on
to 5 x 5cm brass panels
for 0.3Ah pH 1.5

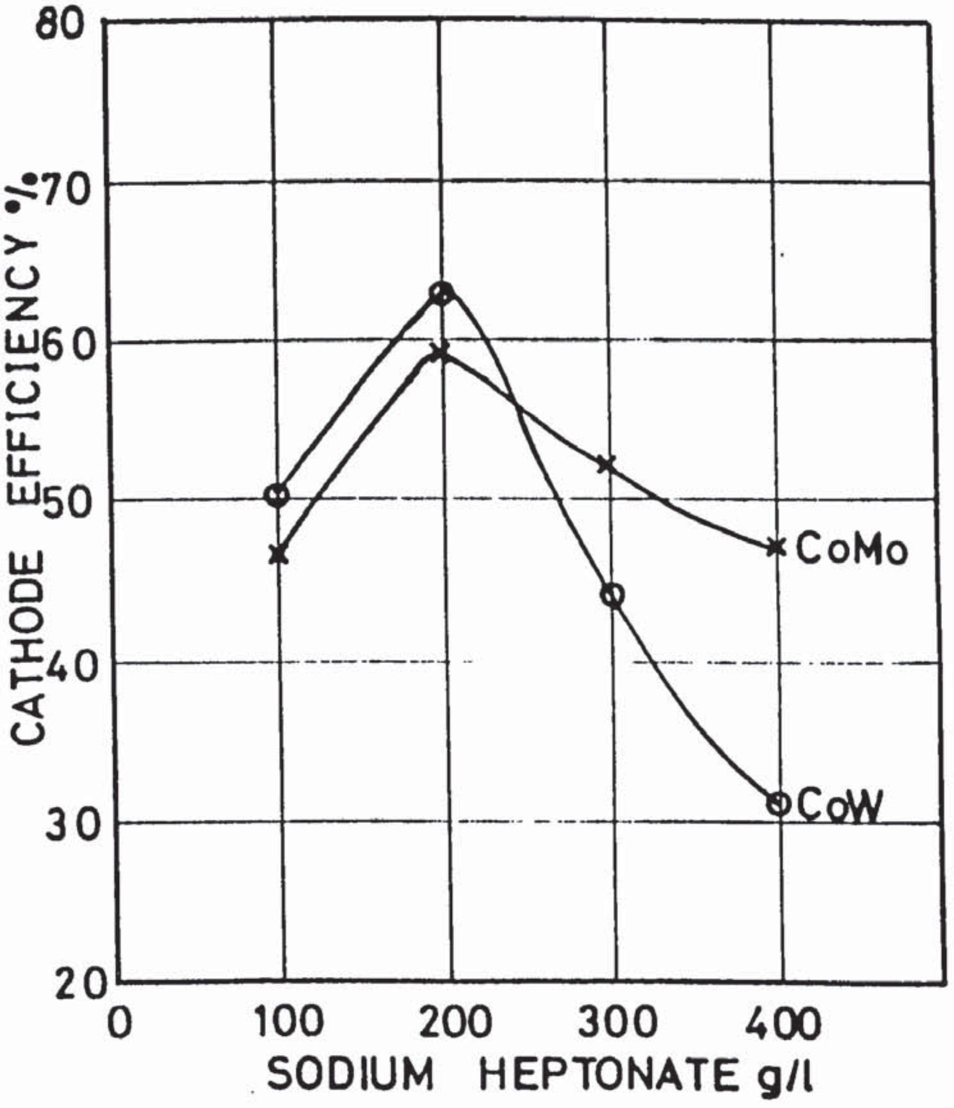
Composition:-
500g/l Cobalt Sulphate
100-400g/l Sodium Heptonate
42.0g/l Acetic Acid
50.4g/l Sodium Tungstate or
Sodium Molybdate.

Fig. 20 illustrates the effect of sodium heptonate concentration on efficiency for the deposits represented by Fig. 19. For both cobalt tungsten and cobalt molybdenum systems, maximum cathode efficiency coincided with a sodium heptonate concentration of 200 g/l. At this level of sodium heptonate, deposition from the cobalt tungsten system proved most efficient at 64%, compared with the cobalt molybdenum system at 57%. Below 200 g/l of sodium heptonate, the cobalt tungsten system remained most efficient, whilst above this level, the efficiency of the cobalt tungsten system fell away rapidly to below that of the cobalt molybdenum system. Examination of the deposits from the above trials showed that solutions containing 200 g/l of sodium heptonate exhibited lower levels of stressing and burning for both systems.

The effect of the concentration of acetic acid on deposit composition can be seen in Fig.21. A fixed concentration of sodium heptonate of 200 g/l was chosen as electrolytes containing this level proved most efficient (Fig.20). Also, the solutions illustrated by Fig.21 contained either 50.4 g/l of sodium tungstate or the equivalent weight of sodium molybdate. Over the range of acetic acid from 10.5 to 84.0 g/l, there was a decrease in the concentration

Fig 20.

Effect of the Concentration of Sodium Heptonate on Cathode Efficiency.

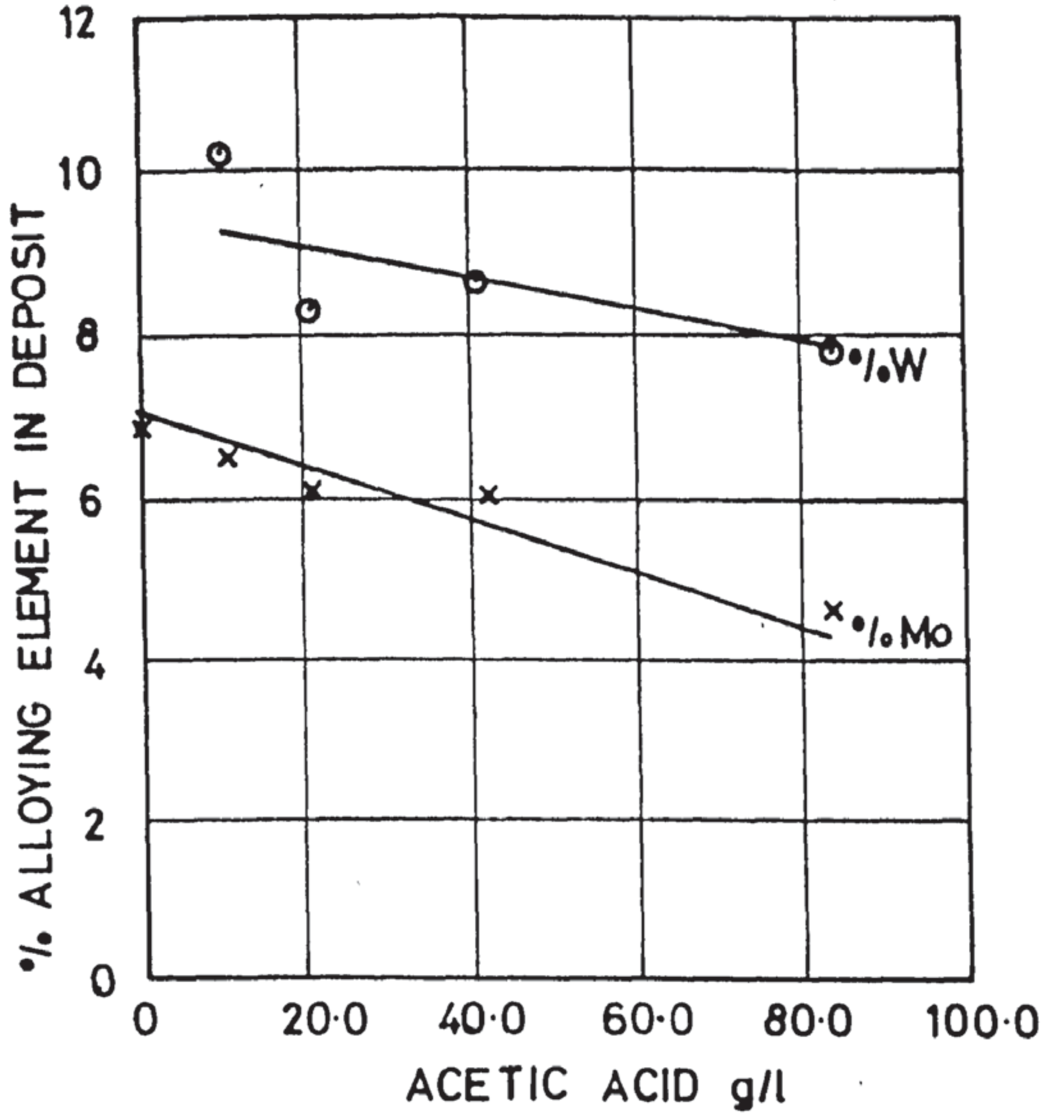


Operating Conditions:-
Brush plated at 17V
on to 5 x 5cm brass
panels for 0.3 Ah
pH 1.5

Composition:-
500g/l Cobalt Sulphate
100-400g/l Sodium Heptonate
42.0g/l Acetic Acid
50.4g/l Sodium Tungstate
or Sodium Molybdate.

Fig 21.

Effect of the Concentration of Acetic Acid on Deposit Composition.



Operating Conditions:-
Brush plated at 17V on
5 x 5cm brass panels for
0.3Ah pH 1.5.

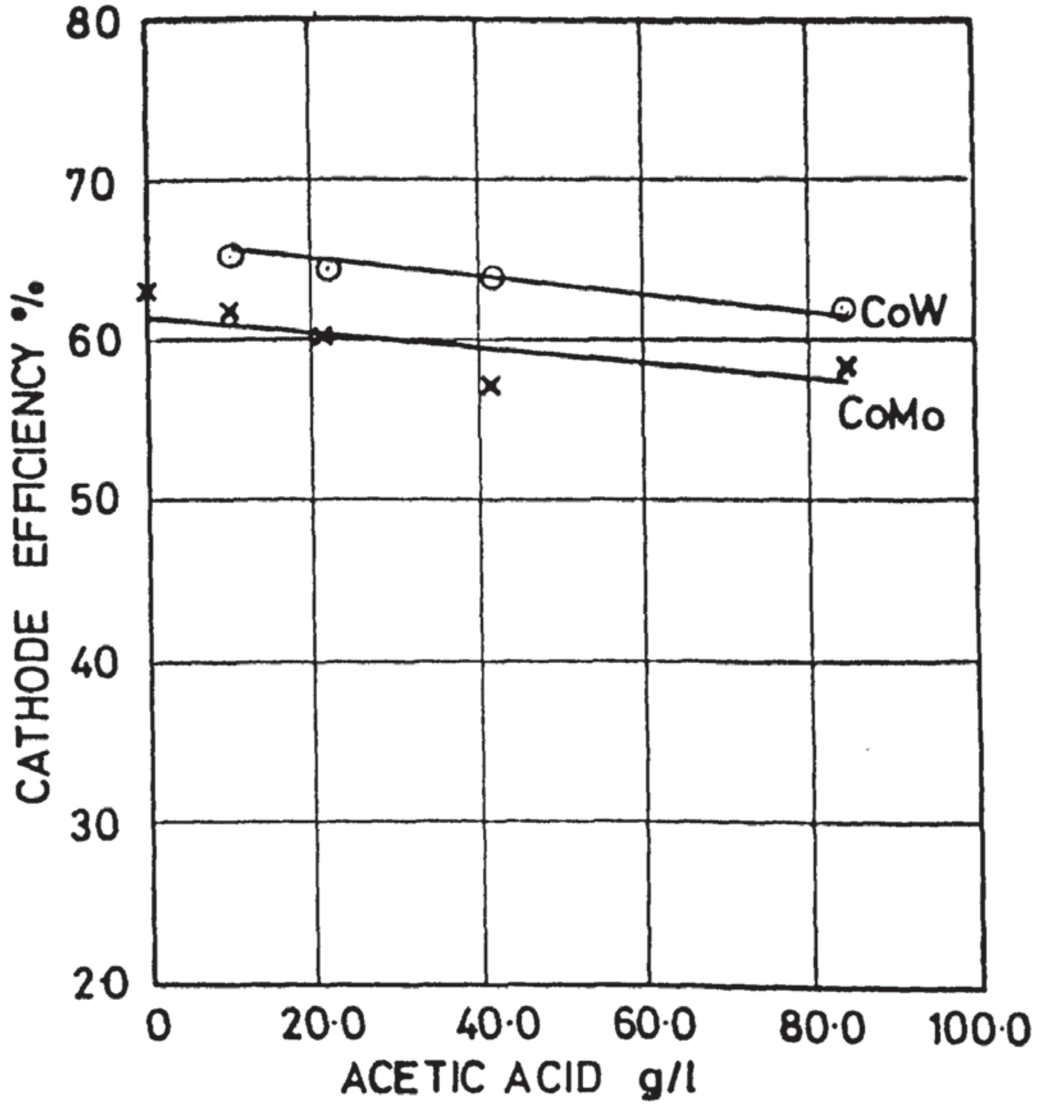
Composition:-
500g/l Cobalt Sulphate
200g/l Sodium Heptonate
0-84g/l Acetic Acid
50.4g/l Sodium Molybdate
or Sodium Tungstate.

of alloying element in the deposit. In the case of the cobalt tungsten deposits this fell from 10.3% to 7.8%, whilst for the cobalt molybdenum deposits the concentration of molybdenum fellfrom 6.9% to 4.6%. Thus over this range of acetic acid concentration, the cobalt tungsten system appeared capable of producing the more highly alloyed deposits. Fig. 22 illustrates the effect on cathode efficiency of these additions of acetic acid. Over the range of acetic acid considered (10.5-84.0 g/l), the overall efficiency of deposition from cobalt tungsten electrolytes was greater than that from the equivalent cobalt molybdenum electrolytes. However, increasing the concentration of acetic acid resulted in a fall in cathode efficiency for both systems. In the case of the cobalt tungsten system, increasing the concentration of acetic acid from 10.5-84.0 g/l reduced the efficiency from 65% to 62%. whilst the resultant fall in efficiency for the cobalt molybdenum system was from 61% to 57%.

Throughout plating trials, it appeared that the addition of glacial acetic acid helped to prevent burning of the deposit due to slow stylus movement. However tables X and XI indicate that cathode efficiency may suffer as a result of additions of acetic acid in excess of 42.0 g/l.

Fig 22.

Effect of the Concentration of Acetic Acid on Efficiency.



Operating Conditions:-
Brush plated at 17V on
5 x 5cm brass panels for
0.3Ah pH 1.5.

Composition:-
500g/l Cobalt Sulphate
200g/l Sodium Heptonate
0-84.0g/l Acetic Acid
50.4g/l Sodium Molybdate
or Sodium Tungstate.

## TABLE X

### Results of Composition Trials on Cobalt Molybdenum Electrolyte

| Sol No | Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Sodium Molybdate g/1 | Acetic Acid g/1 | Mo in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 1 | 500 | 400 | 70.0 | 0 | 9.0 | 70.11 | Burned | 0.2176 |
| 1A | " | " | " | 10.5 | 8.9 | 57.79 | Slight Stress | 0.1798 |
| 1B | " | " | " | 21.0 | 10.9 | 53.96 | " " | 0.1652 |
| 1C | " | " | " | 42.0 | 8.3 | 48.92 | " " | 0.1527 |
| 1D | " | " | " | 84.0 | 9.9 | 50.82 | " " | 0.1556 |
| 2 | " | " | 50.4 | 0 | 11.4 | 69.09 | Slight Stress | 0.2103 |
| 2A | " | " | " | 10.5 | 8.9 | 53.14 | " " | 0.1648 |
| 2B | " | " | " | 21.0 | 6.5 | 48.12 | " " | 0.1526 |
| 2C | " | " | " | 42.0 | 7.3 | 47.33 | Sound | 0.1490 |
| 2D | " | " | " | 84.0 | 5.6 | 44.91 | Sound | 0.1437 |
| 3 | " | " | 25.2 | 0 | 7.1 | 56.53 | Slight Stress | 0.1782 |
| 3A | " | " | " | 10.5 | 6.2 | 70.17 | Stressed | 0.1594 |
| 3B | " | " | " | 21.0 | 6.3 | 51.87 | Stressed | 0.1656 |
| 3C | " | " | " | 42.0 | | | | 0.1755 |
| 3D | " | " | " | 84.0 | 5.7 | 48.39 | Sound | 0.1542 |
| 4 | " | " | 12.6 | 0 | 3.8 | 68.8 | Stressed | 0.2145 |
| 4A | " | " | " | 10.5 | 5.7 | 57.33 | Slight Stress | 0.1840 |
| 4B | " | " | " | 21.0 | 5.2 | 54.89 | " " | 0.1764 |
| 4C | " | " | " | 42.0 | 4.2 | 52.76 | " " | 0.1710 |
| 4D | " | " | " | 84.0 | 3.7 | 48.11 | " " | 0.1559 |
| 5 | " | 300 | 70.0 | 0 | 9.0 | 61.87 | Burned | 0.1920 |
| 5A | " | " | " | 10.5 | 8.3 | 66.43 | Stressed | 0.2082 |
| 5B | " | " | " | 21.0 | 8.0 | 63.27 | " | 0.1980 |
| 5C | " | " | " | 42.0 | 5.0 | 53.67 | " | 0.1717 |
| 5D | " | " | " | 84.0 | 6.0 | 48.72 | " | 0.1558 |

## TABLE X Cont'd

### Results of Composition Trials on Cobalt Molybdenum Electrolyte

| Sol No | Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Sodium Molybdate g/1 | Acetic Acid g/1 | Mo in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 6 | 500 | 300 | 50.4 | 0 | 9.5 | 70.88 | Slight Stress | 0.2191 |
| 6A | " | " | " | 10.5 | 6.6 | 52.58 | Sound | 0.1667 |
| 6B | " | " | " | 21.0 | 6.2 | 54.55 | Sound | 0.1730 |
| 6C | " | " | " | 42.0 | 5.8 | 52.23 | Slight Stress | 0.1660 |
| 6D | " | " | " | 84.0 | 4.6 | 64.14 | Slight Stress | 0.2078 |
| 7 | " | " | 25.2 | 0 | 10.4 | 68.15 | Stressed | 0.2092 |
| 7A | " | " | " | 10.5 | 4.7 | 51.98 | " | 0.1672 |
| 7B | " | " | " | 21.0 | 5.0 | 65.76 | " | 0.2104 |
| 7C | " | " | " | 42.0 | 3.9 | 54.25 | Sound | 0.1756 |
| 7D | " | " | " | 84.0 | 3.7 | 54.80 | Slight Stress | 0.1770 |
| 8 | " | " | 12.6 | 0 | 9.4 | 65.54 | Stressed | 0.2030 |
| 8A | " | " | " | 10.5 | 1.6 | 53.20 | " | 0.1756 |
| 8B | " | " | " | 21.0 | 2.2 | 57.90 | " | 0.1909 |
| 8C | " | " | " | 42.0 | 2.3 | 56.41 | " | 0.1860 |
| 8D | " | " | " | 84.0 | 2.4 | 56.29 | " | 0.1858 |
| 9 | " | 200 | 70.0 | 0 | 8.0 | 50.06 | Burned | 0.1567 |
| 9A | " | " | " | 10.5 | 6.5 | 62.40 | Stressed | 0.1978 |
| 9B | " | " | " | 21.0 | 9.3 | 45.66 | Burned | 0.1412 |
| 9C | " | " | " | 42.0 | 6.2 | 66.47 | Burned | 0.1994 |
| 9D | " | " | " | 84.0 | 5.2 | 49.65 | Sound | 0.1598 |
| 10 | " | " | 50.4 | 0 | 6.9 | 63.0 | Slight Stress | 0.1995 |
| 10A | " | " | " | 10.5 | 6.5 | 62.4 | Slight Stress | 0.2052 |
| 10B | " | " | " | 21.0 | 6.1 | 60.51 | Slight Stress | 0.1924 |
| 10C | " | " | " | 42.0 | 6.0 | 57.25 | Sound | 0.1822 |
| 10D | " | " | " | 84.0 | 4.6 | 59.36 | Sound | 0.1922 |

## TABLE X Cont'd

### Results of Composition Trials on Cobalt Molybdenum Electrolyte

| Sol No | Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Sodium Molybdate g/1 | Acetic Acid g/1 | Mo in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 11 | 500 | 200 | 25.2 | 0 | 6.4 | 78.13 | Slight Stress | 0.2477 |
| 11A | " | " | " | 10.5 | 3.2 | 68.23 | " " | 0.2227 |
| 11B | " | " | " | 21.0 | 4.0 | 60.89 | " " | 0.1972 |
| 11C | " | " | " | 42.0 | 5.2 | 59.24 | " " | 0.1898 |
| 11D | " | " | " | 84.0 | 4.2 | 56.81 | " " | 0.1832 |
| 12 | " | " | 12.6 | 0 | 10.3 | 73.75 | Severe Stress | 0.2265 |
| 12A | " | " | " | 10.5 | 3.6 | 75.61 | Stressed | 0.2455 |
| 12B | " | " | " | 21.0 | 5.3 | 71.5 | " | 0.2195 |
| 12C | " | " | " | 42.0 | 3.2 | 63.63 | " | 0.2069 |
| 12D | " | " | " | 84.0 | 2.3 | 56.56 | " | 0.1862 |
| 13 | " | 100 | 70.0 | 0 | 11.5 | 48.27 | Burned | 0.1468 |
| 13A | " | " | " | 10.5 | | | Burned | 0.1433 * |
| 13B | " | " | " | 21.0 | | | Severe Stress | 0.1066 * |
| 13C | " | " | " | 42.0 | | | " " | 0.1078 * |
| 13D | " | " | " | 84.0 | 4.4 | 37.62 | " " | 0.1218 |
| 14 | " | " | 50.4 | 0 | 4.4 | 55.64 | Burned | 0.1794 |
| 14A | " | " | " | 10.5 | 7.0 | 32.96 | Stressed | 0.1044 |
| 14B | " | " | " | 21.0 | 5.5 | 39.85 | Slight Stress | 0.1275 |
| 14C | " | " | " | 42.0 | 3.1 | 46.93 | " " | 0.1530 |
| 14D | " | " | " | 84.0 | 3.9 | 51.36 | " " | 0.1610 |
| 15 | " | " | 25.2 | 0 | 8.5 | 73.11 | Stressed | 0.2278 |
| 15A | " | " | " | 10.5 | 7.8 | 48.46 | " | 0.1518 |
| 15B | " | " | " | 21.0 | 5.8 | 58.39 | " | 0.1860 |
| 15C | " | " | " | 42.0 | 4.3 | 57.14 | Sound | 0.1846 |
| 15D | " | " | " | 84.0 | 3.0 | 54.0 | Sound | 0.1770 |

## TABLE X Cont'd

### Results of Composition Trials on Cobalt Molybdenum Electrolyte

| Sol No | Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Sodium Molybdate g/1 | Acetic Acid g/1 | Mo in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 16 | 500 | 100 | 12.6 | 0 | 9.1 | 70.76 | Stressed | 0.2194 |
| 16A | " | " | " | 10.5 | 5.7 | 69.85 | Slight Stress | 0.2226 |
| 16B | " | " | " | 21.0 | 3.5 | 59.94 | Sound | 0.1947 |
| 16C | " | " | " | 42.0 | 3.8 | 58.69 | Sound | 0.1410 |
| 16D | " | " | " | 84.0 | 1.9 | 54.04 | Sound | 0.1790 |

**Operating Conditions:-**

Brush plated at 17V, 5x5cm brass panel for 0.3A/h
pH 1.5

* Deposits too thin for analysis.

## TABLE XI

### Results of Composition Trials on Cobalt Tungsten Electrolytes.

| Sol No | Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Sodium Tungstate g/1 | Acetic Acid g/1 | W in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 1 | 500 | 400 | 70.0 | 0 | 9.1 | 72.4 | Stressed | 0.2426 |
| 1A | " | " | " | 10.5 | 11.2 | 47.49 | " | 0.1415 |
| 1B | " | " | " | 21.0 | 12.6 | 38.06 | " | 0.1280 |
| 1C | " | " | " | 42.0 | 10.5 | 42.55 | " | 0.1429 |
| 1D | " | " | " | 84.0 | 12.0 | 35.51 | " | 0.1197 |
| 2 | " | " | 50.4 | 0 | 8.6 | 69.6 | " | 0.2336 |
| 2A | " | " | " | 10.5 | 10.4 | 44.07 | " | 0.1484 |
| 2B | " | " | " | 21.0 | 9.6 | 33.89 | " | 0.1137 |
| 2C | " | " | " | 42.0 | 10.8 | 31.38 | " | 0.1058 |
| 2D | " | " | " | 84.0 | 6.9 | 33.52 | " | 0.1122 |
| 3 | " | " | 25.2 | 0 | 8.0 | 61.4 | " | 0.2060 |
| 3A | " | " | " | 10.5 | 6.3 | 51.26 | " | 0.1718 |
| 3B | " | " | " | 21.0 | 7.1 | 36.29 | " | 0.1214 |
| 3C | " | " | " | 42.0 | 5.0 | 52.26 | " | 0.1751 |
| 3D | " | " | " | 84.0 | 6.1 | 38.21 | " | 0.1280 |
| 4 | " | " | 12.6 | 0 | 5.3 | 54.13 | Slight Stress | 0.1816 |
| 4A | " | " | " | 10.5 | 3.5 | 31.95 | " " | 0.1110 |
| 4B | " | " | " | 21.0 | 3.0 | 42.16 | " " | 0.1415 |
| 4C | " | " | " | 42.0 | 2.6 | 31.85 | " " | 0.1066 |
| 4D | " | " | " | 84.0 | 1.8 | 37.11 | " " | 0.1246 |
| 5 | " | 300 | 70.0 | 0 | 15.8 | 70.50 | Stressed | 0.2371 |
| 5A | " | " | " | 10.5 | 10.7 | 51.62 | " | 0.1730 |
| 5B | " | " | " | 21.0 | 11.5 | 62.73 | " | 0.2110 |
| 5C | " | " | " | 42.0 | 9.6 | 39.07 | Slight Stress | 0.1308 |
| 5D | " | " | " | 84.0 | 8.9 | 34.35 | " " | 0.1156 |

## TABLE XI Cont'd

### Results of Composition Trials on Cobalt Tungsten Electrolytes

| Sol No | Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Sodium Tungstate g/1 | Acetic Acid g/1 | W in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 6 | 500 | 300 | 50.4 | 0 | 13.7 | 66.9 | Slight Stress | 0.2255 |
| 6A | " | " | " | 10.5 | 10.7 | 39.63 | Stressed | 0.1334 |
| 6B | " | " | " | 21.0 | 11.5 | 51.83 | " | 0.1741 |
| 6C | " | " | " | 42.0 | 8.3 | 44.40 | " | 0.1490 |
| 6D | " | " | " | 84.0 | 5.8 | 46.65 | " | 0.1566 |
| 7 | " | " | 25.2 | 0 | 11.7 | 58.0 | " | 0.1949 |
| 7A | " | " | " | 10.5 | 5.9 | 43.19 | " | 0.1444 |
| 7B | " | " | " | 21.0 | 6.6 | 45.58 | " | 0.1530 |
| 7C | " | " | " | 42.0 | 7.6 | 52.57 | " | 0.1768 |
| 7D | " | " | " | 84.0 | 5.5 | 33.36 | " | 0.1121 |
| 8 | " | " | 12.6 | 0.8 | 5.6 | 62.30 | " | 0.2093 |
| 8A | " | " | " | 10.5 | 3.7 | 37.46 | " | 0.1252 |
| 8B | " | " | " | 21.0 | 3.0 | 35.98 | " | 0.1202 |
| 8C | " | " | " | 42.0 | 2.6 | 38.66 | " | 0.1300 |
| 8D | " | " | " | 84.0 | 2.6 | 32.75 | " | 0.1126 |
| 9 | " | 200 | 70.0 | 0 | 10.5 | 67.0 | Burned | 0.2249 |
| 9A | " | " | " | 10.5 | 6.3 | 73.18 | " | 0.2460 |
| 9B | " | " | " | 21.0 | 7.6 | 74.66 | Stressed | 0.2508 |
| 9C | " | " | " | 42.0 | 8.5 | 66.25 | " | 0.2224 |
| 9D | " | " | " | 84.0 | 8.0 | 59.05 | " | 0.1980 |
| 10 | " | " | 50.4 | 0 | | | | |
| 10A | " | " | " | 10.5 | 10.3 | 65.50 | Slight Stress | 0.2200 |
| 10b | " | " | " | 21.0 | 8.3 | 64.60 | " " | 0.2168 |
| 10C | " | " | " | 42.0 | 8.7 | 64.0 | Sound | 0.2172 |
| 10D | " | " | " | 84.0 | 7.8 | 61.90 | Sound | 0.2082 |

## TABLE XI Cont'd

### Results of Composition Trials on Cobalt Tungsten Electrolytes

| Sol No | Cobalt Sulphate g/1 | Sodium Heptonate g/1 | Sodium Tungstate g/1 | Acetic Acid g/1 | W in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 11 | 500 | 200 | 25.2 | 0 | | | | |
| 11A | " | " | " | 10.5 | 4.7 | 71.98 | Stressed | 0.2418 |
| 11B | " | " | " | 21.0 | 4.0 | 71.31 | " | 0.2386 |
| 11C | " | " | " | 42.0 | 3.5 | 43.40 | Slight Stress | 0.1456 |
| 11D | " | " | " | 84.0 | 4.4 | 61.34 | " " | 0.2060 |
| 12 | " | " | 12.6 | 0 | 15.6 | 51.84 | Stressed | 0.1743 |
| 12A | " | " | " | 10.5 | 3.5 | 57.74 | " | 0.1934 |
| 12B | " | " | " | 21.0 | 3.2 | 65.08 | Slight Stress | 0.2182 |
| 12C | " | " | " | 42.0 | 3.6 | 62.30 | " " | 0.2084 |
| 12D | " | " | " | 84.0 | 3.2 | 56.10 | " " | 0.1880 |
| 13 | " | 100 | 70.0 | 0 | 10.4 | 55.1 | Burned | 0.1845 |
| 13A | " | " | " | 10.5 | 4.9 | 79.76 | Stressed | 0.2676 |
| 13B | " | " | " | 21.0 | 7.6 | 39.30 | " | 0.1320 |
| 13C | " | " | " | 42.0 | 6.7 | 60.34 | " | 0.2020 |
| 13D | " | " | " | 84.0 | 7.0 | 51.74 | " | 0.1738 |
| 14 | " | " | 50.4 | 0 | 15.6 | 55.5 | Severe Stress | 0.1866 |
| 14A | " | " | " | 10.5 | 8.0 | 51.81 | " " | 0.1738 |
| 14B | " | " | " | 21.0 | 8.9 | 48.29 | " " | 0.1624 |
| 14C | " | " | " | 42.0 | 7.3 | 47.83 | Stressed | 0.1604 |
| 14D | " | " | " | 84.0 | 5.9 | 41.85 | " | 0.1408 |
| 15 | " | " | 25.2 | 0 | 14.6 | 60.6 | " | 0.2038 |
| 15A | " | " | " | 10.5 | 8.9 | 33.93 | Severe Stress | 0.1141 |
| 15B | " | " | " | 21.0 | 5.2 | 43.73 | " " | 0.1463 |
| 15C | " | " | " | 42.0 | 5.9 | 59.10 | " " | 0.2104 |
| 15D | " | " | " | 84.0 | 5.5 | 58.27 | Stressed | 0.1952 |

## TABLE XI Cont'd

### Results of Composition Trials on Cobalt Tungsten Electrolytes

| Sol No | Cobalt Sulphate g/l | Sodium Heptonate g/l | Sodium Tungstate g/l | Acetic Acid g/l | W in deposit % | Cathode Efficiency % | Deposit Quality | Wt of deposit g |
|---|---|---|---|---|---|---|---|---|
| 16 | 500 | 100 | 12.6 | 0 | 13.6 | 63.30 | Burned | 0.2126 |
| 16A | " | " | " | 10.5 | 5.7 | 63.02 | Stressed | 0.2114 |
| 16B | " | " | " | 21.0 | 6.3 | 59.79 | Sound | 0.2002 |
| 16C | " | " | " | 42.0 | 5.1 | 35.60 | Stressed | 0.1198 |
| 16D | " | " | " | 84.0 | 5.3 | 72.59 | Stressed | 0.2434 |

Operating Conditions:-

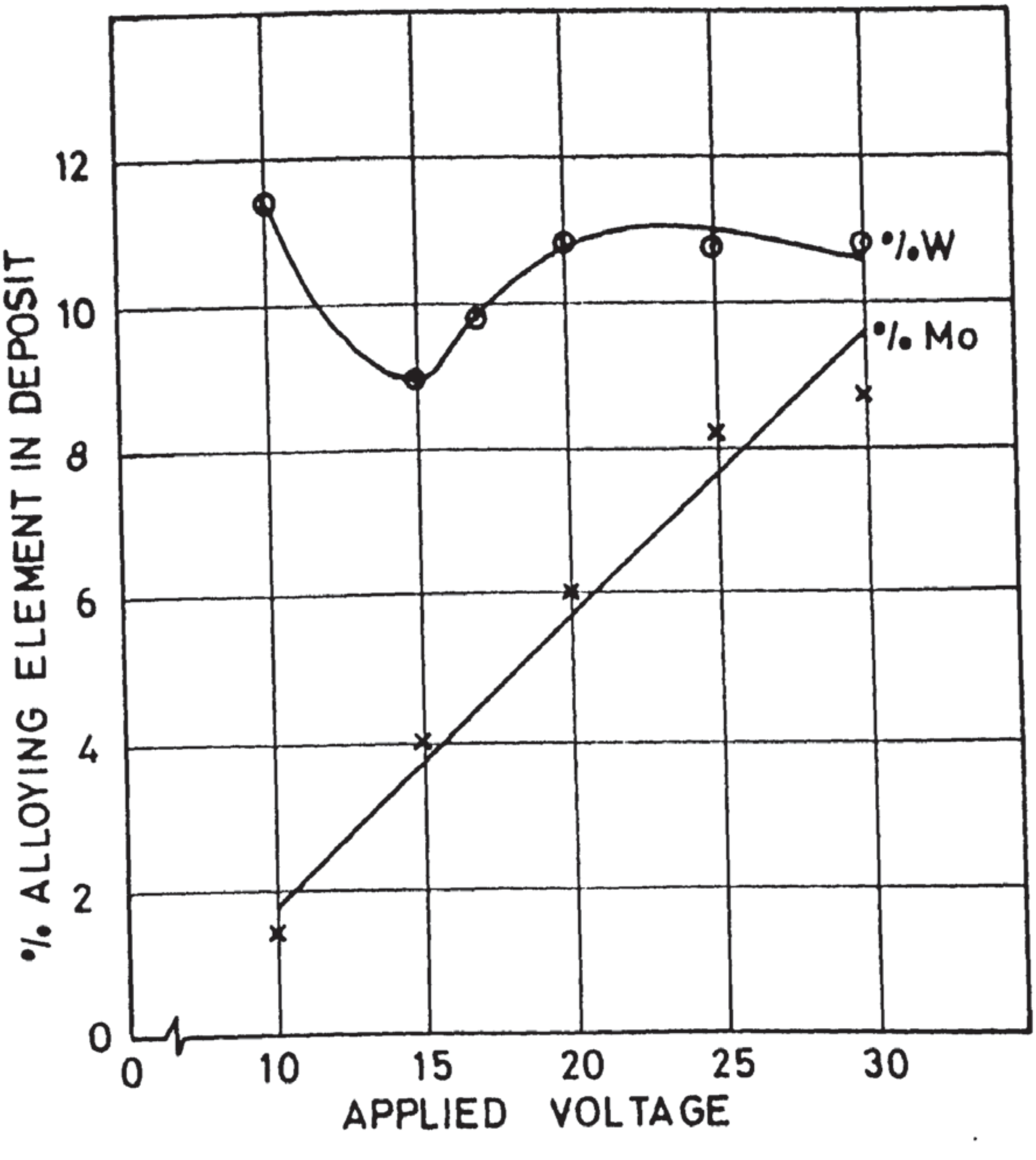
Brush plated at 17V on 5 x 5cm brass panels
for 0.3 A/H.
pH 1.5

## 15.3 Effect of Voltage on Deposition Characteristics of Cobalt Molybdenum and Cobalt Tungsten Electrolytes.

The results of investigations into the effect of deposition voltage upon composition and efficiency can be seen in table XII. Fig 23 illustrates the effect of voltage on composition, for cobalt-tungsten and cobalt-molybdenum deposits. The behaviour of the cobalt-tungsten system appeared to be different from the cobalt-molybdenum system at low voltages. When brush plated at 10V, cobalt-molybdenum deposits contained 1.20% Mo whilst the equivalent cobalt tungsten deposits contained 11.4% W. An increase in applied voltage results in an initial fall in the tungsten content of the Co-W deposits to a minimum of 8.9% W at 15 volts, followed by an increase to approximately 11.0% at voltages in excess of 20V. Over the same voltage range the molybdenum content of the Co-Mo deposits steadily increased from 1.2% at 10 volts to 8.70% at 30V.

Fig 23.

Effect of Applied Voltage upon deposit composition.



Operating Conditions:-
Brush plated at 10-30V
on to 5cm x 5cm brass
panels for 0.3Ah
pH 1.5

Composition:-
500g/l Cobalt Sulphate
200g/l Sodium Heptonate
42.0g/l Acetic Acid
50.4g/l Sodium Molybdate
or Sodium Tungstate.

# TABLE XII

## Results of Voltage Trial

### Cobalt Molybdenum System

| Voltage | Weight Deposited g | Mo in Deposit % | Cathode Efficiency % | Deposit Quality |
|---|---|---|---|---|
| 10 | 0.1422 | 1.20 | 42.84 | Sound |
| 15 | 0.1741 | 4.0 | 53.74 | Sound |
| 20 | 0.1874 | 6.0 | 58.80 | Slight Stress |
| 25 | 0.1848 | 8.30 | 59.13 | " " |
| 30 | 0.1668 | 8.70 | 53.55 | " " |

### Cobalt Tungsten System

| Voltage | Weight Deposited g | W in Deposit % | Cathode Efficiency | Deposit Quality |
|---|---|---|---|---|
| 10 | 0.2072 | 11.4 | 61.71 | Sound |
| 15 | 0.2346 | 8.9 | 69.85 | " |
| 17 | 0.2374 | 9.9 | 70.90 | " |
| 20 | 0.2282 | 10.8 | 67.94 | Slight Stress |
| 25 | 0.2174 | 10.7 | 64.70 | Stressed |
| 30 | 0.2192 | 10.7 | 65.27 | " |

Operating Conditions

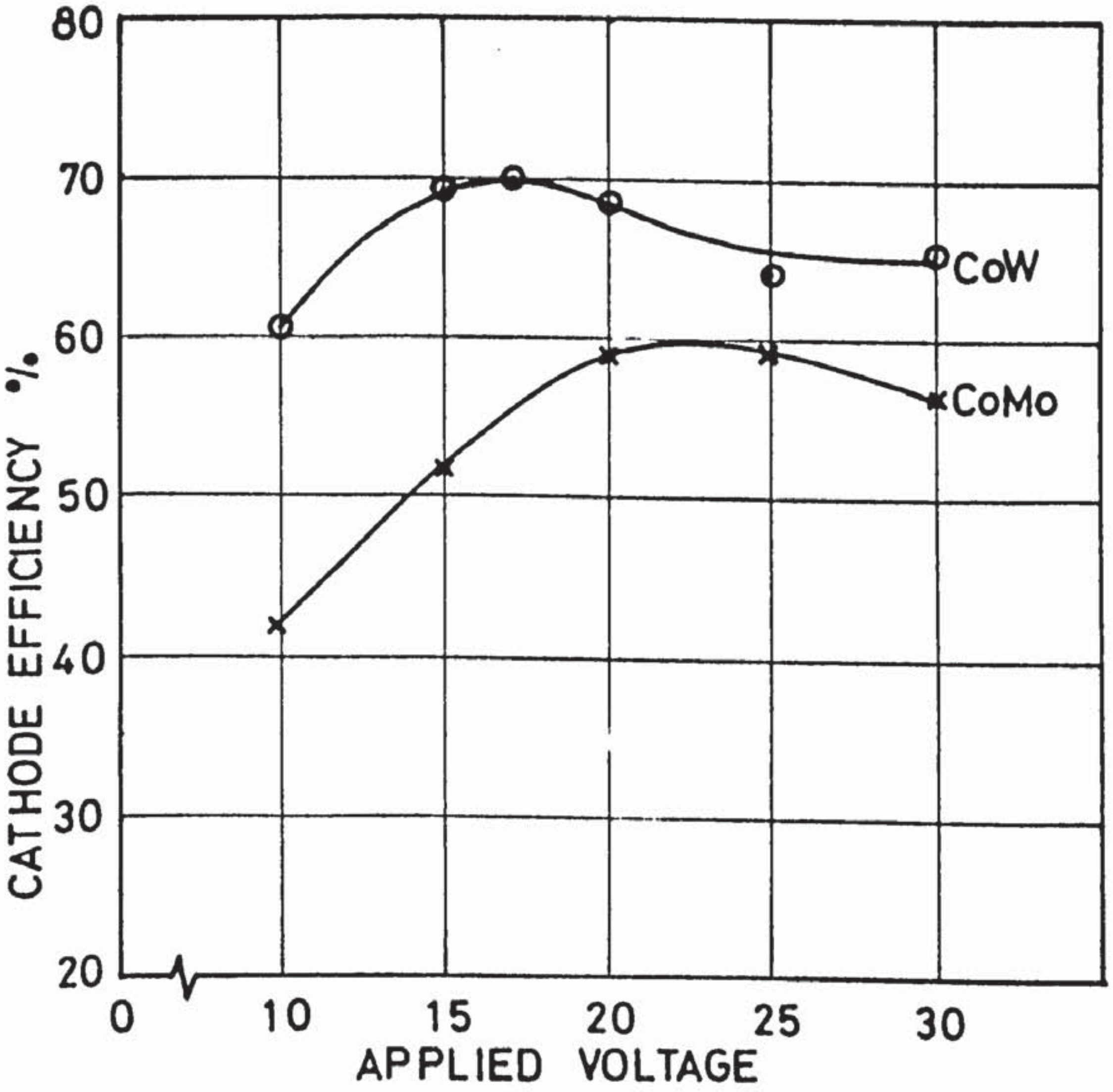
pH 1.5, deposition on to 5cm x 5cm brass panels for 0.3 Ah.

Fig 24 shows the effect of applied voltage on cathode efficiency for the two systems. The maximum efficiency of the cobalt tungsten system of 71% was attained at 17 volts, whilst the maximum for the cobalt molybdenum system was approximately 60% corresponding to 22 volts.

Optimum deposit quality for the two systems fell in the range 10-20 V, however operating voltages of less than 15 volts led to lengthy deposition times.

Fig 24

Effect of Applied Voltage upon cathode efficiency.



Operating Conditions:-
Brush plated at 10-30v
on to 5cm x 5cm brass
panels for 0.3 Ah
pH 1.5

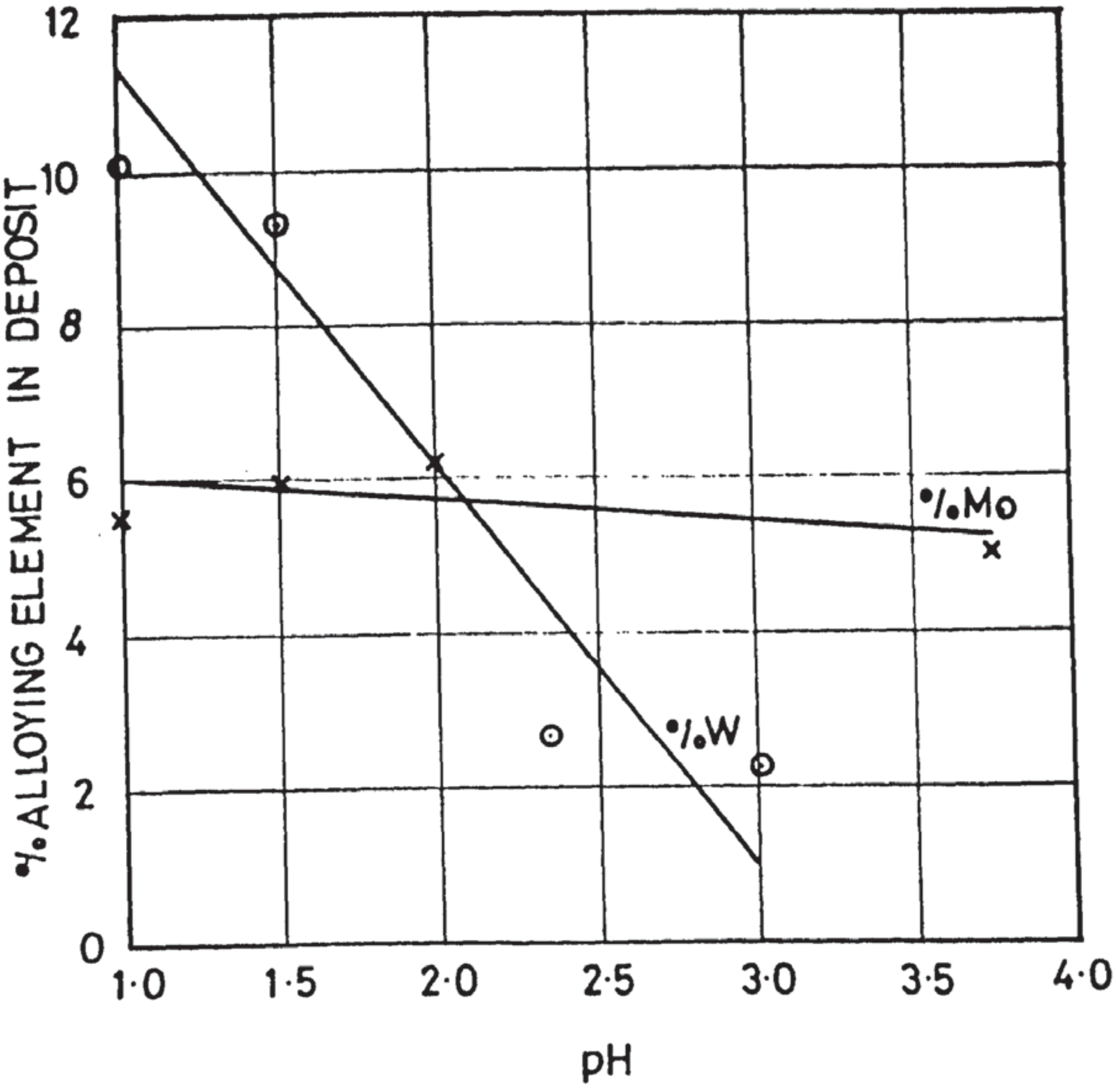
Composition:-
500 g/l Cobalt Sulphate
200 g/l Sodium Heptonate
42.0 g/l Acetic Acid
50.4 g/l Sodium Molybdate
or Sodium Tungstate.

## 15.4. Effect of pH on Deposition Characteristics of Cobalt Molybdenum and Cobalt Tungsten Electrolytes.

The results of the investigation into the effects of pH on deposition characteristics are shown in table XIII. Fig. 25 illustrates the effect of pH on deposit composition for the two systems. From this, it can be seen that variations of pH have a greater effect on the composition of deposits from the cobalt tunsten system than on those from the cobalt molybdenum electrolytes. The molybdenum content of the Co-Mo deposits varied from 5.0% to 6.2% over the pH range 1.0-3.75. However, over a pH range of 1.0 - 3.02, the tungsten content of the Co-W deposits fell sharply from 10.1% to 2.2%. Fig 26 shows the effect on efficiency of these variations in pH. At all levels of pH, the cobalt tungsten electrolytes proved most efficient, having cathode efficiencies between 66.48% at pH 1.0 and 83.5% at pH 3.02. The efficiency of the cobalt molybdenum electrolytes over the pH range of 1.0 - 3.75 increased from 56.9% to 75.3%. Thus, for both systems, efficiency increased with increasing pH over the range of pH chosen. However, electrolytes from the cobalt tungsten system exhibited higher overall efficiency. The quality of deposits obtained

Fig 25.

Effect of pH on deposit composition.

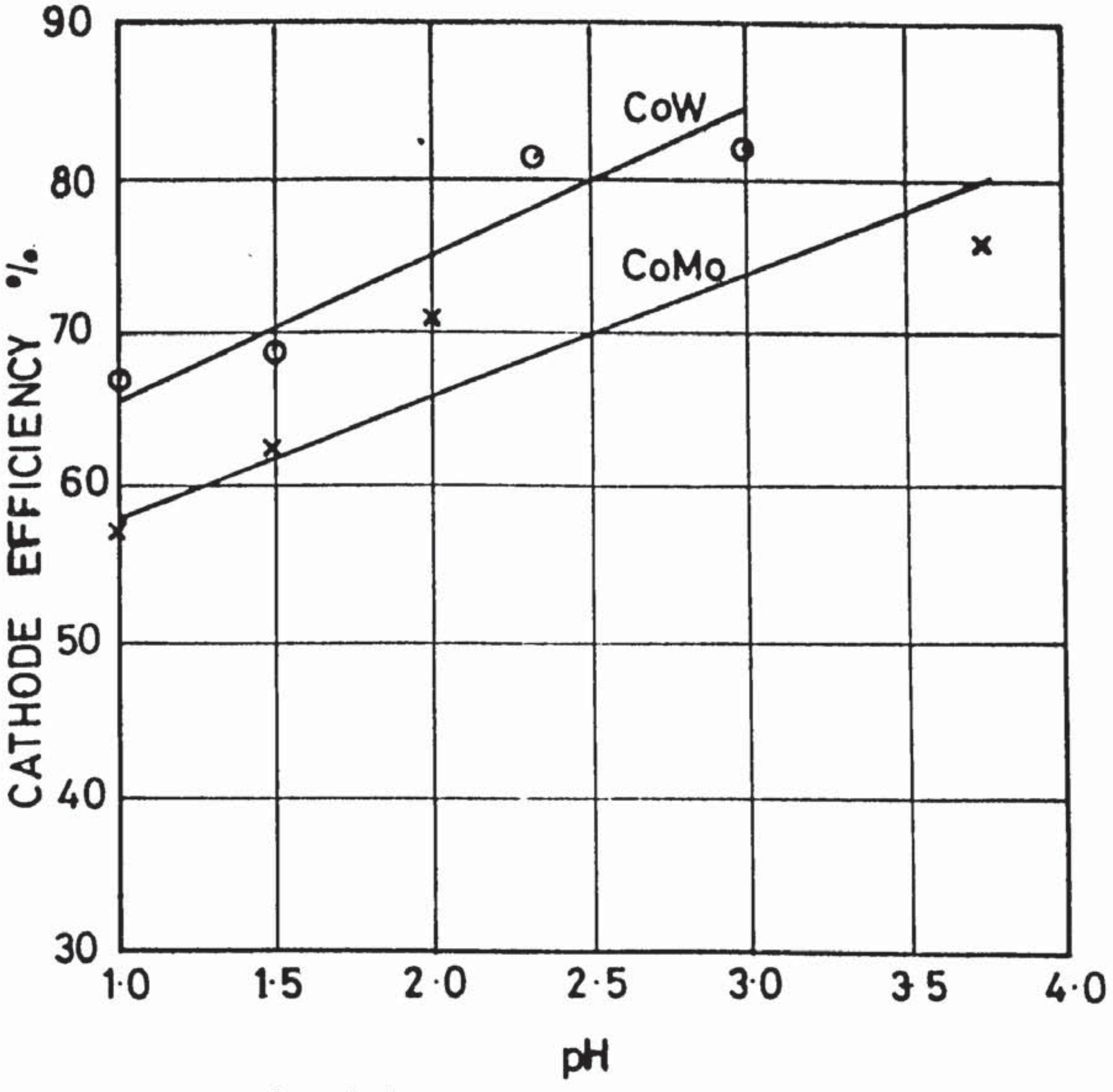


Operating Conditions:-
Brush plated at 17V
on to 5cm x 5cm brass
panels for 0.3 Ah
pH 1.0 - 3.75

Composition:-
500 g/l Cobalt Sulphate
200 g/l Sodium Heptonate
42.0 g/l Acetic Acid
50.4 g/l Sodium Molybdate
or Sodium tungstate.

Fig 26.

Effect of pH on Cathode efficiency



Operating Conditions:-
Brush plated at 17V
on to 5cm x 5cm brass
panels for 0.3 Ah.
pH 1.0-3.75

Composition:-
500 g/l Cobalt Sulphate
200 g/l Sodium Heptonate
42.0 g/l Acetic Acid
50.4 g/l Sodium Molybdate
or Sodium Tungstate.

# TABLE XIII

## Results of pH Trial

### Cobalt Molybdenum System

| pH | Weight Deposited g | Mo in Deposit % | Cathode Efficiency % | Deposit Quality |
|---|---|---|---|---|
| 1.0 | 0.1822 | 5.5 | 56.90 | Sound |
| 1.5 | 0.1986 | 5.9 | 62.36 | Sound |
| 2.0 | 0.2244 | 6.2 | 70.59 | Slightly Stressed |
| 3.75 | 0.2420 | 5.0 | 75.26 | Stressed |

### Cobalt-Tungsten System

| pH | Weight Deposited g | W in Deposit | Cathode Efficiency % | Deposit Quality |
|---|---|---|---|---|
| 1.0 | 0.2230 | 10.1 | 66.48 | Sound |
| 1.5 | 0.2293 | 9.3 | 68.30 | |
| 2.31 | 0.2740 | 2.6 | 81.65 | Stressed |
| 3.02 | 0.2804 | 2.2 | 83.5 | Severe Stress |

throughout the trial indicated that minimum stressing and burning could be expected in the pH range 1.0-2.0.

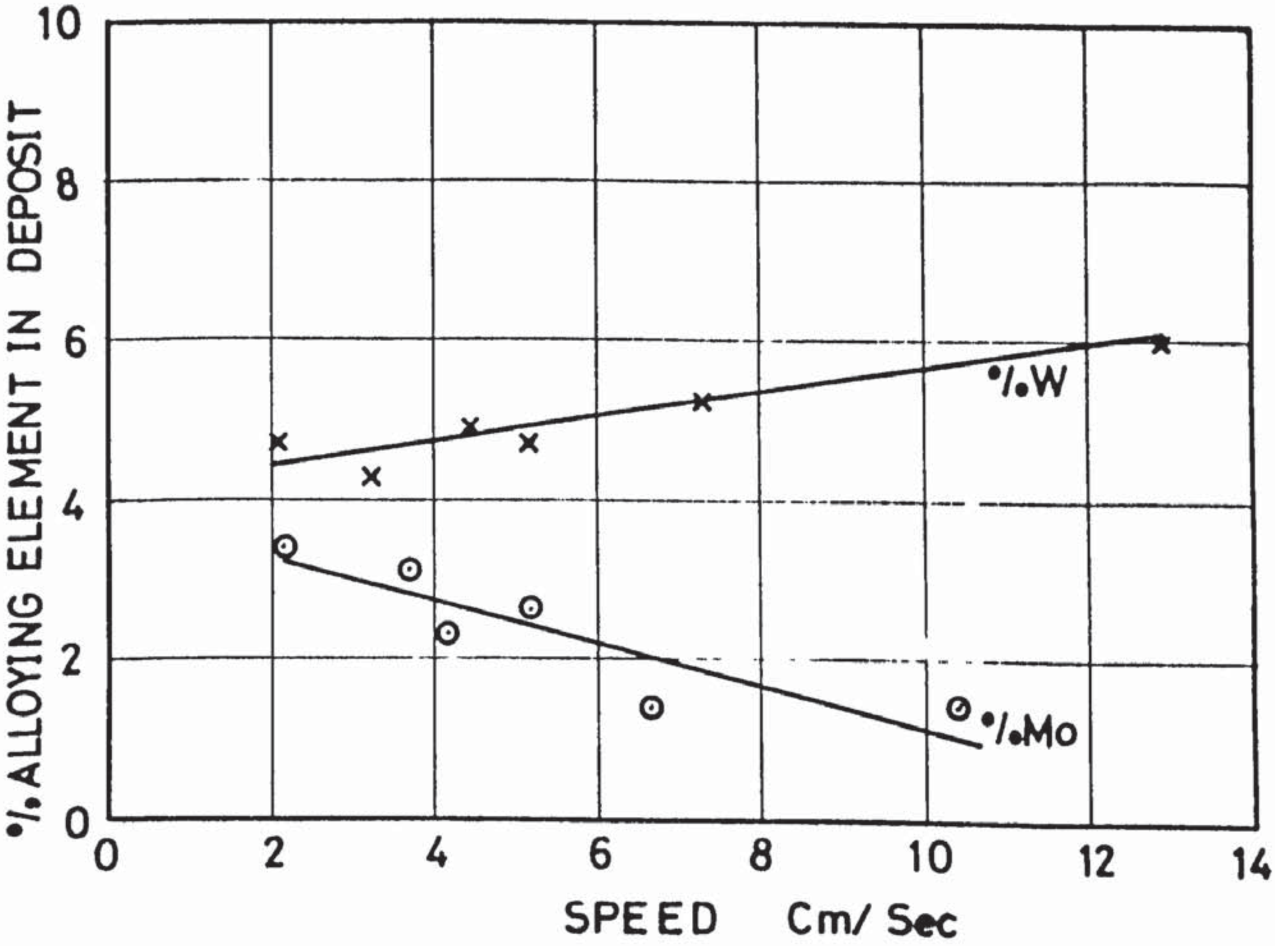
## 15.5. Effect of Speed and Pressure.

The results of the investigation into the effects of stylus speed and pressure are shown in tables XIV and XV respectively.

The effect of stylus speed upon deposit composition is illustrated by Fig. 27, where it can be seen that an increase in relative stylus speed resulted in deposits containing a higher level of tungsten from cobalt tungsten electrolytes. However, in the case of cobalt molybdenum electrolytes, such an increase in stylus speed resulted in a lower concentration of molybdenum being incorporated in the deposit. Over the range of stylus speed chosen (2-12 cm/sec), the level of alloying element in the deposits produced was significantly lower than in trials carried out by "hand" brush plating. In "hand" trials, using solutions of the same composition deposits containing 6% Mo and 8% W were produced. The concentration of alloying element in deposits obtained over the range of speeds used varied from 1.4-3.4% Mo and 4.3-6.0% W. However, it should be noted that the majority of "hand" brush plating operations took place at 17V whilst the speed and pressure trials were operated at 15V. Fig. 28

Fig 27.

Effect of Relative Stylus speed on Deposit Composition

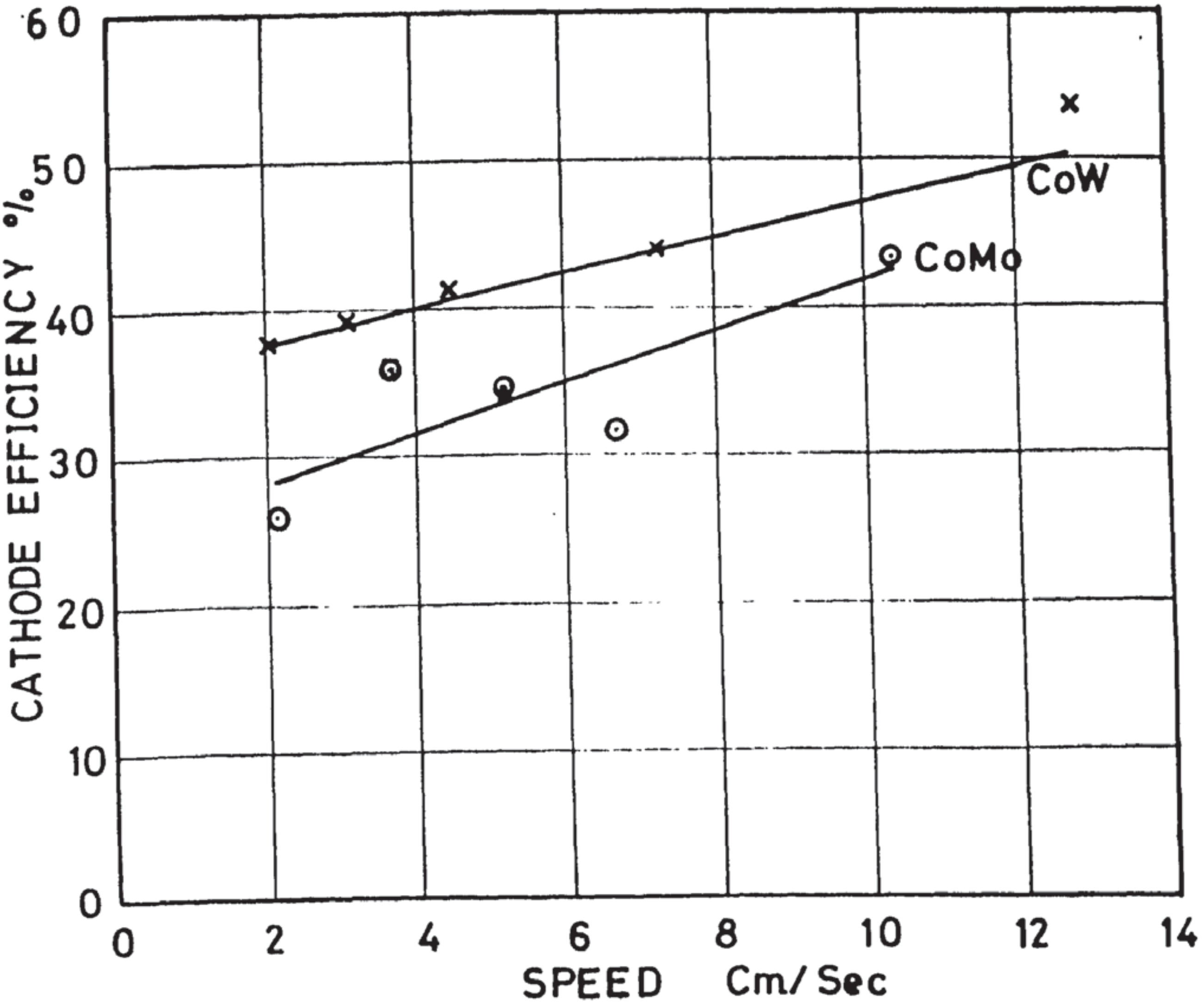


Operating Conditions:-
Brush plated at 15v on
to 20cm diameter brass
discs for 0.3 Ah.
pH 1.5

Composition:-
500 g/l Cobalt Sulphate
200 g/l Sodium Heptonate
42.0 g/l Acetic Acid
50.4 g/l Sodium Tungstate
or Sodium Molybdate.

Fig 28.

Effect of Relative Stylus speed on cathode efficiency



Operating Conditions:-
Brush plated at 15v
on to 20cm diameter
brass discs for 0.3Ah
pH 1.5

Composition:-
500 g/l Cobalt Sulphate
200 g/l sodium Heptonate
42.0 g/l Acetic Acid
50.4 g/l Sodium Molybdate
or Sodium Tungstate.

## TABLE XIV

### Effect of Stylus Speed on CathodeEfficiency and Deposit Composition.

### Cobalt Molybdenum System

| Speed<br>Cm/Sec | Weight Deposited<br>g | Mo in Deposit<br>% | Cathode Efficiency<br>% |
|---|---|---|---|
| 10.36 | 0.144 | 1.4 | 43.46 |
| 6.74 | 0.105 | 1.4 | 31.57 |
| 5.18 | 0.114 | 2.6 | 34.78 |
| 4.24 | 0.165 | 2.3 | 50.24 |
| 3.70 | 0.117 | 3.1 | 35.93 |
| 2.17 | 0.084 | 3.4 | 25.84 |

### Cobalt Tungsten System

| Speed<br>Cm/sec | Weight Deposited<br>g | W in Deposit<br>% | Cathode Efficiency<br>% |
|---|---|---|---|
| 12.9 | 0.169 | 6.0 | 50.38 |
| 7.32 | 0.147 | 5.2 | 43.82 |
| 4.54 | 0.138 | 4.9 | 41.14 |
| 3.16 | 0.132 | 4.3 | 39.36 |
| 2.07 | 0.128 | 4.7 | 38.17 |

**Operating Conditions:-**

pH 1.5
Voltage 15V

## TABLE XV

## Effect of Stylus Pressure on Cathode Efficiency and Deposit Composition.

### Cobalt Molybdenum System

| Pressure $g/cm^2$ | Weight Deposited g | Mo in Deposit % | Cathode Efficiency % |
|---|---|---|---|
| 125.8 | 0.084 | 1.1 | 25.34 |
| 92.7 | 0.087 | 1.5 | 26.23 |
| 63.5 | 0.123 | 0.9 | 36.97 |
| 46.0 | 0.075 | 1.5 | 22.66 |

### Cobalt Tungsten System

| Pressure $g/cm^2$ | Weight Deposited g | W in Deposit % | Cathode Efficiency % |
|---|---|---|---|
| 125.8 | 0.099 | 7.3 | 27.46 |
| 92.7 | 0.093 | 6.3 | 25.93 |
| 63.5 | 0.105 | 7.5 | 28.96 |
| 46.0 | 0.120 | 4.7 | 34.03 |

Operating Conditions:-

pH 1.5

Voltage 15V

ilustrates the effect of speed on the cathode efficiency for deposition of these alloys. Thus, it can be seen that over the range of speed chosen, increasing stylus speed resulted in an increase of cathode efficiency for both systems, the cobalt tungsten system having the highest overall efficiency. By comparison with deposition from equivalent solutions "hand" brush plated, the cathode efficiency of both systems was somewhat lower. Hand brush plating of electrolytes of the same composition gave efficiencies in the range 60-65%, compared with 25-55% over the speed range selected.

Table XIV indicates that over the range considered, increases in applied stylus pressure had little effect on either deposit composition or cathode efficiency. The level of alloying element in the deposits produced being of a similar order to those obtained in the "speed" trial.

## 15.6. Results of the Comparison of the Developed Cobalt Tungsten Electrolyte with a Proprietary Solution and Determination of Experimental Variability.

Table XVI gives the cathode efficiency and deposit composition on various substrates for the developed cobalt tungsten solution and a proprietary equivalent. For each trial, six panels were plated under identical

## TABLE XVI

### Cathode Efficiency and Deposit Composition on Various Substrates

| | Proprietary Co-W Solution | | Developed Co-W Solution | | | | | |
|---|---|---|---|---|---|---|---|---|
| pH | 1.7 | | 1.5 | | 1.5 | | 1.5 | |
| Voltage | 11 | | 17 | | 17 | | 17 | |
| Substrate | Brass | | Brass | | Mild Steel | | No 5 Die Steel | |
| | Effic . % | % W | Effic.% | % W | Effic. % | % W | Effic. % | % W |
| | 76.01 | 5.7 | 74.30 | 8.5 | 70.13 | 8.5 | 42.71 | 15.2 |
| | 73.87 | 5.8 | 66.55 | 10.6 | 61.50 | 9.8 | 55.89 | 14.7 |
| | 65.86 | 6.8 | 72.08 | 9.6 | 70.65 | 8.6 | 61.79 | 10.00 |
| | 65.86 | 6.8 | 66.61 | 10.7 | 56.16 | 10.6 | 63.42 | 10.20 |
| | 70.87 | 6.8 | 71.98 | 9.8 | 56.44 | 11.6 | 62.89 | 12.10 |
| | 65.53 | 7.6 | 73.88 | 10.3 | 58.41 | 12.8 | 65.23 | 10.00 |
| Mean | 69.67 | 6.58 | 70.90 | 9.92 | 62.22 | 10.31 | 58.67 | 12.03 |
| S.D. | 4.59 | 0.72 | 3.47 | 0.82 | 6.62 | 1.70 | 8.45 | 2.40 |

operating conditions in order to assess experimental variability.

The most notable feature of the proprietary cobalt tungsten electrolyte was that its recommended operating voltage of 11V, resulted in deposition times approximately twice as long as those required by the developed solution operating at 17V, in order to produce deposits of equivalent thickness.

On equivalent brass substrates, the proprietary electrolyte produced deposits containing less tungsten than the deposits from the developed cobalt tungsten electrolyte (6.58% and 9.92%respectively). Also at 69.67%, the proprietary electrolyte had marginally inferior cathode efficiency.

These results also show the effect of brush plating the developed cobalt tungsten electrolyte on to three different substrates. The mean concentration of tungsten in deposits on brass, mild steel, and No 5 die steel was 9.92, 10.31, and 12.03 respectively. Thus, the composition of the cobalt tungsten deposits appeared dependent on the substrate material. Similarly, the cathode efficiency for deposition appeared to be sensitive to the substate material. Mean efficiency for deposition on brass, mild steel and No 5 die steel were calculated as 70.90, 62.22, and 58.67 respectively. Hence an increase in concentration of tungsten in the deposit resulted in a lower cathode efficiency.

During deposition, the proprietary cobalt tungsten electrolyte appeared to produce more highly stressed deposits, as deflection of the test panels was noticed and slight exfoliation of the deposit occured. However, cracking was noticed in deposits from the proprietary solution and the developed cobalt tungsten electrolyte.

# 16. RESULTS OF INVESTIGATIONS INTO COATING PROPERTIES.

## 16.1. Structure of Cobalt and Cobalt Alloy Brush Plated Deposits.

The results obtained from X-ray diffraction of the cobalt and cobalt alloy deposits are recorded in table XVII. Diffraction data is also included for the brass substrate on which the coatings were deposited. For each diffraction trace obtained, the $2\theta$ angles were recorded for diffraction peaks and the "d" spacings were calculated. An estimation of relative intensity of the peaks was made, and recorded in the table. Attempts were then made to "index" the diffraction data by reference to the ASTM Powder Diffraction File.

In the case of samples A, B and C, the "d" spacings were indexed as mixtures of FCC and CPH cobalt. The "d" spacings of FCC and CPH cobalt as recorded in the ASTM Powder Diffraction File are as follows:-

FCC Cobalt (Stable above 450°C) ASTM Powder
Diffraction Ref 15-806

| dÅ |
|---|
| 2.05 |
| 1.77 |
| 1.25 |
| 1.07 |
| 1.02 |

CPH Cobalt (Stable at Room Temperature ASTM Powder
Diffraction Ref 5-0727

| dÅ |
|---|
| 2.17 |
| 2.02 |
| 1.91 |
| 1.48 |
| 1.25 |
| 1.15 |
| 1.08 |
| 1.07 |
| 1.05 |
| 1.02 |

Hence, at room temperature the brush plated cobalt only deposits appeared to have a mixed structure consisting of C.P.H and F.C.C. Cobalt. Certain of the less intense peaks in some of the samples were identified as originating from the brass substrate. However, indexing of the alloy deposits was less successful. After a considerable search in the Powder Diffraction File, non of the alloy deposits were indexed. It was then decided to consult the ASTM Alphabetical index in order to compare the "d" spacings of various cobalt compounds, with those obtained experimentally. Although "d" spacings of the following were compared with the experimentally derived values, indexing again proved impossible.

Cobalt Molybdenum and Tungsten Elements and Compounds found in ASTM Alphabetical Index.

| W Metal (4-0806) | Mo Metal (4-0809) |
|---|---|
| dÅ | dÅ |
| 2.24 | 2.23 |
| 1.29 | 1.29 |
| 1.58 | 1.57 |

| $Co_3W$ (2-1298) | $Co_7W_6$ (2-1091) | $CoS_2$ (3-0772) | $Co_4S_3$ (2-1338) | $Co_6S_5$ (2-1459) |
|---|---|---|---|---|
| dÅ | dÅ | dÅ | dÅ | dÅ |
| 1.95 | 2.38 | 2.75 | 1.76 | 1.76 |
| 3.00 | 2.18 | 2.46 | 2.99 | 2.99 |
| 2.21 | 2.08 | 1.66 | 2.28 | 1.91 |

In conclusion, although it has been determined that cobalt brush plated deposits appear to have a mixed CPH and FCC structure at room temperature, the structures of the cobalt alloy deposits remain unknown.

## TABLE XVII

### Results of X-Ray Diffraction of Cobalt and Cobalt Alloy Deposits.

**Sample A Co Only**

| 20 | dĀ | Intensity |
|---|---|---|
| 48.8 | 2.17 | 3 (CPH Co) |
| 49.7 | 2.13 | 7 (Brass Subst) |
| 51.8 | 2.04 | 4 (FCC Co) |
| 52.3 | 2.03 | 5 (CPH Co) |
| 56.0 | 1.91 | 9 (CPH Co) |
| 86.7 | 1.30 | 2 (Brass Subst) |
| 91.6 | 1.25 | 1 (FCC or CPH Co) |
| 107.0 | 1.11 | 8 (Brass Subst) |
| 114.4 | 1.07 | 6 (FCC Co) |

**Sample B Co Only**

| 20 | dĀ | Intensity |
|---|---|---|
| 49.7 | 2.13 | 2 (Brass Subst) |
| 52.3 | 2.03 | 1 (CPH Co) |
| 55.8 | 1.91 | 3 (CPH Co) |
| 60.4 | 1.78 | 4 (CPH Co) |
| 86.7 | 1.30 | 5 (Brass Subst) |
| 91.8 | 1.25 | 6 (CPH or FCC Co) |

**Sample C Co Only.**

| 20 | dA | Intensity |
|---|---|---|
| 49.0 | 2.16 | 1 (CPH Co) |
| 51.1 | 2.07 | 4 |
| 52.0 | 2.04 | 2 (FCC Co) |
| 52.8 | 2.01 | 3 (CPH Co) |
| 54.1 | 1.97 | 4 |
| 86.6 | 1.31 | 5 (Brass Subst) |
| 91.4 | 1.25 | 6 (CPH or FCC Co) |

**Sample D Co 10% Mo.**

| 20 | dA | Intensity |
|---|---|---|
| 48.6 | 2.18 | 1 |
| 49.8 | 2.13 | 4 |
| 51.5 | 2.06 | 3 |
| 55.0 | 1.94 | 6 |
| 55.7 | 1.91 | 5 |
| 86.5 | 1.31 | 2 |
| 90.5 | 1.26 | 8 |
| 107.0 | 1.11 | 7 |

## TABLE XVII Cont'd.

## Results of X-Ray Diffraction of Cobalt and Cobalt Alloy Deposits.

### Sample E Co 5.3% Mo

| $2\theta$ | dÅ | Intensity |
|---|---|---|
| 48.5 | 2.18 | 4 |
| 49.7 | 2.13 | 2 |
| 51.6 | 2.06 | 2 |
| 86.6 | 1.31 | 1 |
| 93.0 | 1.23 | 5 |
| 107.0 | 1.11 | 3 |

### Sample F Co 15% W

| $2\theta$ | dÅ | Intensity |
|---|---|---|
| 48.5 | 2.18 | 6 |
| 48.9 | 2.16 | 6 |
| 49.7 | 2.13 | 5 |
| 51.2 | 2.07 | 4 |
| 52.0 | 2.04 | 2 |
| 52.5 | 2.02 | 3 |
| 53.7 | 1.99 | 6 |
| 54.8 | 1.95 | 6 |
| 86.7 | 1.30 | 1 |
| 106.9 | 1.11 | 7 |
| 107.3 | 1.11 | 7 |

### Sample G Co 19% W

| $2\theta$ | dÅ | Intensity |
|---|---|---|
| 48.8 | 2.17 | 4 |
| 49.1 | 2.15 | 3 |
| 49.8 | 2.13 | 2 |
| 52.0 | 2.04 | 3 |
| 86.6 | 1.31 | 1 |
| 91.0 | 1.26 | 5 |
| 91.5 | 1.25 | 5 |
| 107.0 | 1.11 | 5 |

### Sample H Co 8.15% Mo

| $2\theta$ | dÅ | Intensity |
|---|---|---|
| 48.7 | 2.17 | 1 |
| 51.5 | 2.06 | 3 |
| 51.8 | 2.04 | 3 |
| 55.0 | 1.94 | 4 |
| 86.5 | 1.31 | 2 |
| 90.5 | 1.26 | 5 |

## TABLE XVII Cont'd.

**Results of X-Ray Diffraction of Cobalt and Cobalt Alloy Deposits.**

| Sample i Co 6.35%Mo | | | Sample j Co 10.8%W | | |
|---|---|---|---|---|---|
| 20 | dÅ | Intensity | 20 | dÅ | Intensity |
| 49.0 | 2.16 | 1 | 48.7 | 2.17 | 1 |
| 52.2 | 2.04 | 3 | 50.0 | 2.12 | 4 |
| 55.0 | 1.94 | 4 | 51.6 | 2.06 | 3 |
| 86.5 | 1.31 | 2 | 52.0 | 2.04 | 5 |
| 91.6 | 1.25 | 5 | 86.5 | 1.31 | 2 |
| 107.3 | 1.11 | 6 | 107.0 | 1.11 | 6 |
| 117.0 | 1.05 | 7 | | | |

| Sample k Co 10.3%W | | | Brass Substrate | | |
|---|---|---|---|---|---|
| 20 | dÅ | Intensity | 20 | dÅ | Intensity |
| 47.0 | 2.25 | 6 | 49.7 | 2.13 | 2 |
| 48.5 | 2.18 | 6 | 58.0 | 1.85 | 4 |
| 49.5 | 2.13 | 3 | 86.5 | 1.31 | 1 |
| 49.8 | 2.13 | 2 | 107.0 | 1.11 | 3 |
| 50.5 | 2.10 | 6 | | | |
| 52.0 | 2.04 | 4 | | | |
| 54.5 | 1.96 | 6 | | | |
| 58.0 | 1.85 | 6 | | | |
| 86.6 | 1.31 | 1 | | | |
| 107.0 | 1.11 | 5 | | | |

## 16.2. Transmission Electron Microscopy.

Fig 29 shows T.E.M photographs of a cobalt brush plated deposit. As can be seen from Fig 29(a) the grain size appeared extremely fine and could not be resolved at the magnification of x 100 K. At a higher magnification of x 500 K (Fig 29(b)) grain boundaries could be resolved, thus enabling an estimate of grain size to be made. By taking the magnification into account the polygonal grains in the centre of Fig 29(b) were estimated as having an approximate diameter of $10^{-6}$cm. Further inspection of the T.E.M photographs of the cobalt deposits revealed that there was very little variation in grain size, as compared with the cobalt molybdenum deposits.

Fig 30 shows T.E.M photographs of a cobalt molybdenum deposit containing 2.8% molybdenum. At x 200 K magnification (Fig 30(a)) the grains could be resolved, the grain size being apparently much greater than that of the cobalt deposit. An increase of magnification to x 400 K revealed a much greater variation in grain size throughout the sample than was observed with the cobalt deposits. The mean grain diameter of the cobalt molybdenum alloy was estimated at $5.7 \times 10^{-6}$cm. Thus, it could be concluded that the cobalt molybdenum alloys showed evidence of possessing a much larger and more variable grain size than the cobalt only deposits.

Fig 29.

Transmission electron photomicrographs of cobalt brush plated deposits.

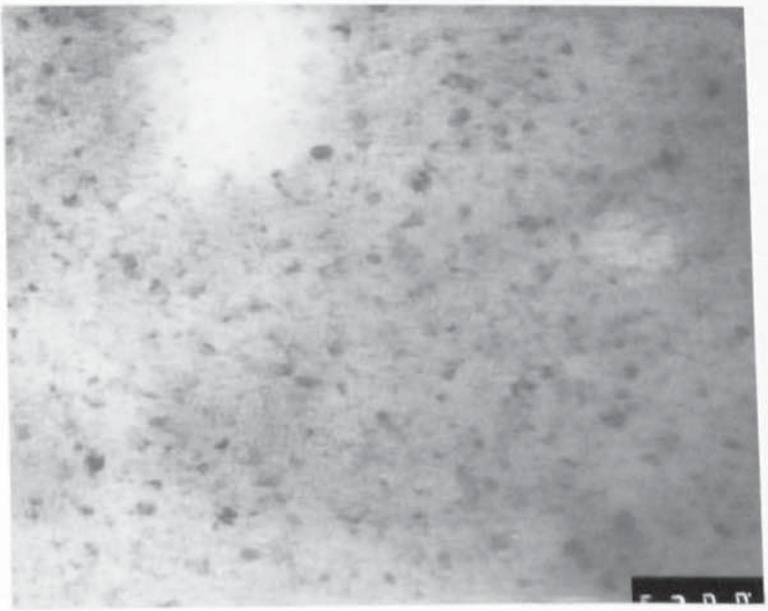


Fig 29a. Cobalt deposit x 100K.

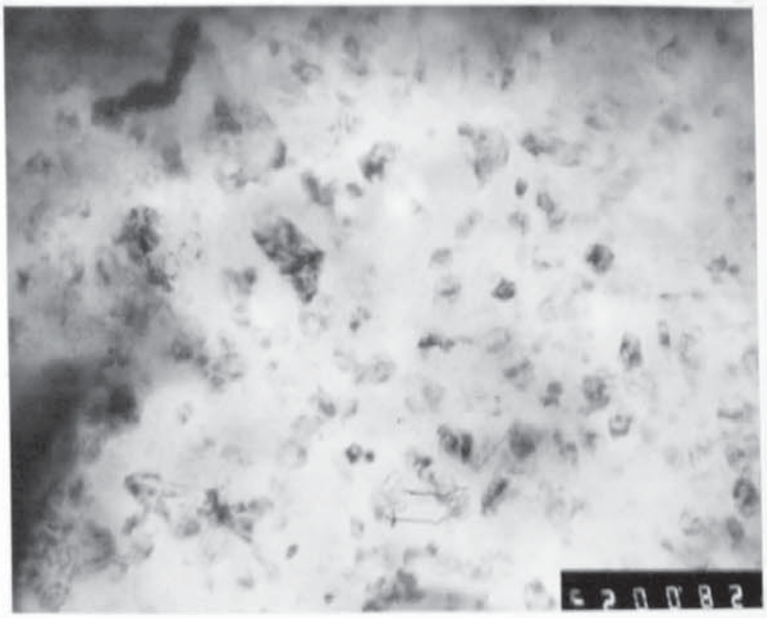


Fig 29b. Cobalt deposit x 500K.

Fig 30.

Transmission electron photomicrographs of cobalt molybdenum brush plated deposits

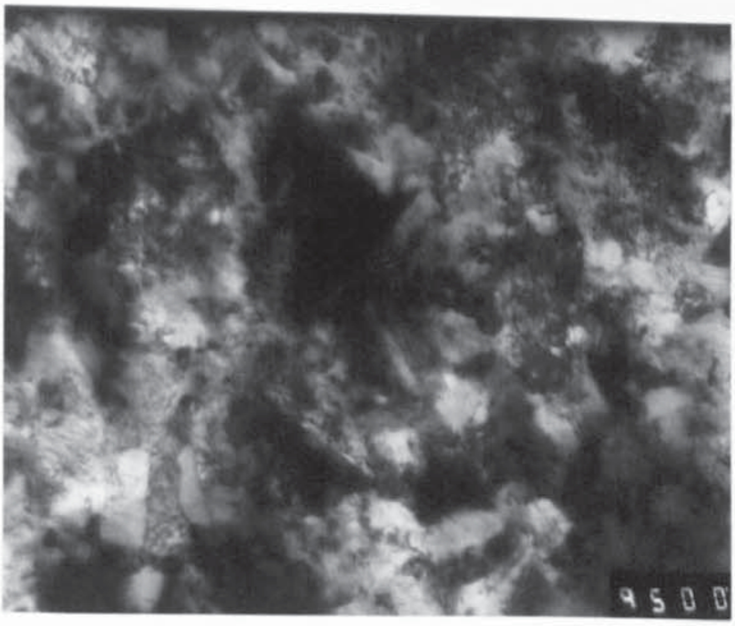


Fig 30a. Co 2.8%Mo Deposit x 200K.

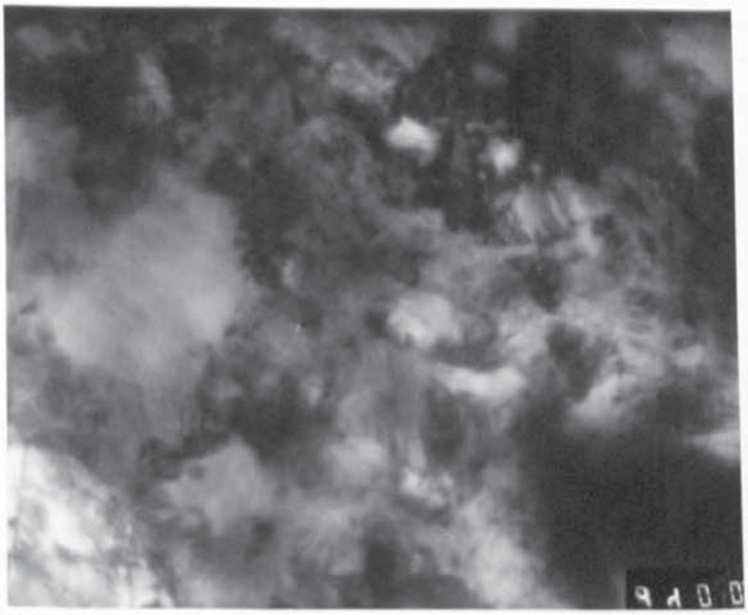


Fig 30b. Co 2.8%Mo Deposit x 400K.

## 16.3. Scanning Electron Microscopy

Scanning electron microscope photographs of a selection of the brush plated electrodeposits are shown in Figs 31-34.

Fig 31 demonstrates the effect on surface topography of brush plating a Co W alloy on to a smooth brass substrate, (Fig 31a) and also on to a grit blasted die steel substrate (Fig 31b). In both cases, it can be seen that the deposit is cracked, but there appears to be little evidence of exfoliation.

Fig 32(a) illustrates the grit blasted surface of a No 5 die steel prior to brush plating. Fig 32(b) shows a similar surface after being plated with a cobalt tungsten alloy. Thus a nodular deposit growth is observed having a slight smoothing effect on the surface.

Cobalt and cobalt molybdenum deposits can be seen in Fig 33a and 33b respectively. Both of these were laid down on smooth brass substrates. Again, evidence of cracking can be seen but little sign of poor adhesion. The cobalt molybdenum deposit depicted in Fig 33(b) appears to show signs of "brush marks" from the plating operation.

The photographs illustrated in Fig 34(a) and 34(b) show the cobalt molybdenum and the cobalt tungsten deposits at higher magnification (X5K).

To obtain these photographs a tilt angle of 70° was adopted, as the deposits were extremely smooth and their topographical features could not be resolved on normal viewing. Further investigations were made with the aid of the scanning electron microscope when the wear ring of an experimental hot forged die was examined. (Section 17.2).

Fig 31.

Scanning electron photomicrographs of cobalt tungsten deposits.

Fig 31a. Cobalt tungsten deposit on brass substrate x 500.

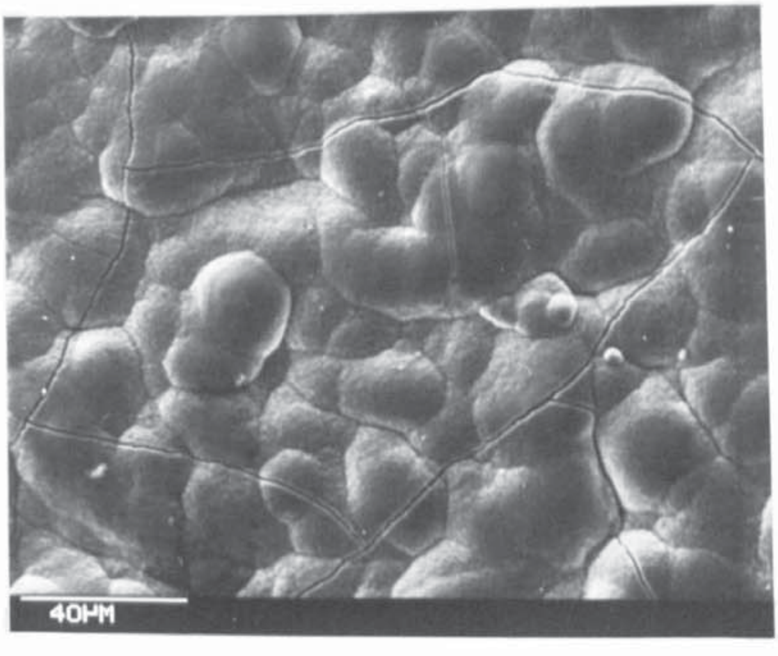


Fig 31b. Cobalt tungsten deposit on grit blasted die steel substrate x 500.

Fig 32.

Scanning electron photomicrographs demonstrating the effect of brush plating a cobalt tungsten alloy on to a grit blasted No. 5 die steel substrate.

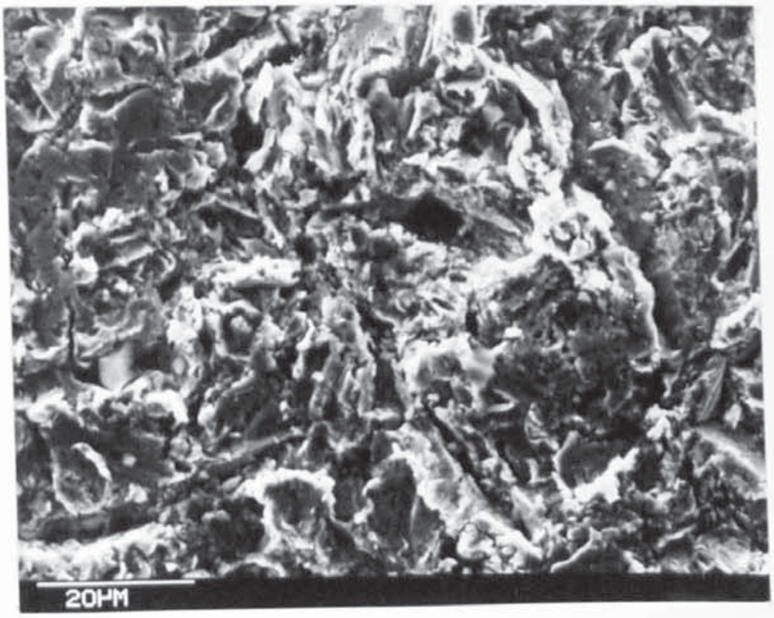
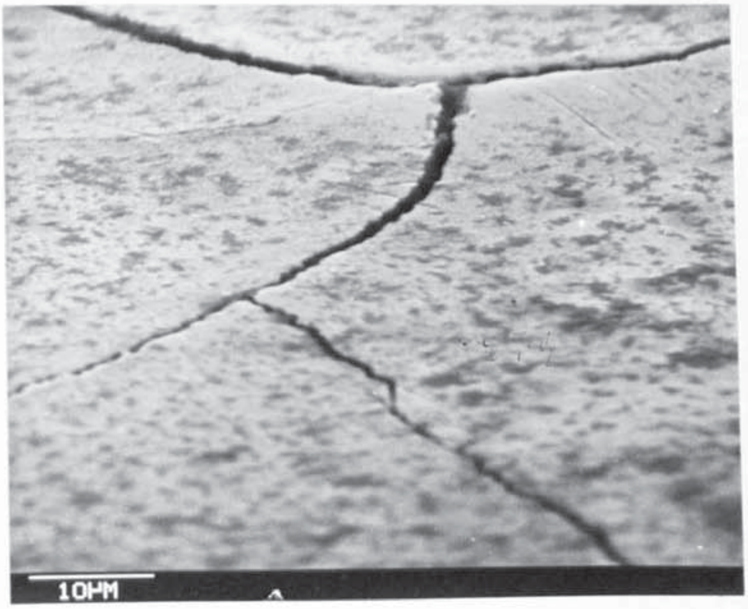


Fig 32a. Grit blasted No. 5 die steel surface (unplated) x 1K.

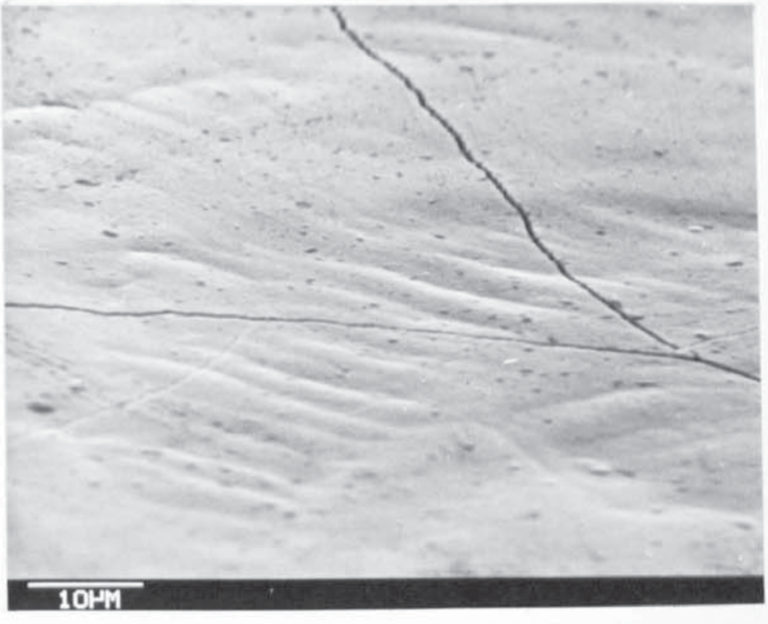
Fig 32b. Die steel surface after brush plating with 13μm of cobalt tungsten alloy.

Fig 33.

Scanning electron photomicrographs of cobalt and cobalt molybdenum deposits.



33a. Cobalt deposit on brass substrate x2K.



33b. Cobalt molybdenum deposit on brass substrate x 2K.

Fig 34.

Scanning electron photomicrographs of cobalt tungsten and cobalt molybdenum deposits.

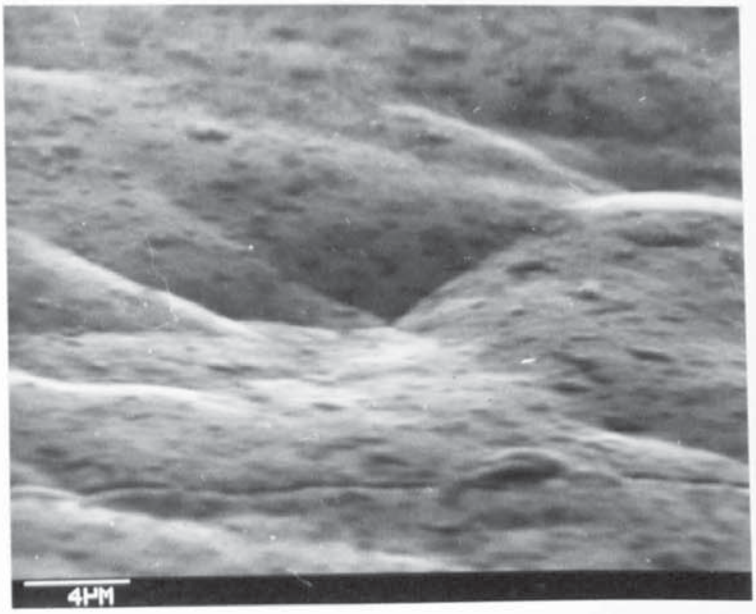


Fig 34a. Cobalt molybdenum deposit on brass substrate x 5K.

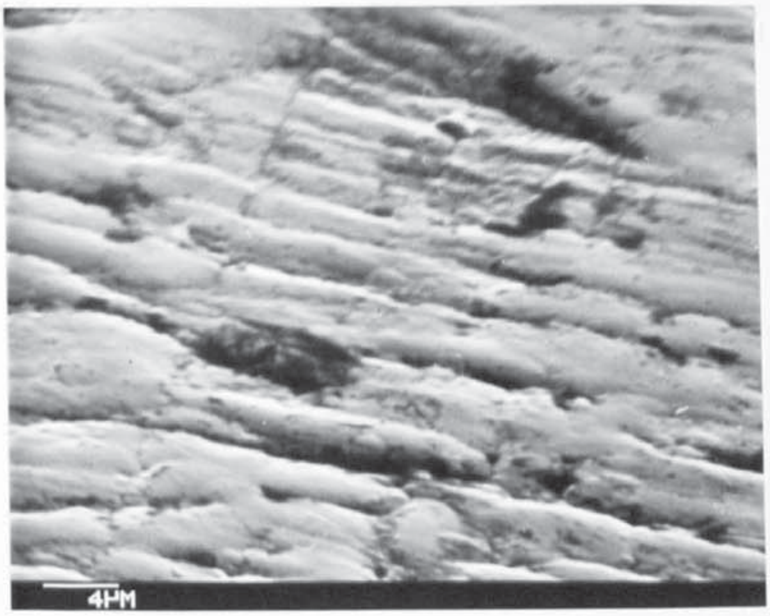


Fig 34b. Cobalt tungsten deposit on brass substrate x 5K.

## 16.4 Hardness of Brush Plated Deposits.

The hardness and composition of cobalt tungsten deposits on various substrates is shown in table XVIII. Vickers microhardness tests (20g) were carried out on six deposits produced under identical conditions. Deposits obtained from the developed CoW electrolyte (section 12.2) were hardness tested having brass, mild steel and die steel substrates. As a comparison, deposits obtained from a proprietary CoW electrolyte were also hardness tested. Unfortunately restricted availability of the commercially produced solution only permitted deposition on a brass substrate, hence comparison of results could only be made with the deposits on brass obtained from the developed electrolyte. The concentration of tungsten in the electrodeposit is also given, so that the relationship between % W in the deposit and hardness can be observed.

From these results, it can be seen that the proprietary CoW electrolytes produced coatings having a lower hardness compared with the deposits from the developed CoW solution (674 compared with 778). Mean values of the six hardness tests were evaluated as individual results appeared to have little correlation with composition.

It could then be observed that the deposits on the die steel which contained the highest levels

## TABLE XVIII

### Hardness and composition of CoW Brush plated deposits on various substrates

| | Deposits Obtained from Proprietary Electrolyte | | Deposits obtained from developed CoW Electrolyte (Section 12.2) | | | | | |
|---|---|---|---|---|---|---|---|---|
| Substrate | Brass | | Brass | | Mild Steel | | Die Steel | |
| | %W | VPN 20g | %W | VPN 20g | %W | VPN 20g | %W | VPN 20g |
| | 5.7 | 743 | 8.5 | 618 | 8.5 | 834 | 15.2 | 834 |
| | 5.8 | 715 | 10.6 | 743 | 9.8 | 869 | 14.7 | 740 |
| | 6.8 | 599 | 9.6 | 834 | 8.6 | 715 | 10.0 | 642 |
| | 6.8 | 642 | 10,7 | 780 | 10.6 | 655 | 10.2 | 869 |
| | 6.8 | 665 | 9.8 | 840 | 11.6 | 743 | 12.1 | 995 |
| | 7.6 | 678 | 10.3 | 851 | 12.8 | 780 | 10.0 | 760 |
| Mean | 6.58 | 673.7 | 9.92 | 777.7 | 10.31 | 766.0 | 12.03 | 806.7 |

of tungsten (12.03%) had the highest hardness of 806.7 VPN.

On an equivalent substrate, the proprietary CoW solution produced deposits of a lower hardness compared to the developed electrolyte. The higher tungsten content of deposits laid down on mild steel and die steel was reflected in increased deposit hardness. There was insufficient time available to carry out microhardness tests on all of the cobalt molybdenum deposits produced, but the hardness of the majority of the CoMo alloy deposits lay in the range 650-1000 VPN.

## 16.5. Levelling Properties of Cobalt Molybdenum Deposits.

Details of the abraded and brush plated steel panel referred to in section 13.7, are shown in table XIX. Also given, is a table of surface roughness results determined on the abraded and brush plated surfaces. In the case of the "as rolled" and "grit blasted" surfaces, brush plating with cobalt molybdenum to a "silky feel" resulted in considerable degree of levelling. Further deposition to 1.0 $Ah/dm^2$ resulted in slight re-roughening of the surface but the brush plated finish was still smoother than the unplated surfaces. However, areas of the steel panel abraded to 320 grit and 600 grit actually became rougher on

## TABLE XIX

## Surface Roughness Determinations of Brush Plated Deposits.

### Details of abraded and brush plated steel panel.

| | | | | |
|---|---|---|---|---|
| C | F | I | L | PLATED TO 1Ah/dm$^2$ |
| B | E | H | K | PLATED TO A "SILK FEEL" |
| A | D | G | J | UNPLATED |
| As Rolled Sheet. | Shot Blasted | Abraded 320 Grit | Abraded 600 Grit | |

### Surface Roughness Results

| Area on Panel | C.L.A.µm | Area on Panel | C.L.A.µm |
|---|---|---|---|
| A | 1.1 | G | 0.45 |
| B | 0.8 | H | 0.65 |
| C | 0.9 | I | 0.75 |
| D | 2.3 | J | 0.4 |
| E | 1.82 | K | 0.45 |
| F | 2.0 | L | 0.72 |

brush plating with the cobalt molybdenum alloys. Hence it appears that the levelling properties of brush plated cobalt alloy deposits depend on the initial surface roughness of the substrate. The grit blasted surface, having a CLA roughness of 2.3µm benefited most by the application of a brush plated deposit to a "silky feel" having a measured CLA roughness of 1.82µm. Application of the deposit to an abraded surface having a CLA roughness of 0.45µm resulted in surface roughness increasing to 0.65µm after plating to a "silky feel".

# 17. RESULTS OF INVESTIGATIONS INTO WEAR PERFORMANCE OF COATINGS.

## 17.1 Pin and Disc Wear Testing

The results of the pin and disc wear measurements are shown in table XX. In addition to the results presented, several wear tests had to be abandoned due to fatigue failure of the wear pin. Although still quite firmly clamped by the upper portion of the pin, the fractured section of the pin in contact with the rotating disc gave rise to chattering and hence invalid wear test results. As in most tests the dynamic coefficient of friction varied over the period of testing; average values have been recorded.

The unplated BH 13 steel pin gave a wear rate of $9.1 \times 10^{-7}$ mm cm$^{-1}$, with a dynamic coefficient of friction of 0.77. A significant improvement in wear performance was obtained by the application of 12µm of cobalt molybdenum, resulting in a wear rate of $3.9 \times 10^{-7}$ mm cm$^{-1}$ with a coefficient of friction of 0.39. A similar effect was obtained by the application of 12µm of brush plated cobalt tungsten alloy, resulting in a wear rate of $3.8 \times 10^{-7}$ mm cm$^{-1}$ with a coefficient of friction of 0.38.

## TABLE XX

### Results of Pin and Disc Wear Tests.

| Wear Pin Treatment | Wear $\text{mm.cm}^{-1}$ | Mean Coefficient of Dynamic Friction. |
|---|---|---|
| Untreated Pin | $9.1\text{x}10^{-1}$ | 0.77 |
| Brush Plated CoMo alloy 12µm | $3.9\text{x}10^{-7}$ | 0.39 |
| Brush Plated CoW alloy 12µm | $3.8\text{x}10^{-7}$ | 0.38 |
| Electroless Ni + chromium carbide - composite covering | $2.4\text{x}10^{-7}$ | 0.27 |

For comparison purposes, results were obtained for an equivalent wear test on an electroless nickel deposit containing chromium carbide particles. The wear rate of this system was measured as $2.4 \times 10^{-7}$ mm $cm^{-1}$ with a coefficient of friction of 0.27. Hence, the application of 12µm of the brush plated cobalt molybdenum or cobalt tungsten deposits resulted in a considerable improvement in wear performance and the reduction of dynamic friction. However improvement in wear performance was marginally inferior to that obtained with the electroless nickel composite coating.

## 17.2 Results of the Simulated Hot Forging Tests.

The results of the simulated hot forging tests carried out on a variety of brush plated dies can be seen in table XXI. A result is also given for an unplated Electem No 5 die as a comparison with the plated dies. From these results it can be seen that none of the deposits produced from proprietary brush plating solutions tolerated the forging test as well as the cobalt alloys deposited from electrolytes referred to in 12.2. Of the proprietary electrolytes tested, the Ni-Co deposits exhibited least wear during the test resulting in a mean wear volume of $5.98 \times 10^{-3} cm^3$. The Ni-W coating gave the worst wear performance resulting in a measured wear

## TABLE XXI

## Results of the Simulated Hot Forging Tests

| Deposit | Coating Thickness µm | Wear Volume x $10^{-3} Cm^3$ | | |
|---|---|---|---|---|
| | | Top Die | Bottom Die | Mean Value |
| No 5 Die Steel | - | 4.72 | 4.03 | 4.37 |
| +Brushplated CoW | 32 | 11.84 | 6.49 | 9.17 |
| +Brushplated NiW | 23 | 7.50 | 11.53 | 9.57 |
| +Brushplated NiCo | 32 | 6.67 | 5.30 | 5.98 |
| *Brushplated CoMo | 25 | 5.36 | | 5.36 |
| *Brushplated CoMo | 35 | | 1.46 | 1.46 |
| *Brushplated CoMo | 13 | 1.04 | 0.98 | 1.01 |
| *Brushplated CoW | 13 | 1.27 | 2.10 | 1.69 |
| Electroless Ni + Chromium Carbide Particles | | 2.09 | 1.99 | 2.04 |

\+ Deposits produced from commercially available brush plating solutions.

* Deposits produced from the developed electrolytes having formulations as in section 12.2.

volume of $9.57 \times 10^{-3}$ $cm^{-3}$. Of all of the brush plated coatings tested, the deposits obtained from the cobalt alloy electrolytes developed in this work proved most wear resistant. A die set brush plated with the cobalt molybdenum electrolyte referred to in section 12.2 gave a wear volume of $1.01 \times 10^{-3}cm^3$ as compared with $4.37 \times 10^{-3}cm^3$ for the unplated electem No 5 die.

The thickness of the coating appeared to be of importance, as from table XXI it can be seen that the most successful coatings were only 13µm thick. All of the proprietary coatings were applied as recommended by the supplier resulting in deposits 23-35µm thick. It should also be noted that the wear volume results for dies coated with the "developed" CoMo deposit gave inferior performance when plated to thicknesses in excess of 13µm.

Another important factor with respect to wear performance appeared to be the degree of mill scale retention during forging. The dies coated with the CoMo and CoW alloys developed during this work showed little scale retention; consequently minimal descaling was required prior to wear measurement. In fact during forging, scale was observed to build up on these die surfaces, only to be broken away by subsequent blows, leaving the coating bright and clean. Without exception, all of the dies plated with proprietary electrolytes scaled badly, particularly when penetration of the deposit had occured.

The Scanning Electron Microscope was used to investigate the surface characteristics of the bottom die from the cobalt molybdenum plated die set. Fig 35(a) shows the nodular deposit typical of the unworn area of the die. Also shown is the network of cracks common to many brush plated deposits. Fig 35(b) shows the same area as 35(a), where the distribution of molybdenum (white) in the deposit can be seen in the X-ray photograph. Fig 36(a) shows an area of the wear ring where a high degree of relative movement of metal has taken place. The nodular appearance has been eliminated, but the network of surface cracks can still be seen. An X-ray photograph showing molybdenum in white (Fig 36(b)) indicates a more even distribution of molybdenum at the deposit surface. There is also some indication that the overall concentration of molybdenum at the surface has increased. Fig 37(a) shows the central area of the die where there is little evidence of movement of the forged slug. Again, the nodular appearance of the deposit is no longer apparent, but cracking can be seen. Fig 37(b) represents an area of the wear ring where severe abrasion and erosion have taken place. Even

Fig 35.

Scanning electron photomicrographs of unworn area of cobalt molybdenum plated die.

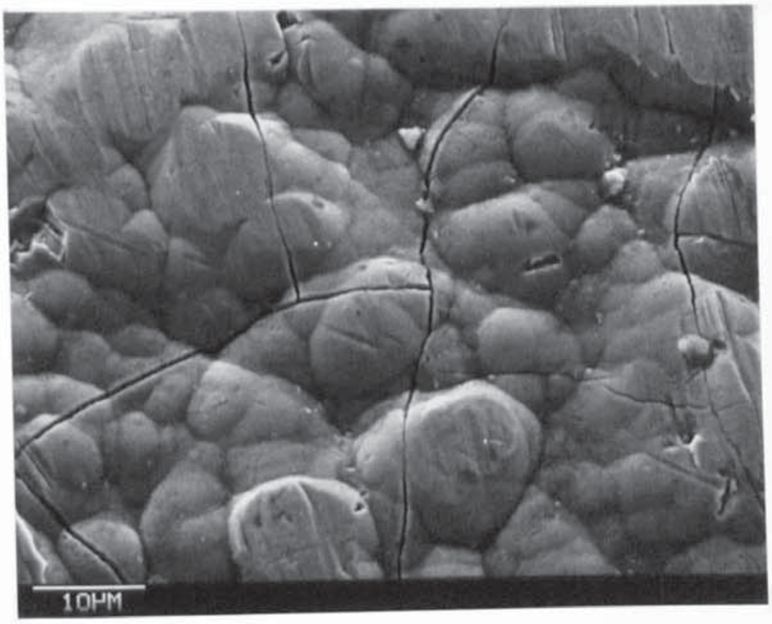


Fig 35a. Unworn area of die x 2K.

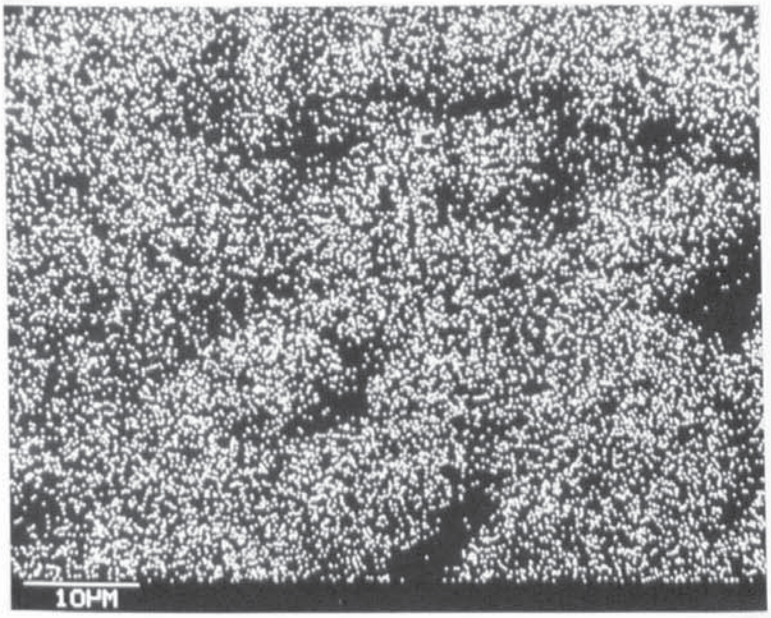


Fig 35b. X-ray photograph of the above area showing the distribution of molybdenum (white). x 2K.

Fig 36.

Scanning electron micrographs of worn area of cobalt molybdenum plated die.

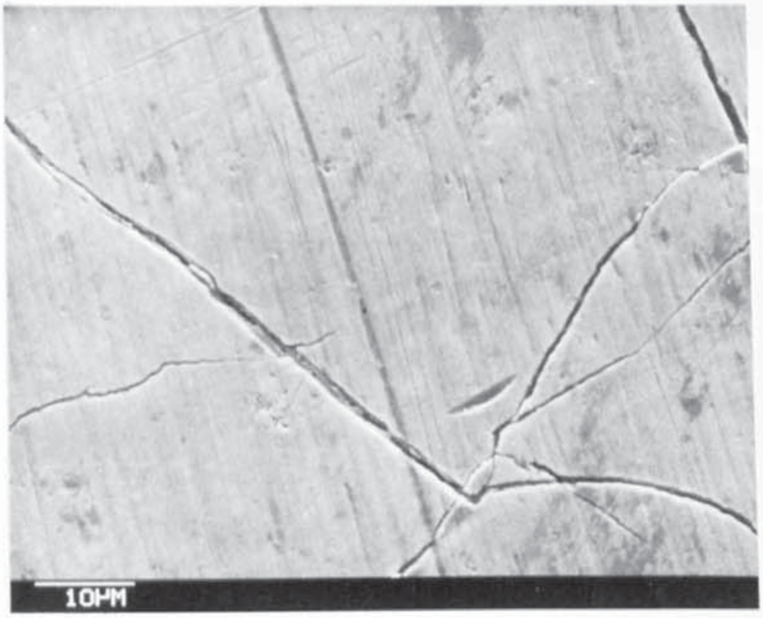


Fig 36a. Wear ring area showing scoring and cracking x 2K.

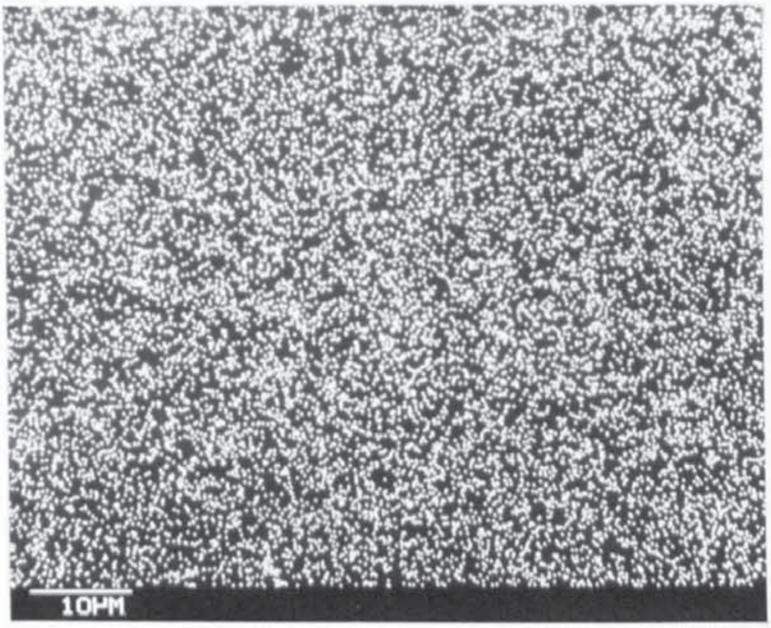


Fig 36b. X-ray photograph of the above area showing distribution of molybdenum (white) x 2K.

# Fig 37.

Scanning electron photomicrographs comparing central area of die with severely abraded area of wear ring.

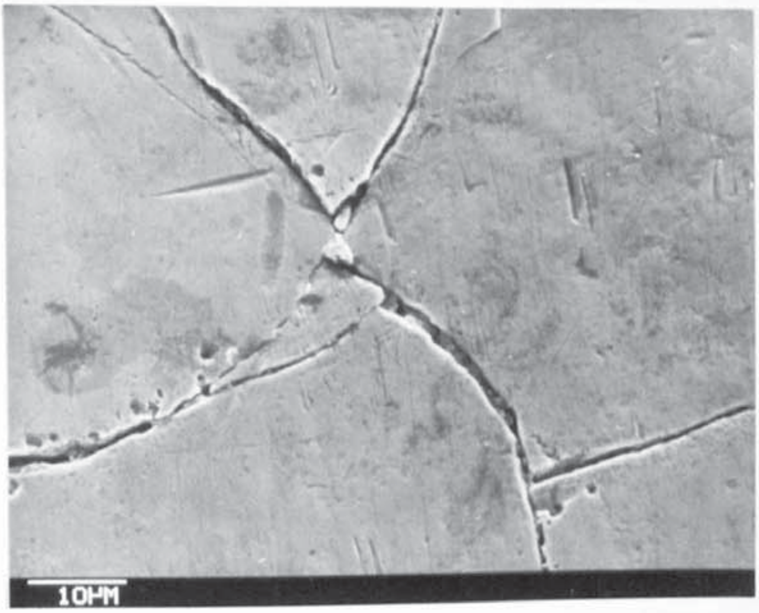


Fig 37a. Central plateau of forged plated die, depicting the flattened nodular deposit; little indication of scoring x 2K.

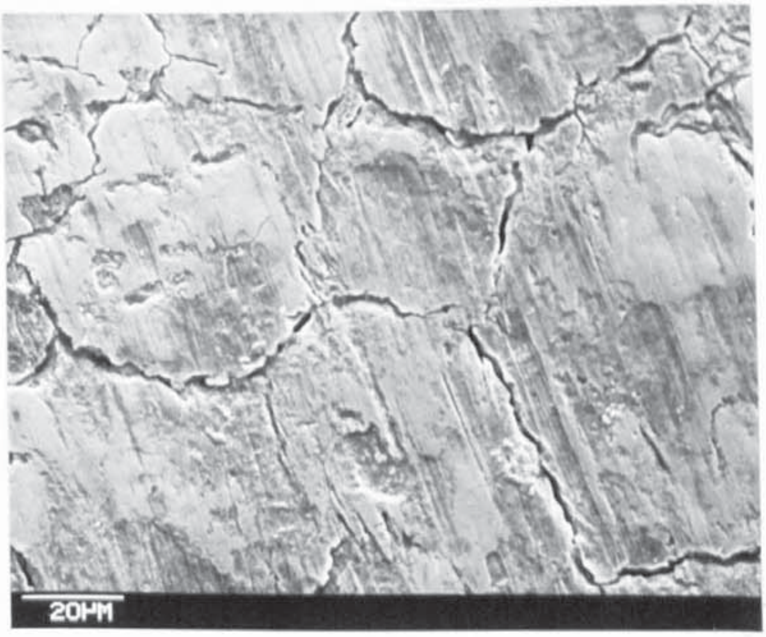


Fig. 37b. Wear ring showing a severely abraded area x 1K.

Fig 38.

Photomicrographs of cross sections of a cobalt molybdenum plated die.

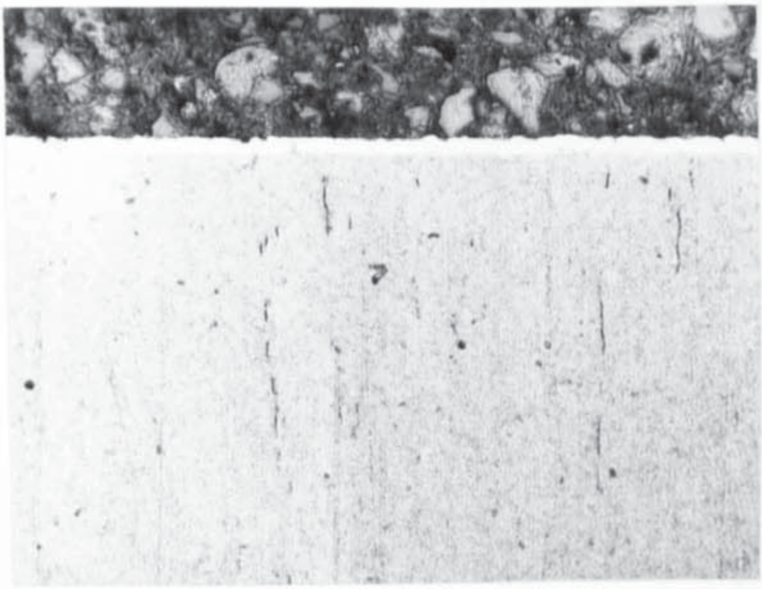


Fig 38a. Cross section of unworn area of cobalt molybdenum plated die x 100.

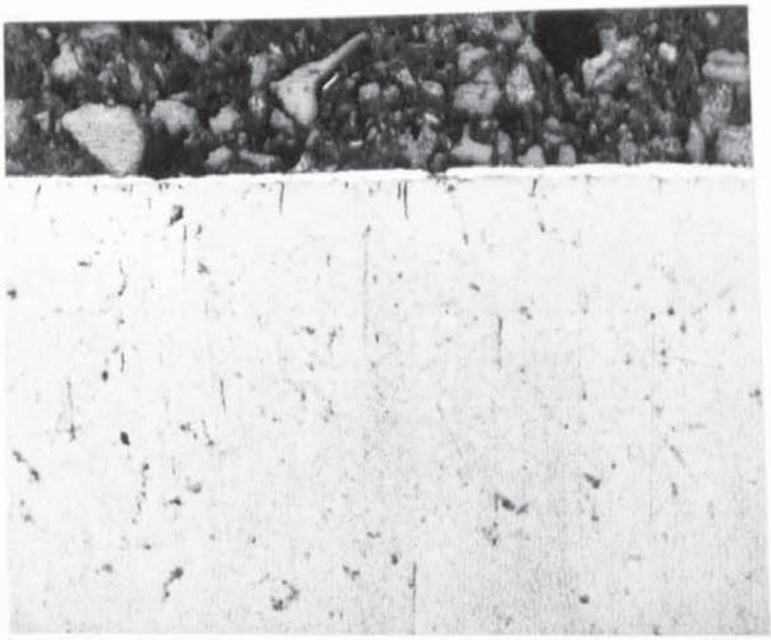


Fig 38b. Cross section of the wear ring of the above die showing erosion of the deposit and cracking of the substrate x 100.

under these extremely arduous conditions the adhesion of the CoMo deposit remained good.

The cobalt molybdenum plated die was then sectioned through the wear ring such that the effect of forging upon the substrate could be seen. Fig 38(a) shows a section of the deposit in an unworn area of the die. An even coating thickness could be observed, with no evidence of poor adhesion. Fig 38(b) is a similar cross section situated in the wear ring of the worn die. From this it can be seen that the coating has worn away evenly, with little indication of surface penetration. Small fatigue cracks were apparent below the surface of the deposit, but there was little evidence to suggest that these were initiated in the deposit.

In conclusion, it appears that optimum wear performance could be obtained by application of a cobalt molybdenum or cobalt tungsten deposit 13µm thick from electrolytes referred to in section 12.2. The cracked nature of the brush plated deposit has little deleterious effect on its wear performance or adhesion.

## 17.3. Results of the Industrial Trials on Hot Forging Dies.

The results of the industrial trials on hot forging dies are presented in table XXII. In all results are recorded for 41 sets of hot forging dies and 19 extrusion inserts. However, a further 15 die sets were plated, but the results were invalid for a variety of reasons. Although ten of these die sets were plated in a satisfactory manner, results of subsequent forging trials were of little value as only part orders were required and the dies were not worn out. A further two die sets were regarded as untypical, as extremely severe grease contamination gave rise to a poor and unrepresentative deposit. The rest of the 15 discounted results were due to poor forging practice, machining or modification of the dies after plating.

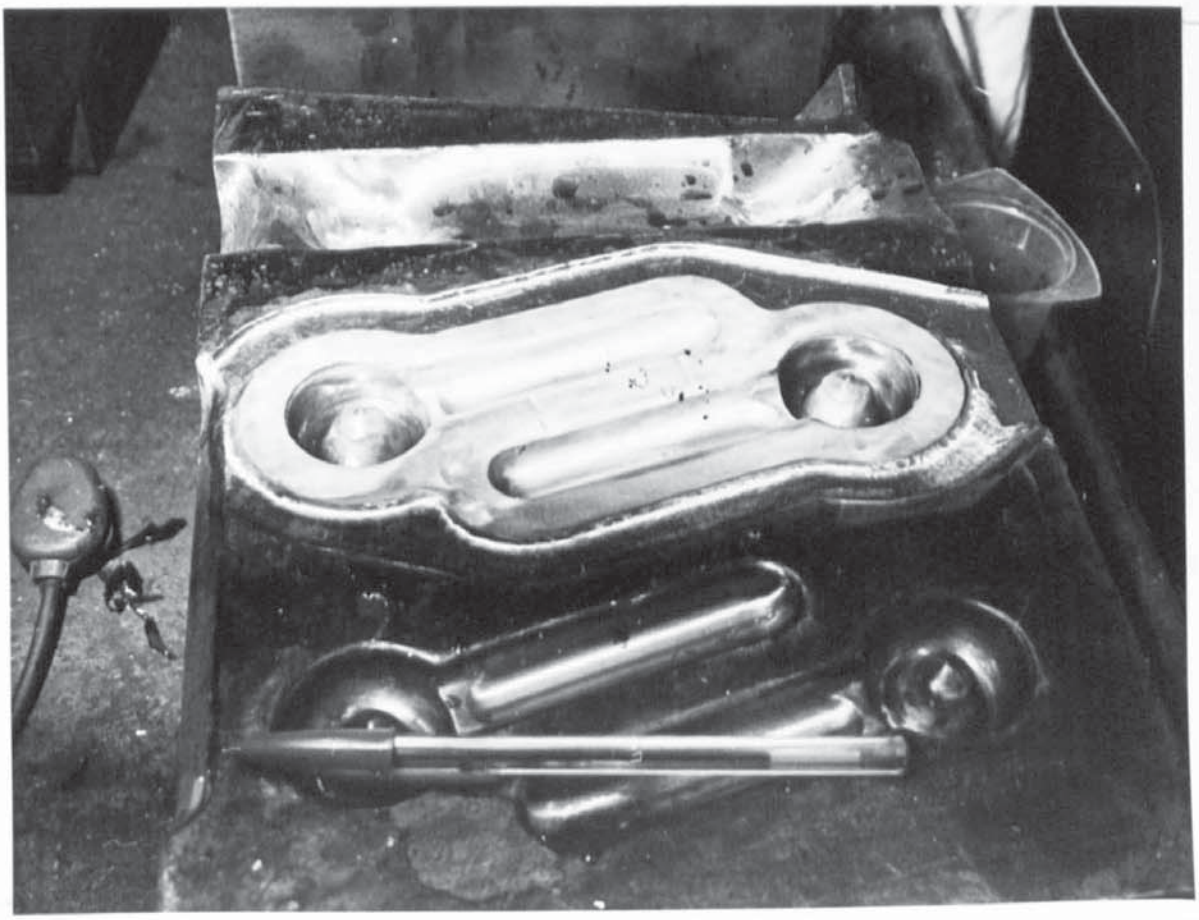
Dies for producing coupling flanges for the automobile industry are illustrated in Fig 39. Three sets were brush plated with 13µm of cobalt molybdenum alloy, a procedure which took 65 minutes for each die. The life of this particular die when unplated can be predicted to within ±6%. Consequently, percentage improvements of 19, 26 and 21% are very significant, especially as the last two results were from dies that were removed from service for

Fig 39.

Dies used for producing coupling flanges for the automobile industry.

Fig 40.

Dies used for producing tract rod pins.



reasons other than wear. When the flat top half of this die was brush plated, its life was increased by 88%.

A short production run prevented a full trial of the die used for producing track rod pins (Fig 40). This die set was brush plated in less than an hour. It was examined by the forge inspection department after being removed from service and it was estimated that the coating had improved its life by at least 25%.

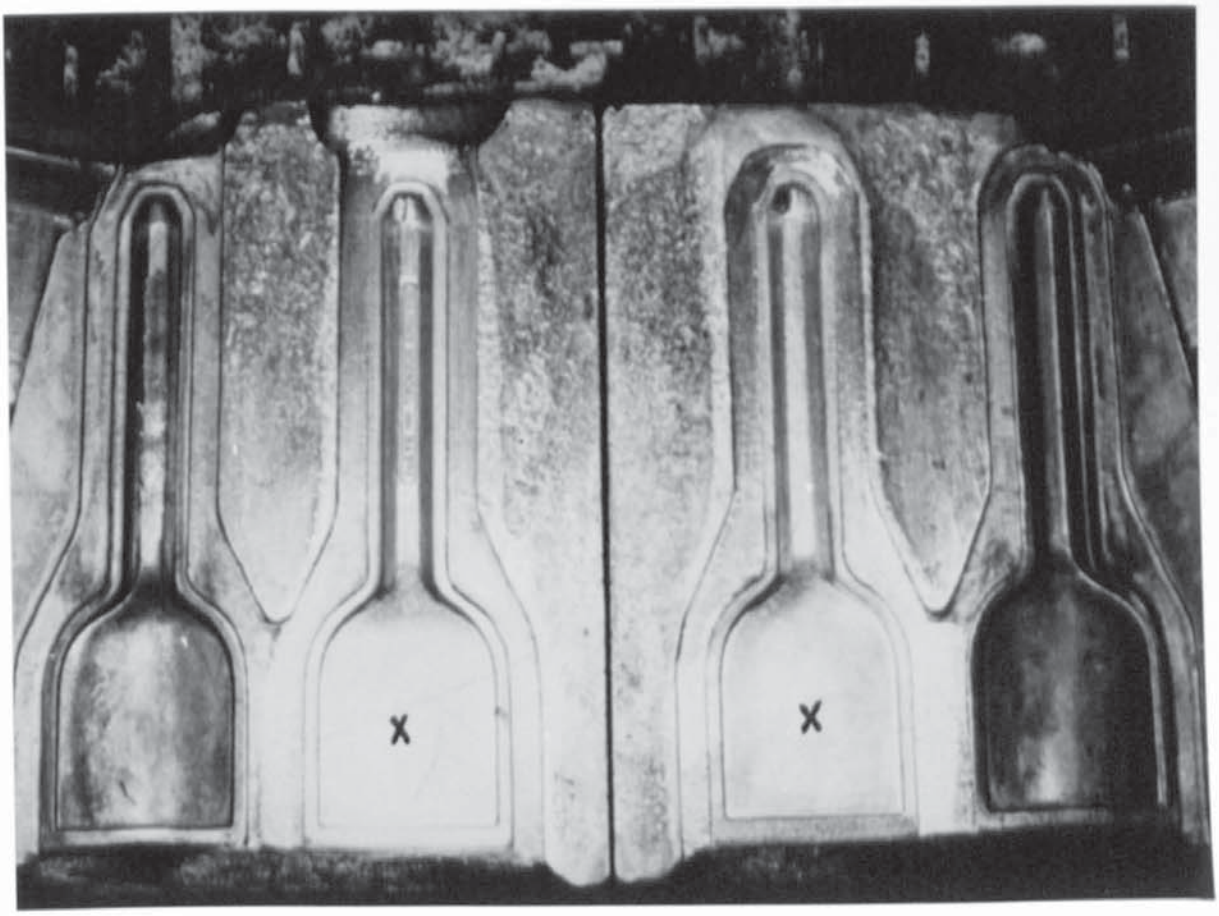
As a direct comparison of performance a plated and an unplated die, the left hand impression only was treated in a die block used for forging bolster chisels (Fig 41). The plated impressions produced 32% more forgings than the unplated, although forged under identical conditions.

A number of turbine blade dies have been plated similar to that illustrated in fig 42. Whilst results are still awaited for the majority of blade dies plated, the results so far obtained appear promising. Application of the cobalt molybdenum coating did not greatly improve die life, but improved forging quality in terms of dimensional accuracy.

Fig 43 shows an extrusion insert in the process of being plated utilizing a rotating lathe type head to hold the workpiece. In this arrangement, the die is rotated and the stylus is held such that the

Fig 41.

Dies used for the production of bolster chisels.



The two impressions marked x were plated with CoMo alloy while the other two were not plated. The brighter finish after plating accounts for the difference in appearance.

Fig 42.

Dies used for the production of turbine blades.

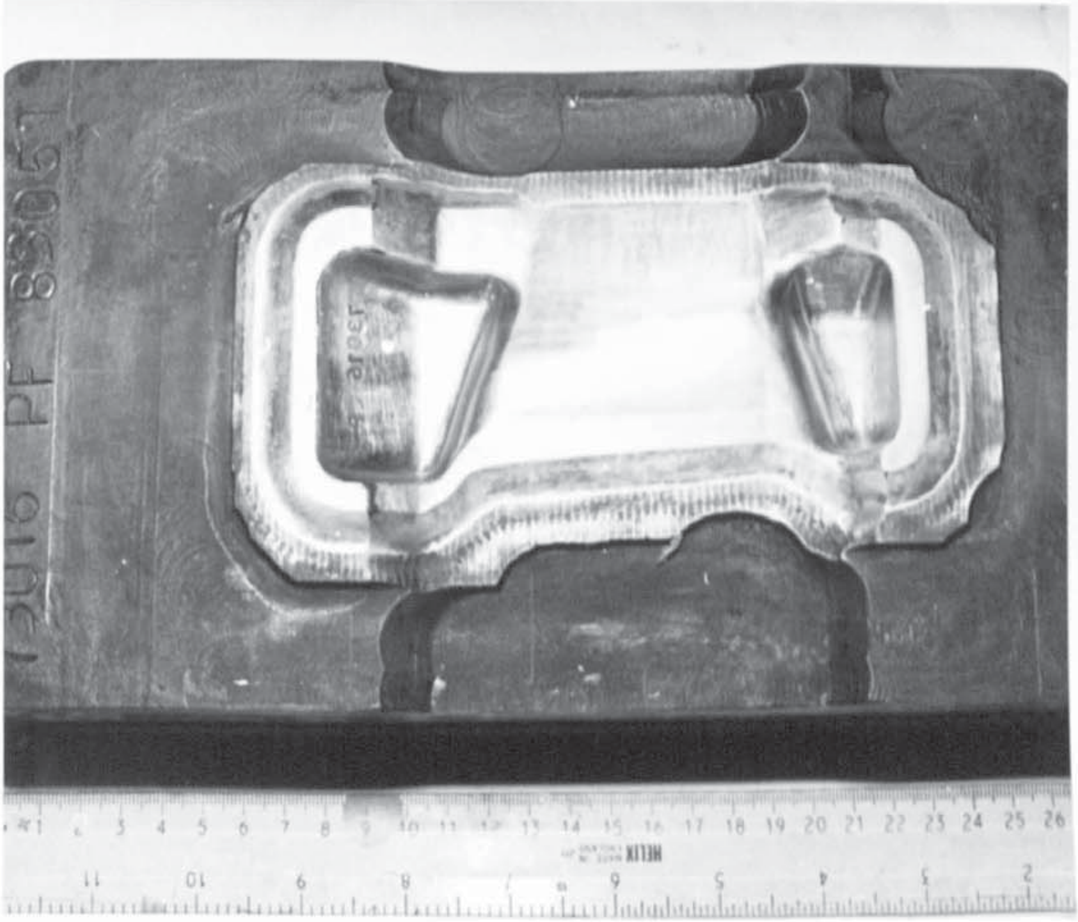
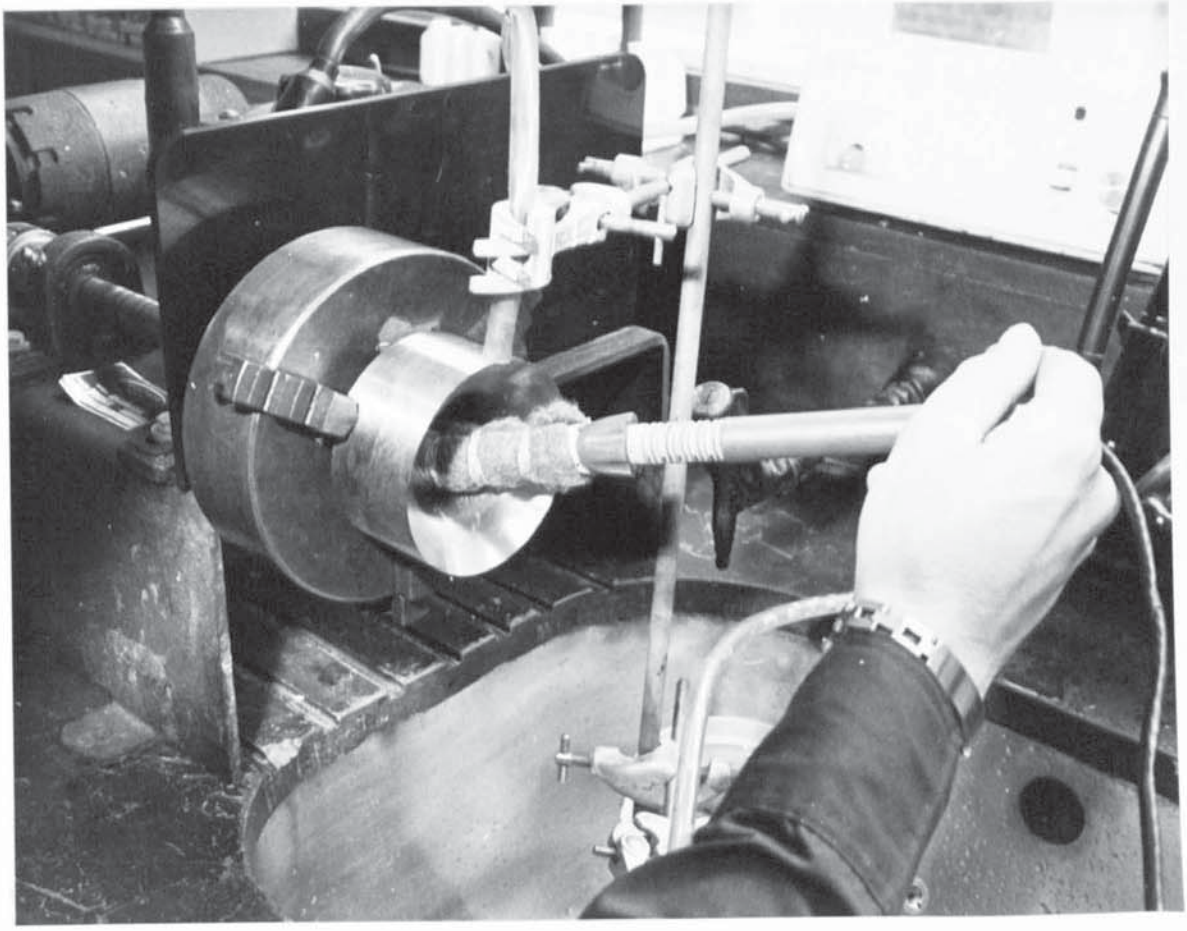


Fig 43.

Application of a rotating head in the brush plating of an extrusion insert.



working area of the workpiece is plated. The type of extrusion insert shown is used in conjunction with a glass lubricant for the extrusion of titanium alloys. Again, application of the cobalt molybdenum electrodeposit did not assist in the extension of die life, but resulted in an improved product.

"Coining" dies of the type illustrated in Fig 44 may have to be "re sunk" after processing only 25 pieces. Such dies are used for the preforming of turbine blades made from Nimonic alloys, where an extrusion of the bar is required. The illustration shows a coining die being brush plated with a shaped, small stylus to enable the deposit to enter the impression. After such a treatment, dies were reported to produce 80-250 pieces.

Extremely large hot foring dies have also been brush plated with the cobalt molybdenum alloy. Fig 45 shows a Ford Transit front axle die being plated with a large stylus. The larger stylus was selected, as flat areas could be plated at a rapid rate, whilst a small stylus was used to plate into inaccessible areas where the large stylus could not reach. Although an increase in die life was obtained with these dies it was not sufficient to make the process an attractive commercial proposition for the company concerned.

Fig 44.

Brush plating a coining die using a specially shaped small stylus.

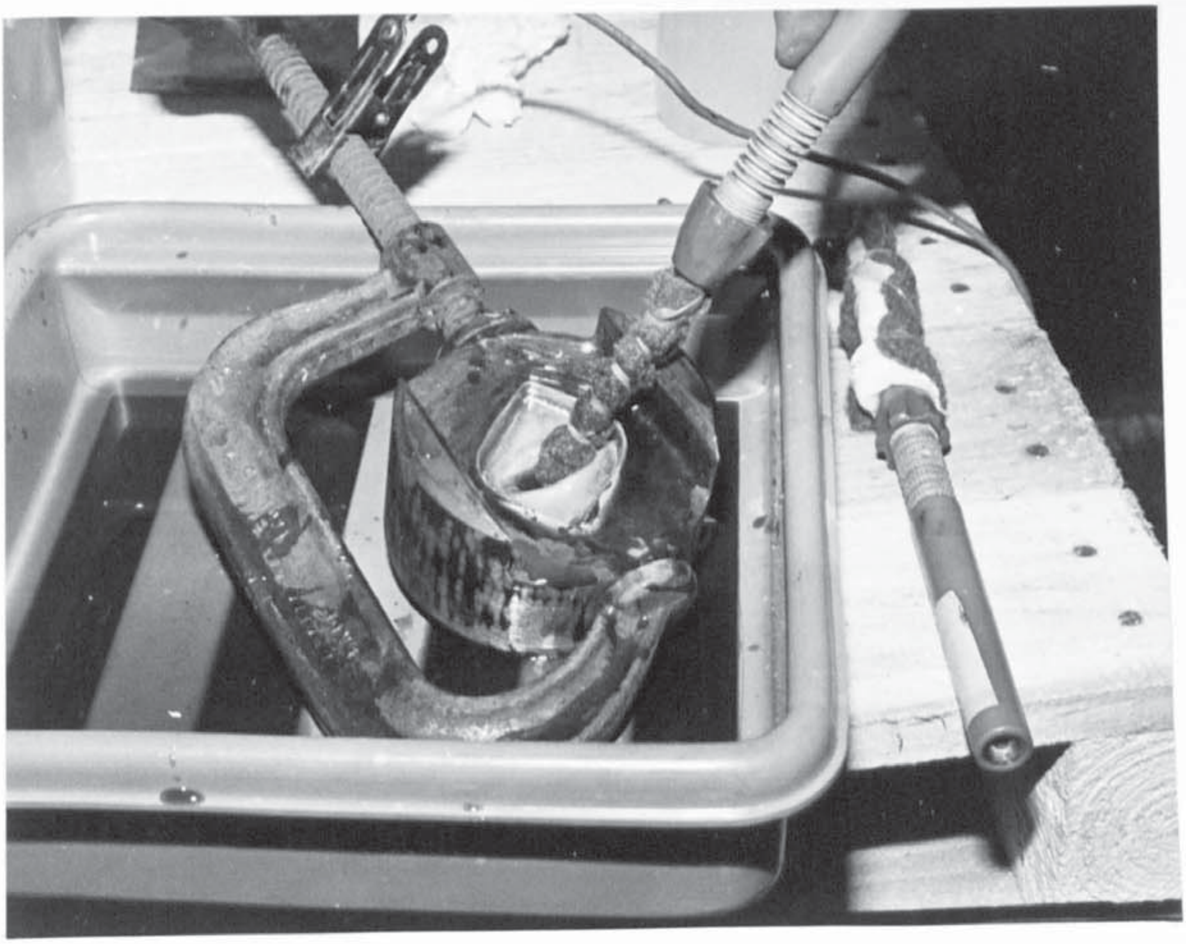
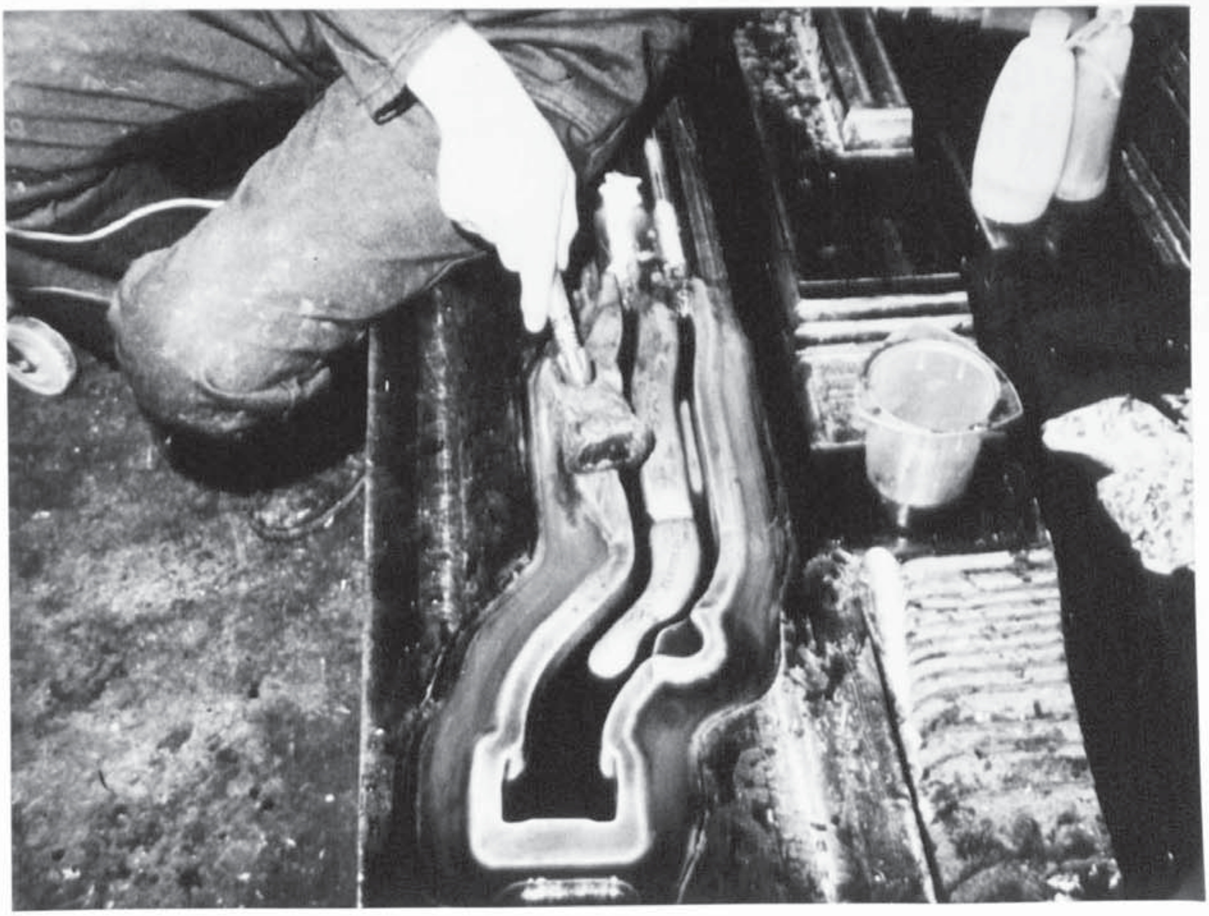


Fig 45.

Use of a large stylus when brush plating a motor vehicle front axle die.



## TABLE XXII

## Results of the Industrial Trials on Hot Forging Dies

| Die Type | No of Sets Plated | Result |
|---|---|---|
| Gear Selector Lever | 1 | 120% improvement in die life compared with an unplated one. |
| Hand Tool Die | 1 | 34% improvement in die life compared with unplated one. |
| Coupling Flange Die | 3 | 20,26 and 21% improvement in die life compared with unplated one. |
| Pipe T piece | 1 | Production ceased, but estimated to increase die life by 25%. |
| Link Pin Die | 1 | " " " |
| Gear blank Dies (nitrided) | 1 | 18% improvement in die life, reduction of sticking of the workpiece to die. |
| Slack adjuster | 1 | No improvement, but failure is normally due to cracking and not erosion. |
| Rocker arm insert | 1 | 13% improvement in die life, compared with unplated die. |

TABLE XXII Cont'd

Results of Industrial Trials on Hot Forging Dies.

| Die Type | No of Sets Plated | Result |
|---|---|---|
| Large Universal Joint Dies | 4 | 1 pair 77% increase in die life.<br>1 pair average life (This pair was Tuft rided giving a poor electrodeposit)<br>2 pairs result awaited. |
| Valve Extrusion Dies | 2 | 1 pair increase in die life.<br>1 pair result awaited |
| Large Universal Joint Dies | 4 | All 4 sets produced less than nitrided dies used as a control. |
| Bolster Chisel Dies | 1 | 32% increase in life compared with unplated dies. |
| Brake Adjuster Dies | 1 | 43% increase in life compared with unplated dies. |
| Open Ended Spanner Die | 1 | Average Life |
| Turbine Blade Dies. (pre-form, coining and finishes) | 6 | 2 sets coining dies produced 80-250 pieces but normal life as low as 25 pieces (NB low life due to production technique - tests discontinued). 1 set finishers 2,200 forged. This is normal life but die will be used again as still in tolerance. |

## TABLE XXI Cont'd

## Results of Industrial Trials on Hot Forging Dies

| Die Type | No of Sets Plated | Result |
|---|---|---|
| Control linkage die | 1 | Plated die ran well, but suddenly failed - possibly due to forging cold bar stock. |
| Turbine blade die | 1 | Used to forge Nimonic alloys, had "normal" life. On removal from forge found to be in tolerance and suitable for further use. |
| Connecting link Rod | 1 | 32% increase in life compared with unplated die. Improved metal flow and lower forging temperature noted. |
| Suspension cup die | 1 | Brush plated over welded areas of die - no problems encountered. Improved die life by 56% over unplated die life. |
| Ford Transit front Axle Dies. | 2 | Improved life but not sufficiently to be viable economically. |

## TABLE XXII Cont'd

## Results of Industrial Trials on Hot Forging Dies.

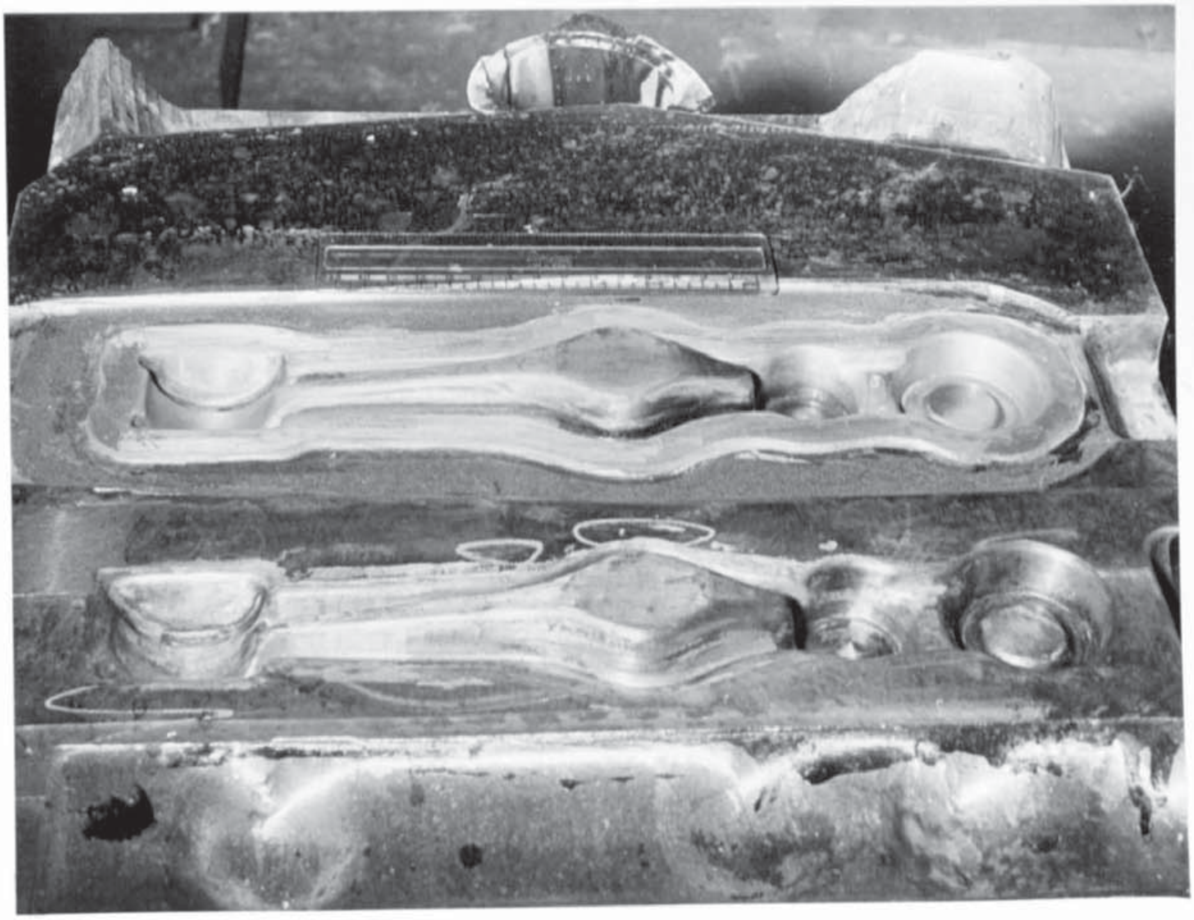
| Die Type | No of Sets Plated | Result |
|---|---|---|
| Extrusion Inserts<br>½" - 2½" dia | 19 | Used for extrusion of titanium for turbine blading. Glass lubricant used. Life not significantly increased but great improvement in surface finish so that scrap rate reduced. |

Cobalt alloy coatings not only improved the wear resistance of dies, but in some cases the ease of metal flow across the die was improved. Fig 46 shows a die used for forging steering link rods which when plated produced 32% more forgings, but because of the improved metal flow the forging temperature could be lowered, giving additional savings on energy costs.

An independant evaluation of the benefits of cobalt alloy brush plating has recently been carried out by a large company engaged in the production of titanium and nimonic forgings for the aircraft industry. Oxidation of the workpiece is a severe problem particularly when forging the nimonic alloys. To overcome this problem, the company involved, nickel plate the nimonic blanks prior to forging. This practice is extremely expensive, as after forging, the nickel is then stripped off and subsequently discarded. After numberous trials involving the use of cobalt molybdenum brush plated dies, it was found possible to forge unplated blanks merely by heating the nimonic stock in an inert atmosphere. The cost of brushplating the dies and the use of an inert-atmosphere for preheating, has been calculated to be considerably less than cost of nickel plating each individual piece. Hence, the company is now using electrolytes of the composition outlined in

Fig 46.

Die used for forging steering link rods for the automobile industry.



Section 12.2 to brush plate dies used for forging nimonic alloys.

## 17.4 Results of the Industrial Trials on Cold Forming Tools.

Cold pressing obviously presented markedly different operating conditions from those involved in hot forging and a different criterion for measuring improvements in "die life" was necessary. Press tools, particularly those used in the automobile industry can have a "life" of between 15-20 years. Being a cold working operation with relatively little metal movement, erosive wear is much lower than in hot forging. A production run for a press-forming tool is rarely halted by out of tolerance dies, but generally by metal 'pick up' on the die causing surface scoring of the components. This scoring may cause rejection of the component for engineering reasons in the case of main stress bearing members or for cosmetic reasons in the case of body panels. In the course of any production run pick-up is removed from the die in situ by hand polishing and at the end of the run the die is removed for major refurbishing. Improvement in the 'life' of the die in this instance is measured in terms of the decrease in down time and not in terms of extra components produced.

In these trials the coatings was applied to specific areas of the press tools which were known to be susceptible to pick-up. These areas were easily identified by reference to a pressing from the end of a production run. The coating was normally applied to the radiused edge and an area of approximately 1-2cm on either side (Fig 47).

Fig 48 shows a die used for a fairly deep draw which is carried out in one operation. This die is built up from steel segments, which is the normal practice with many car component dies and pick-up normally occurs on the radiused edges, particularly at the curved ends.

These dies were used to produce approximately 20,000 pressings and in all cases down time due to scoring was eliminated after plating. Previous production runs of a similar duration using unplated dies incurred at least 1½ hours down-time due to metal pick-up.

Fig 49 shows a small multi segment die of which five segments were plated over their entire working surfaces which included areas of up to 15cm x 15cm. The die is shown after producing approximately 16,000 pressings and again no down-time due to pick-up was experienced. In the unplated condition this die normally requires attention approximately every 3,000 pressings. Fig 50 shows

Fig 47.

Radiused edge of a press tool showing an etching operation.

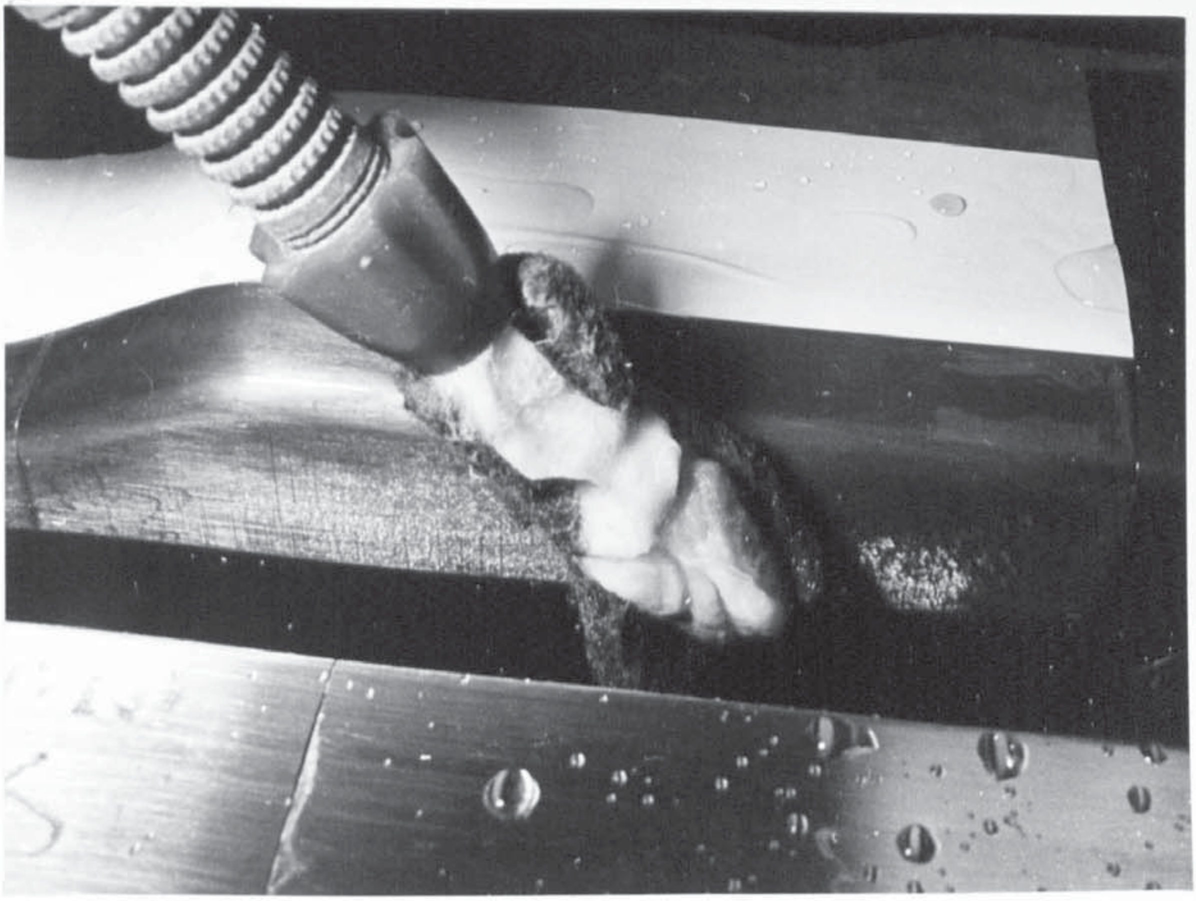


Fig 48.

Pressing tool used for forming a front side member of a motor car.

Fig 49.

Small multisegment press tool used for pressing clutch covers.

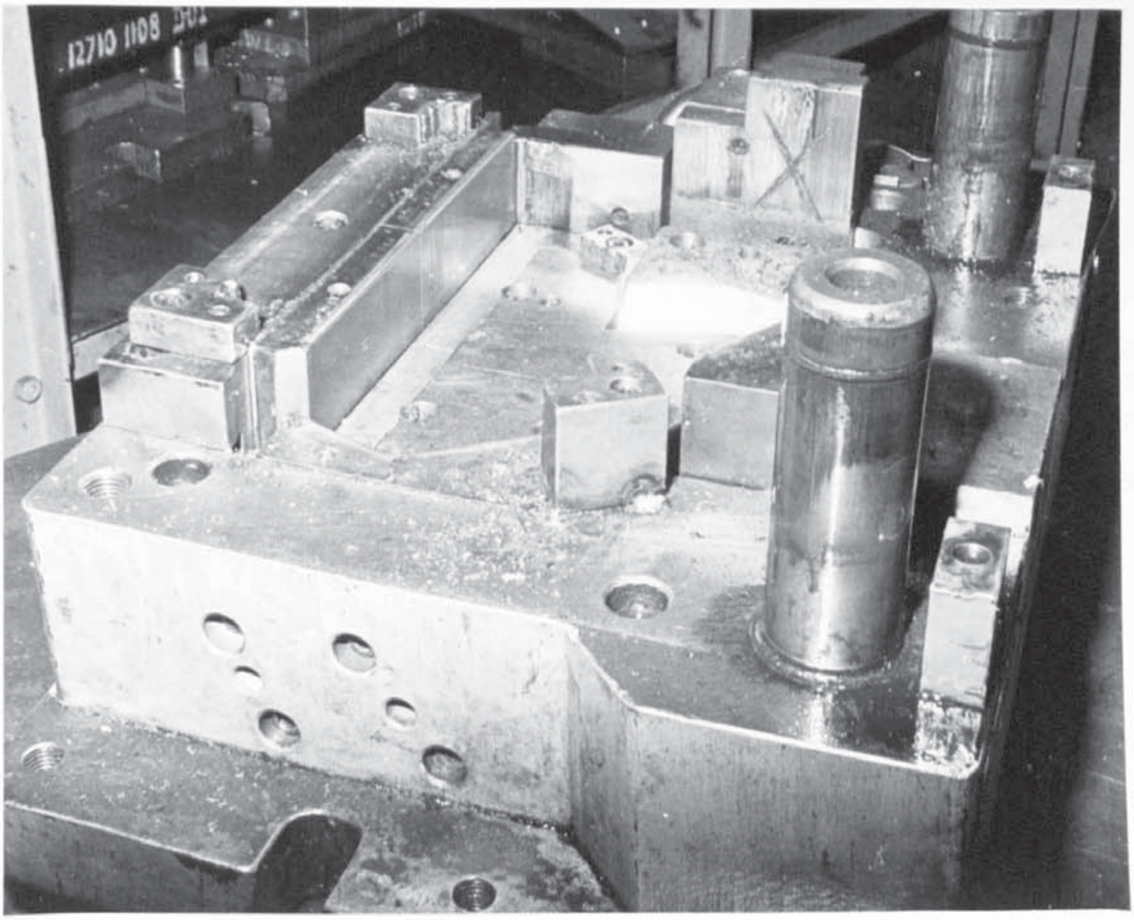
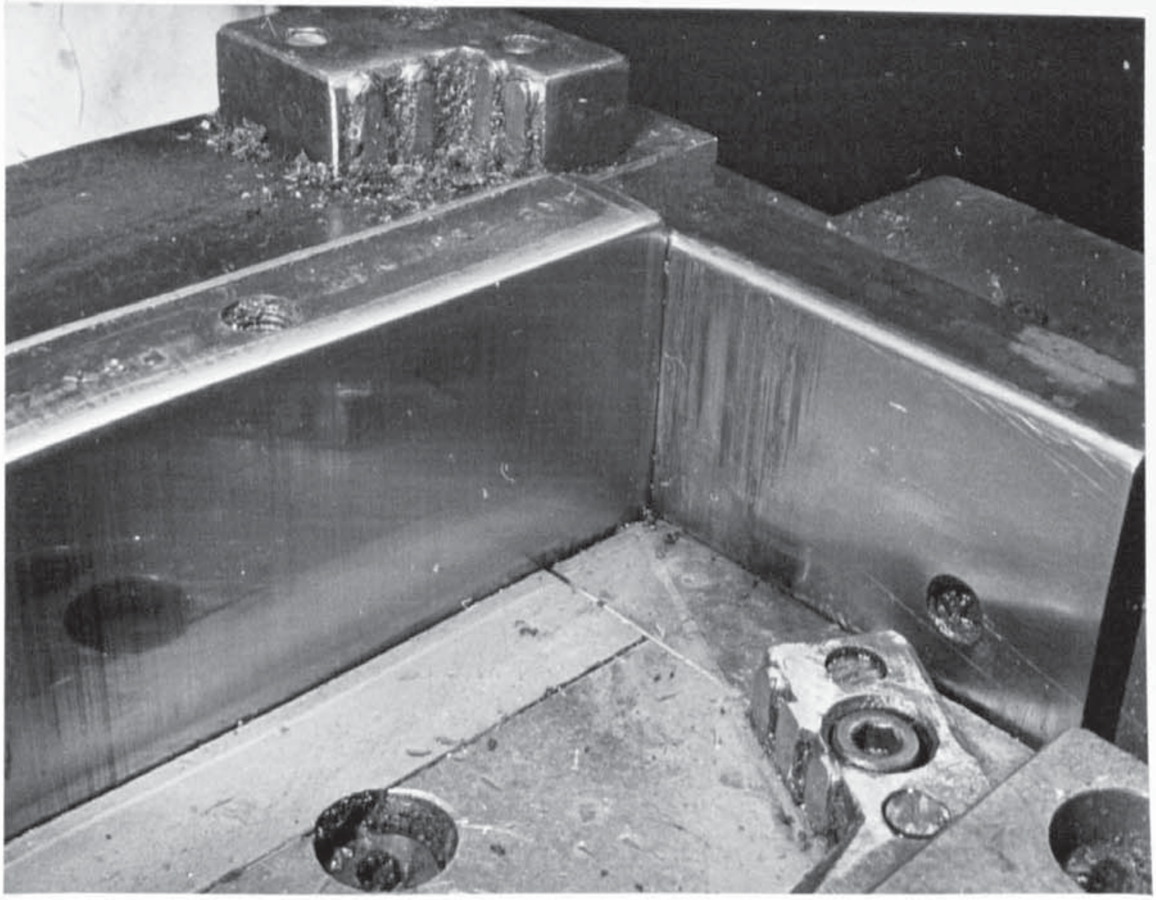


Fig 50.

Close up of press tool of Fig 49 showing scoring.



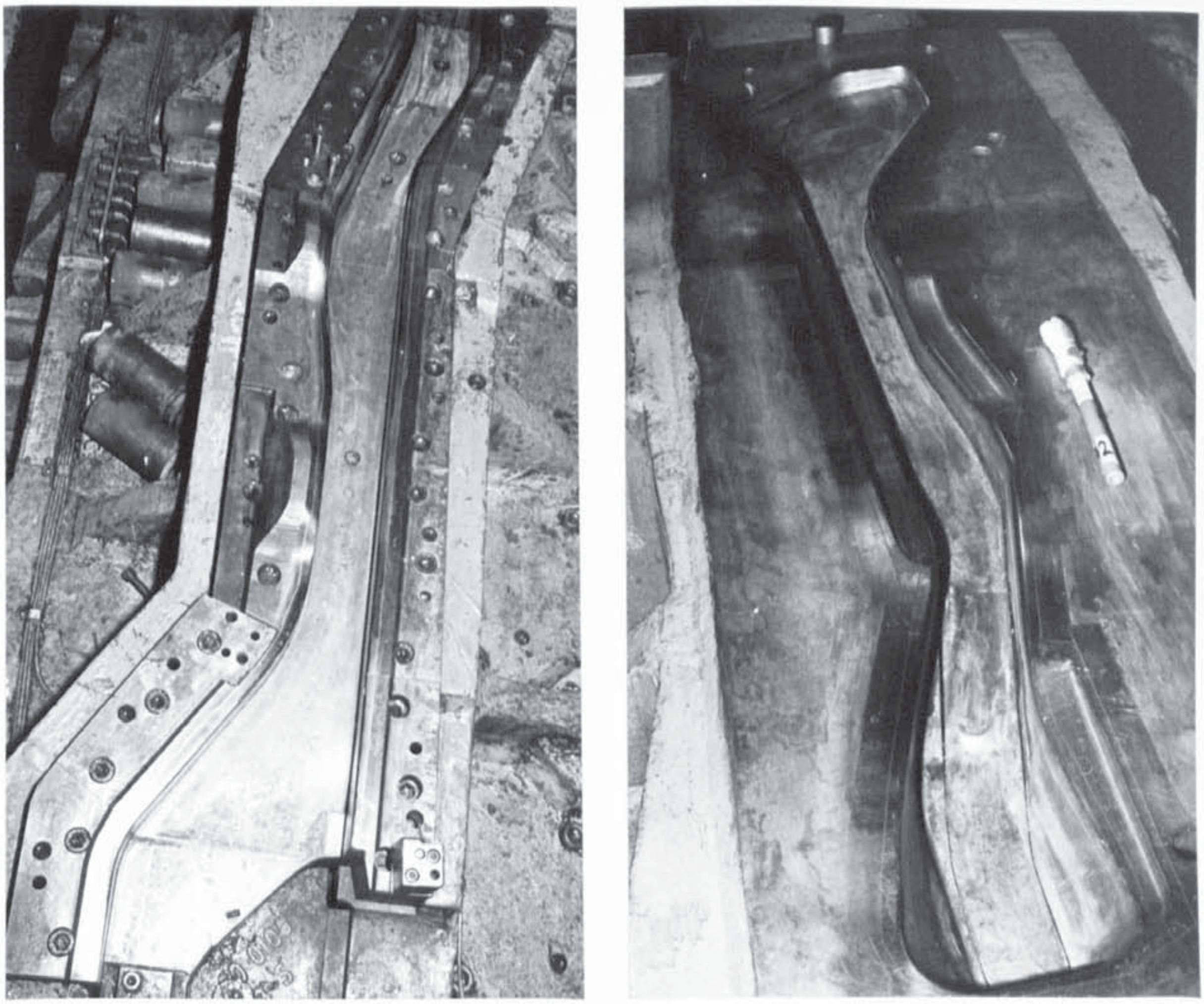
the difference between the plated and unplated areas of this die. The long segment on the left-hand side of the die was plated whereas the small section at right angles to it was unplated. Deterioration of the unplated segment face can be seen clearly.

Many pressings produced in the automobile industry are formed in multi stage operations and therefore several dies in a stand may be susceptible to pick-up. Fig 51 shows two such dies used in a stand of six to produce a fairly deep structural member. It shows both the initial forming die which is a high duty iron casting and the finishing die which is made of steel segments. The plated area can be seen on the radiused edges of both press tools. Approximately 20,000 pressings were produced on these plated dies and again down-time due to pick-up was eliminated. This result however is inconclusive as due to other forming problems, a lubricant was used on the blanks which is not the normal practice.

Lubrication is normal practice for the die shown in Fig 52 as without it, this box section could not be produced. After the die had been brush plated with cobalt/molybdenum alloy, it produced 10,000 pressings without the use of lubricant. This is a significant saving as the lubricant had to be applied by hand, and later had to be removed from the pressing

Fig 51.

Initial and final impressions used for pressing an automobile structural member.

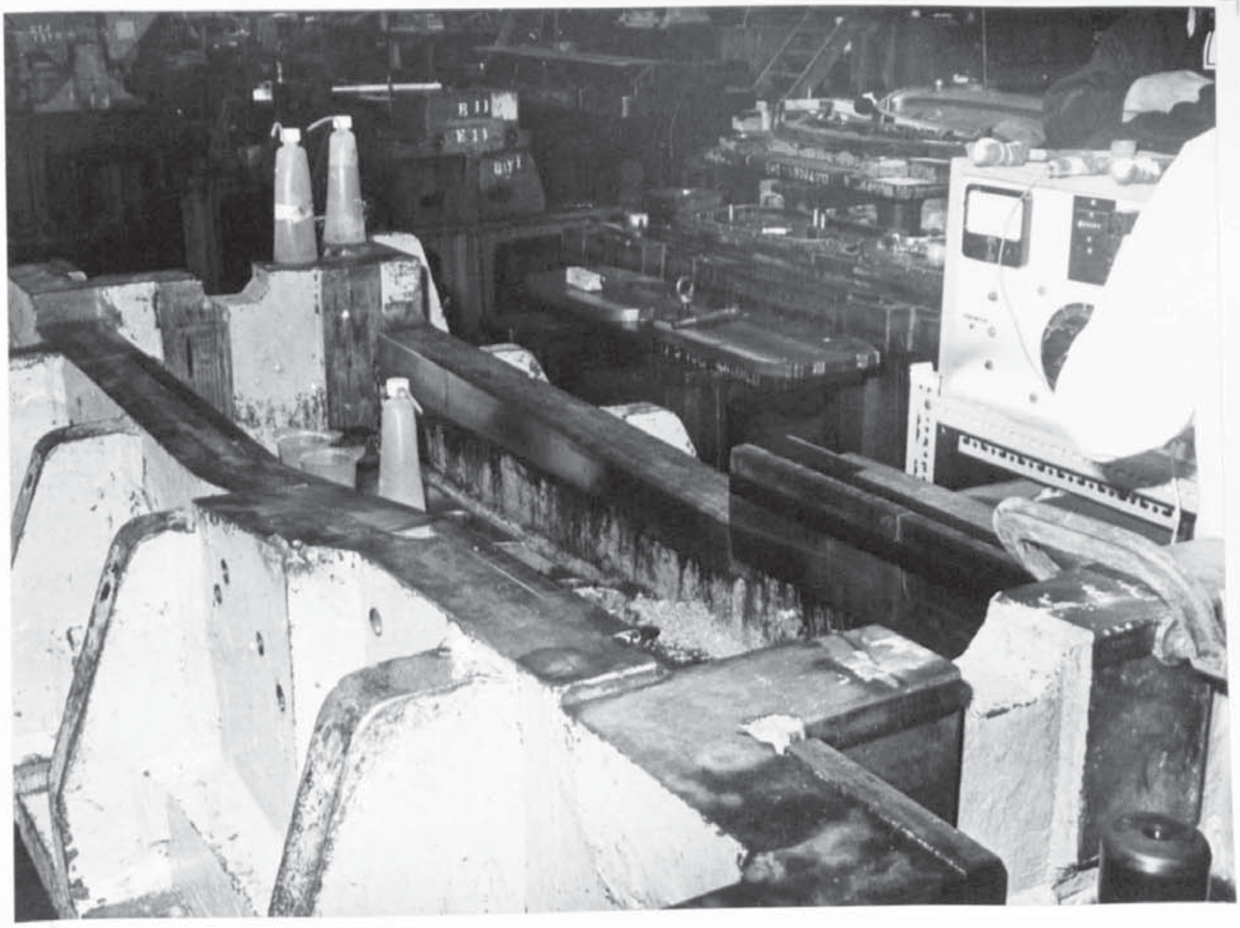


Initial impression, die material cast iron. Brush plated with 13µm of CoMo alloy.

Final impression, segmented steel die. Brush plated with 13µm of CoMo alloy.

Fig 52.

Deep forming die used for pressing car nearside members.



before it could be painted.

In all, the brush plated dies have produced 168,280 pressings with a total down-time due to scoring booked at 6½ hours. The same dies, before they were plated, produced on their last 2 or 3 runs 202,146 pressings but needed 44 hours of stoning to remove the pick-up which caused scoring. This means that a plated die required only 24 minutes down time per 10,000 pressings compared to 130 minutes down-time per 10,000 pressings for an unplated die. As this down-time represents only the time actually 'booked' for die repairs and does not include such factors as run-down and start-up time, the actual overall down-time will be several times larger than this.

# 18. DISCUSSION

## 18.1 Electrolyte Development.

Initial brush plating trials concerned with deposition of cobalt from cobalt sulphate solutions showed that the highest cathode efficiency could be obtained from electrolytes containing 500 g/l cobalt sulphate (Fig.17). Thus as predicted by consideration of high speed plating theory (section 3); increasing metal ion concentration resulted in greater efficiency. In order to obtain maximum efficiency, subsequent brush plating electrolytes were formulated using 500 g/l cobalt sulphate. The lowering of cathode efficiency resulting from additions of sodium heptonate, is also shown in Fig.17. This may be explained by the formation of cobalt ion complexes which make deposition more difficult. A similar effect can be seen in Fig.18 where glacial acetic acid has been added to a 500 g/l cobalt sulphate electrolyte. The upper line represents a fall in efficiency due to the addition of acetic acid, whilst the lower line shows the effect of additions of acetic acid in the presence of 200 g/l sodium heptonate. Thus, a further fall in cathode efficiency is obtained on the addition of both complexing agents. The most important practical implication of this effect is that the minimum amount of complexing agent commensurate with satisfactory plating characteristics and deposit quality should be used in the formulation of alloy brush plating electrolytes.

The effect of sodium heptonate upon deposition characteristics of cobalt-molybdenum and cobalt-tungsten alloys was investigated in the composition trials on these deposits (section 15.2.) Fig 19 illustrates the increased percentage of alloying element obtained in the deposit when raising the concentration of sodium heptonate from 100 to 400 g/l. To examine this effect further, the results plotted in Fig 19 were used to calculate "partial cathode efficiencies" for the deposition of cobalt, tungsten and molybdenum. (Table XXIII)

By plotting these efficiencies against sodium heptonate concentration (Fig.53,54), the effect of additions of the complexing agent are more apparent. The percentage of alloying element in the deposit is also plotted in Figs. 53 and 54 to enable comparisons to be made with the partial efficiencies of cobalt, tungsten, molybdenum and the combined efficiencies of the alloy systems. From Figs. 53 and 54, it can be seen that additions of sodium heptonate result in similar effects on cathode efficiencies for both systems. At 100 g/l of sodium heptonate, the efficiency of deposition of the alloying element is low, as is the efficiency of deposition of cobalt. As deposits obtained at this level of sodium heptonate were stressed

## TABLE XXIII

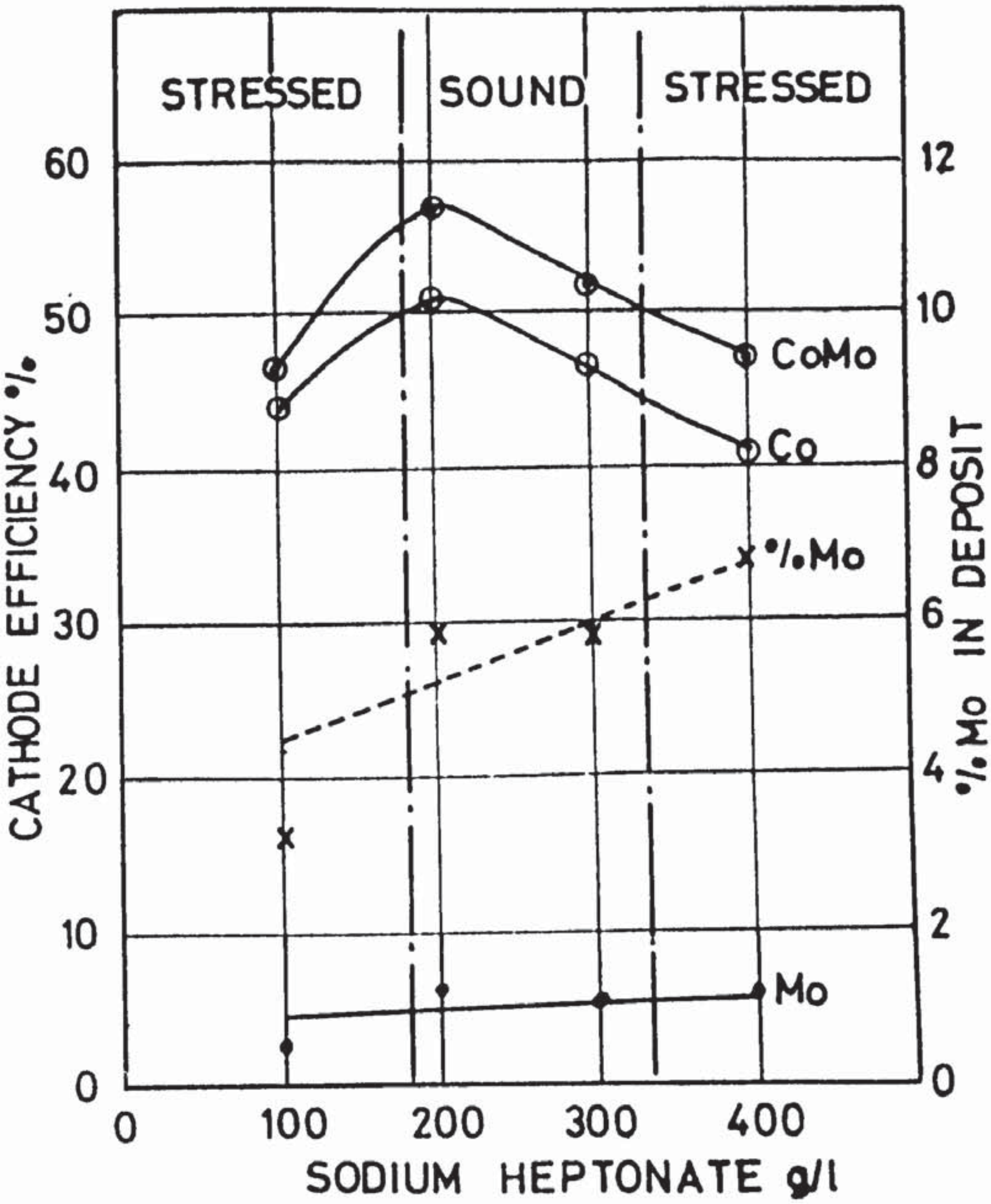
### Effect of Sodium Heptonate on Partial Efficiencies of Cobalt, Tungsten and Molybdenum.

| Sodium Heptonate | Partial Cathode Efficiency % | | Combined Efficiency % |
|---|---|---|---|
| g/l | Mo | Co | CoMo |
| 400 | 6.07 | 41.20 | 47.27 |
| 300 | 5.39 | 46.56 | 51.95 |
| 200 | 6.07 | 51.04 | 57.11 |
| 100 | 2.70 | 43.87 | 46.57 |

| Sodium Heptonate | Partial Cathode Efficiency % | | Combined Efficiency % |
|---|---|---|---|
| g/l | W | Co | CoW |
| 400 | 3.32 | 28.20 | 31.52 |
| 300 | 3.60 | 40.74 | 44.34 |
| 200 | 5.50 | 59.19 | 64.69 |
| 100 | 3.41 | 44.41 | 47.83 |

Fig 53.

Effect of sodium heptonate on the partial efficiencies of cobalt and molybdenum in the deposition of a cobalt molybdenum alloy.

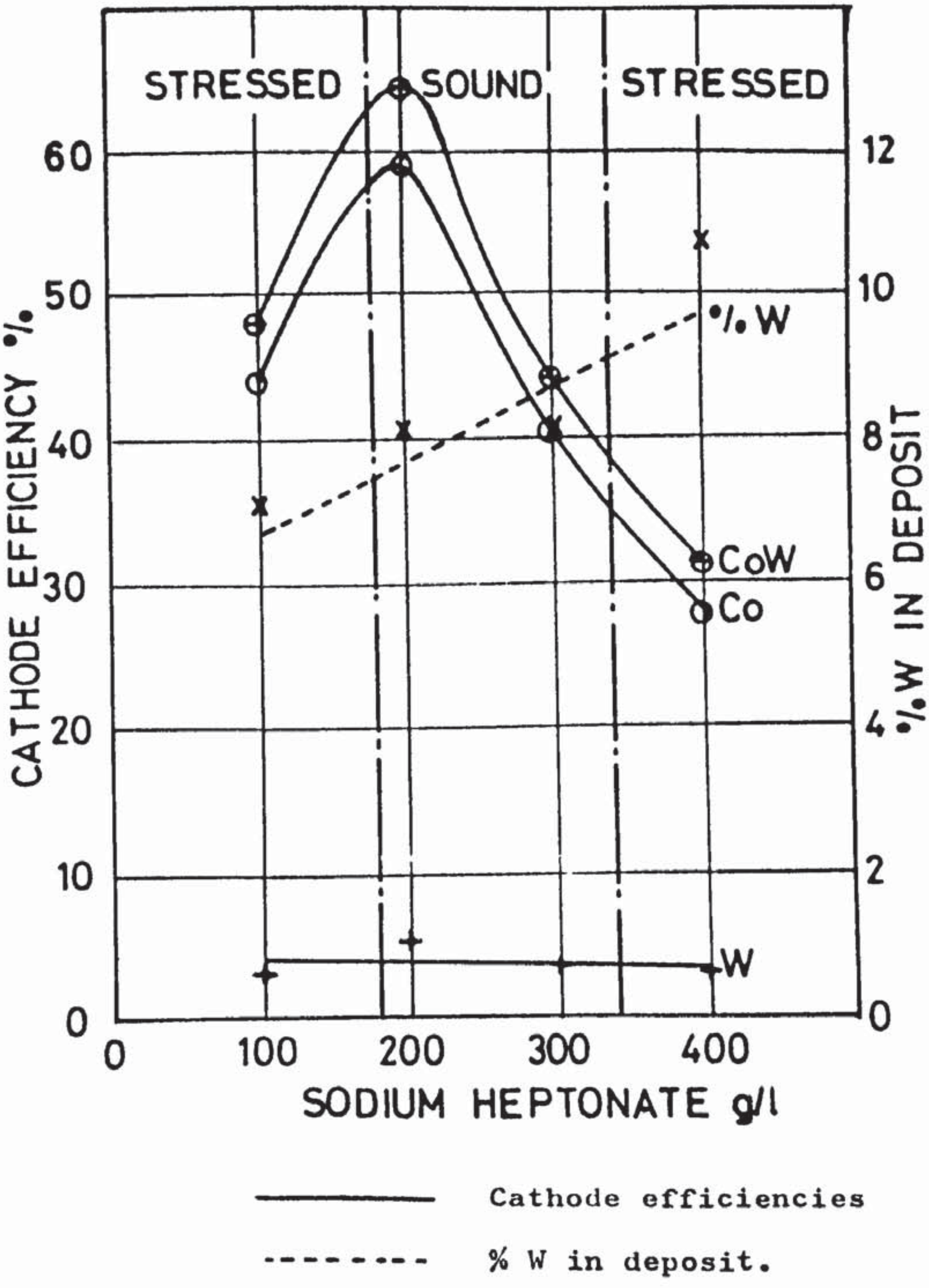


———————— Cathode efficiencies

- - - - - - - % Mo in deposit.

Fig 54.

Effect of sodium heptonate on the partial efficiencies of cobalt and tungsten in the deposition of a cobalt tungsten alloy.



and burned, this may account for a low overall efficiency. Increasing the sodium heptonate concentration to 200 g/l resulted in maximum partial efficiencies for deposition of both cobalt, and alloying elements. At this level of complexing agent, deposits were sound, and it is assumed that sufficient sodium heptonate was present to complex both the cobalt and alloying element adequately. Although additions of sodium heptonate in excess of 200 g/l increased the percentage of alloying element in the deposit this was at the expense of overall efficiency. This effect occurred due to the fact that the efficiency of alloying element deposition remained reasonably constant, whilst the efficiency of the cobalt deposition fell rapidly when 200 g/l of sodium heptonate had been exceeded. Thus the overall effect was to reduce combined efficiency and to increase % alloying element in the deposit. The lowering of the partial efficiency of cobalt deposition at levels of sodium heptonate in excess of 200 g/l was possibly caused by further complexing of the cobalt ion, making its deposition increasingly difficult. Thus, the optimum level of sodium heptonate appeared to be 200 g/l as at this concentration, the partial efficiencies for alloying element deposition and cobalt deposition were at a maximum; sound deposits were also produced.

The effect of increases in concentration of glacial acetic acid are illustrated in Fig 21. For both cobalt tungsten, and cobalt molybdenum systems, increasing the level of acetic acid in the electrolyte, resulted in a lower percentage of alloying element in the deposit. Partial efficiencies for cobalt, molybdenum, and tungsten were calculated for these results, and presented in table XXIV. These were used to plot partial efficiency and combined efficiency versus acetic acid concentration, for the cobalt-molybdenum system Fig 55 and the cobalt-tungsten system Fig 56. The data from Fig 21 has also been superimposed on Fig 55 and 56, such that the percentage of alloying element in the deposit may be considered with respect to partial efficiencies. From Fig 55 and 56, it can be seen that additions of acetic acid resulted in similar behaviour for both systems. An increase in the concentration of acetic acid in the electrolyte depressed the partial efficiency of deposition of molybdenum Fig 55 and tungsten Fig 56. The partial efficiency of cobalt was also reduced, but it should be noted that the reduction in efficiency of cobalt deposition caused by acetic acid was considerably lower than in the case of sodium heptonate, where additions in excess of 200 g/l led to a rapid fall in the partial efficiency of cobalt deposition. This suggests that the acetic acid was more effective in

## TABLE XXIV

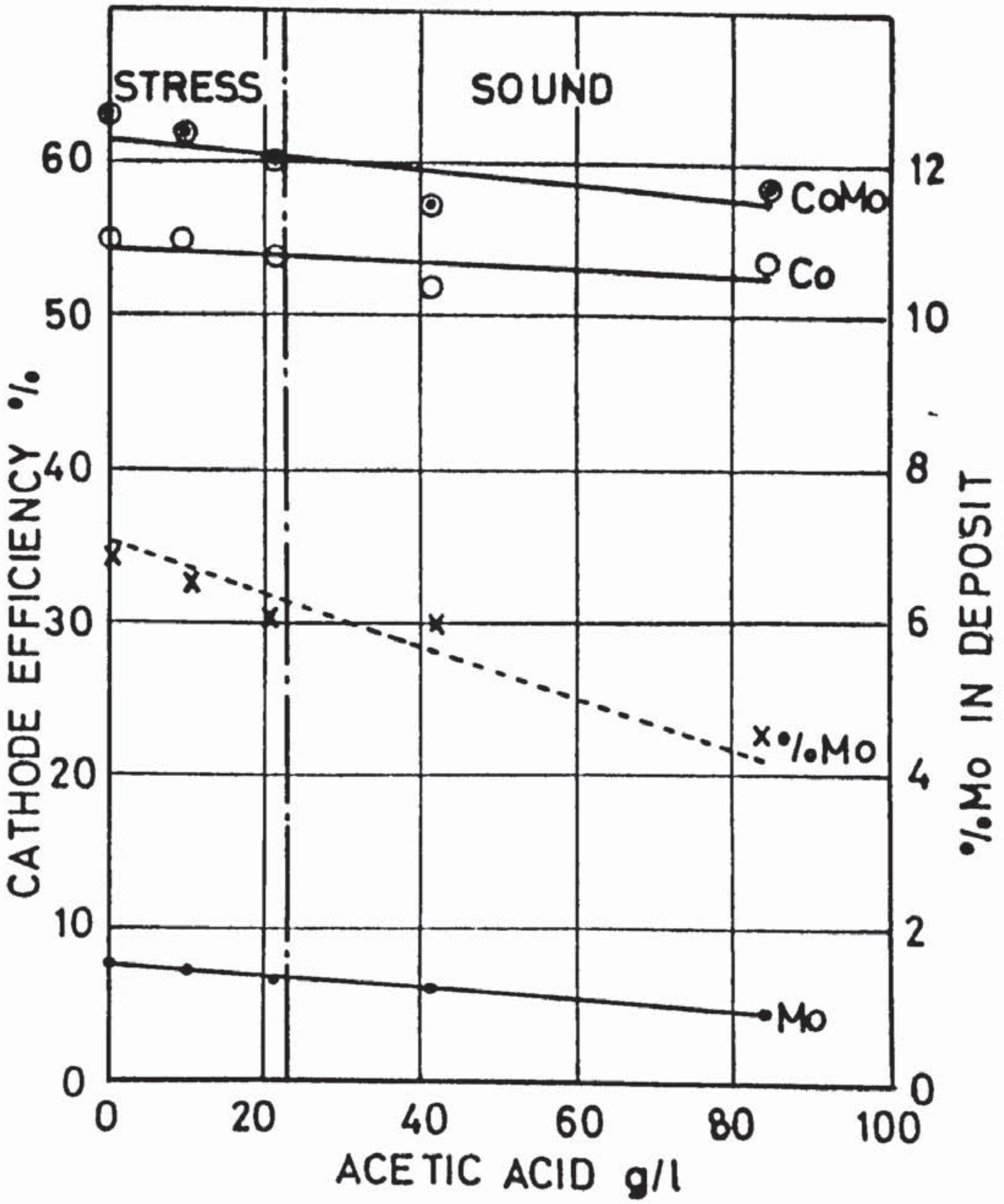
**Effect of Acetic Acid on the Partial Efficiency of Cobalt, Tungsten and Molybdenum.**

| Acetic Acid g/l | Partial Cathode Efficiency % Mo | Co | Combined Efficiency % CoMo |
|---|---|---|---|
| 0 | 7.69 | 55.43 | 63.12 |
| 10.5 | 7.27 | 55.13 | 62.04 |
| 21.0 | 6.57 | 53.94 | 60.51 |
| 42.0 | 6.12 | 51.31 | 57.25 |
| 84.0 | 4.94 | 54.71 | 59.65 |

| Acetic Acid g/l | Partial Cathode Efficiency % W | Co | Combined Efficiency % CoW |
|---|---|---|---|
| 0 | | | |
| 10.5 | 6.59 | 58.89 | 65.48 |
| 21.0 | 5.25 | 59.34 | 64.59 |
| 42.0 | 5.48 | 59.19 | 64.67 |
| 84.0 | 4.72 | 57.31 | 62.07 |

Fig 55.

Effect of acetic acid on the partial efficiencies of cobalt and molybdenum in the deposition of a cobalt-molybdenum alloy.

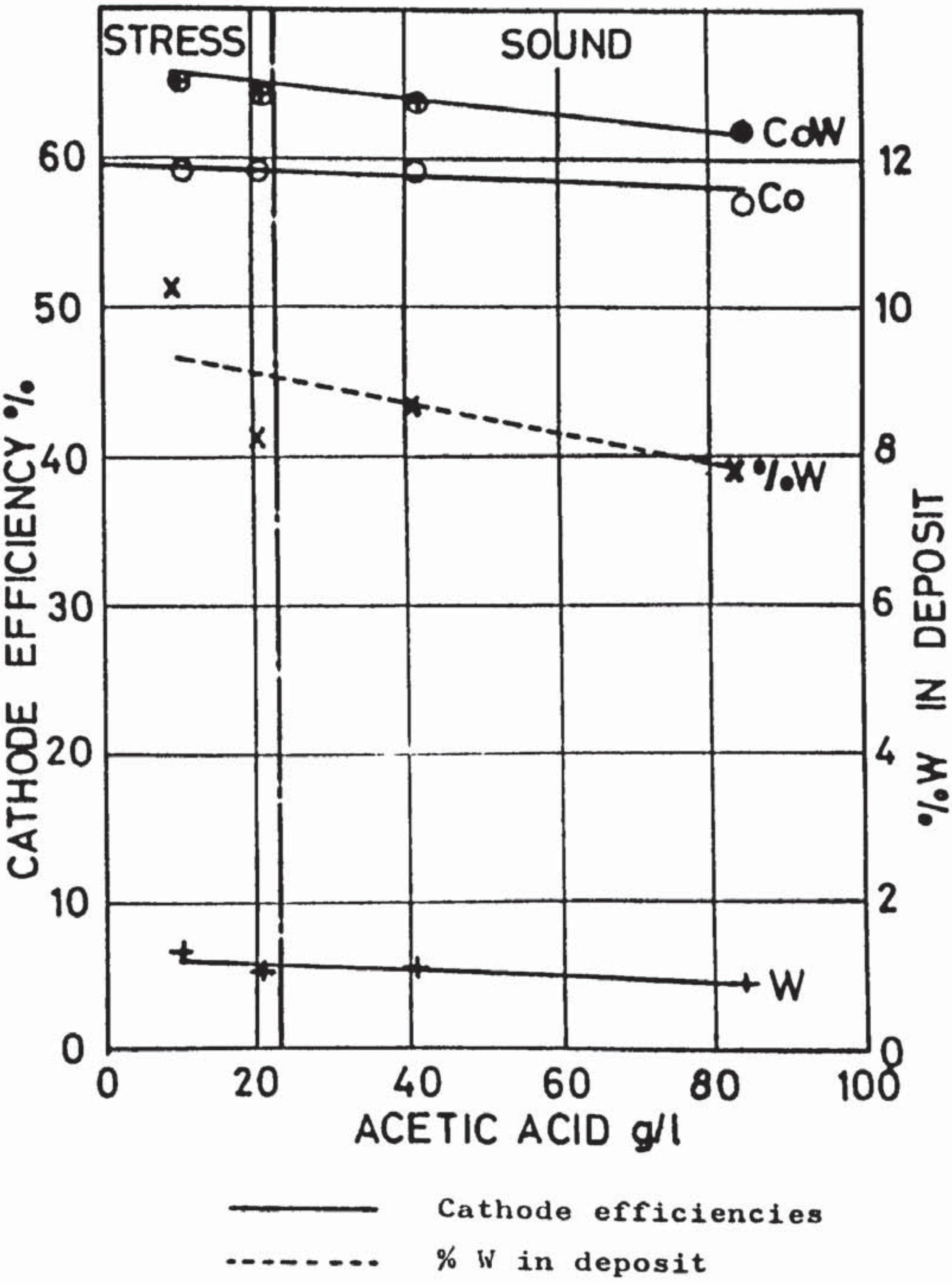


———— Cathode Efficiencies

- - - - - - - - % Mo in deposit.

Fig 56.

Effect of acetic acid on the partial efficiencies of cobalt and tungsten in the deposition of a cobalt-tungsten alloy.



complexing the alloying element than the cobalt. However, the plating trials carried out indicate that at least 21.0 g/l of acetic acid should be used in the electrolyte to prevent "burning" during the early stages of deposition. As a compromise between deposit quality and the percentage of alloying element incorporated into the deposit, 42.0 g/l of acetic acid was considered optimum.

The effect of applied voltage upon deposit composition and cathode efficiency are illustrated in Fig 23 and Fig 24 respectively. From the plot of % alloying element in deposit versus applied voltage, Fig 23, it can be seen that the behaviour of the cobalt-tungsten system differed from that of the cobalt-molybdenum. In the case of tungsten, a minimum occurs at 15V, but ultimately a constant value of about 11% is reached, whereas for molybdenum the percentage of alloying element rises up to 30V where the deposits produced contain approximately 9.5% molybdenum. Partial efficiencies for the voltage trials have been calculated, and presented in table XXV; the appropriate graphs illustrating these results are shown in Fig 57 (cobalt-molybdenum system) and Fig 58 (cobalt-tungsten system). An increase in applied voltage resulted in a considerable increase in the efficiency of molybdenum deposition, (Fig 57), hence although the efficiency of cobalt deposition was a maximum at 20 volts, the overall effect

## TABLE XXV

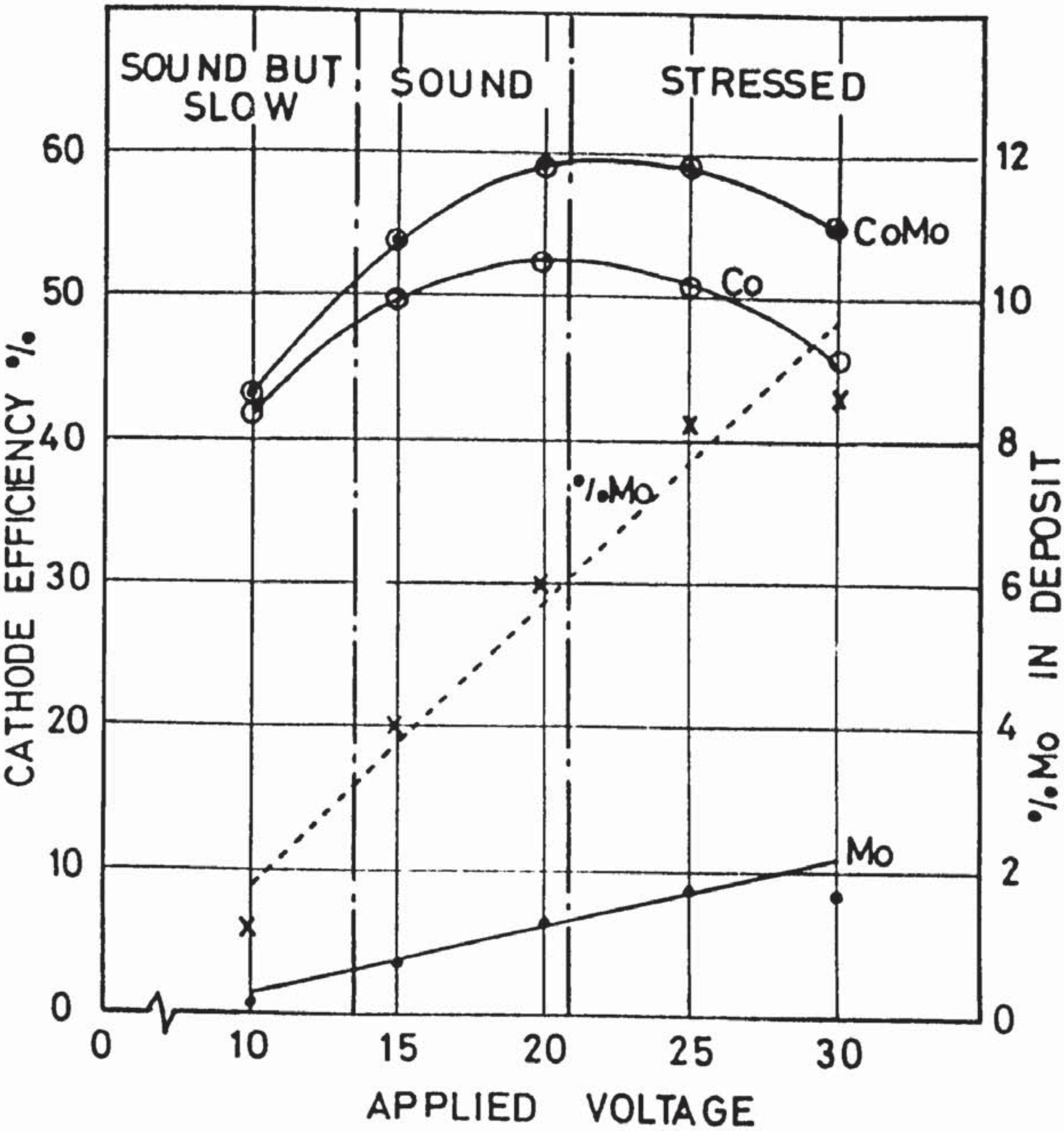
### Effect of applied voltage on the Partial Efficiencies of Cobalt Tungsten and Molybdenum.

| Applied Voltage | Partial Cathode Efficiency % | | Combined Efficiency % |
|---|---|---|---|
| V | Mo | Co | CoMo |
| 10 | 0.95 | 41.89 | 42.84 |
| 15 | 3.92 | 49.82 | 53.74 |
| 20 | 6.27 | 52.53 | 58.80 |
| 25 | 8.62 | 50.51 | 59.13 |
| 30 | 8.17 | 45.37 | 53.55 |

| Applied Voltage | Partial Cathode Efficiency % | | Combined Efficiency % |
|---|---|---|---|
| V | W | Co | CoW |
| 10 | 6.88 | 54.83 | 61.71 |
| 15 | 6.29 | 63.58 | 69.85 |
| 20 | 6.88 | 60.95 | 67.83 |
| 25 | 7.08 | 57.61 | 64.69 |
| 30 | 6.82 | 58.29 | 65.27 |

Fig 57.

Effect of applied voltage on the partial efficiencies of cobalt and molybdenum in the deposition of a cobalt molybdenum alloy.

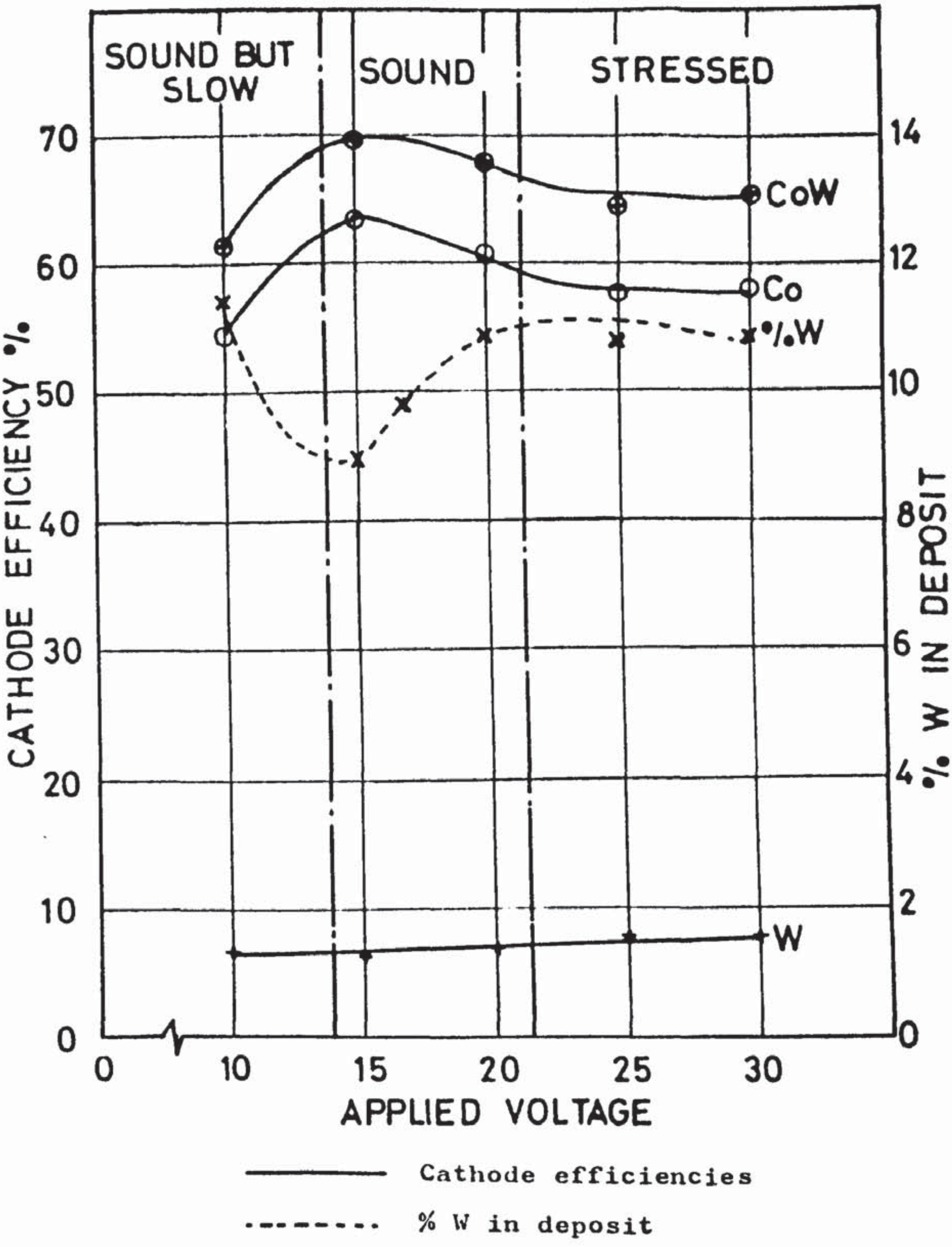


———— Cathode efficiencies

------- % Mo in deposit

Fig 58.

Effect of applied voltage on the partial efficiencies of cobalt and tungsten in the deposition of a cobalt tungsten alloy.



was a sharp increase in percentage of molybdenum incorporated in the deposit. Thus it can be concluded that in the cobalt-molybdenum system, increases in applied voltage appears to have a marked effect on the partial efficiency of molybdenum deposition, and this becomes evident in a greater percentage of molybdenum in the deposit. There is little effect of applied voltage on the partial efficiency of tungsten deposition (Fig 58). However a peak in partial efficiency of cobalt deposition at 15V resulted in the percentage of tungsten in the deposition falling to a minimum. Thus, consideration of the partial efficiencies of the two systems has shown that the variation in the percentage of alloying element in the deposits occurs for different reasons. The influence of applied voltage on the efficiency of tungsten deposition is minimal, whereas an increase in applied voltage greatly increases the efficiency of molybdenum deposition. Over the range 10-20 volts, sound deposits were obtained for both systems, although plating at voltages lower than 12 V resulted in lengthy periods of deposition being required to attain coatings of the desired thickness. In excess of 20 V, deposits became stressed, possibly due to heating effects. In practice, an operating voltage of 17 volts was adopted as it appeared the best compromise between speed of operation and deposit quality.

The effect of pH upon deposit composition and cathode efficiency has been illustrated in Figs 25 and 26 respectively. Increases in pH resulted in a decrease in the percentage of tungsten obtained in the cobalt-tungsten deposits, whilst the percentage of molybdenum in the cobalt-molybdenum deposits appeared to be independant of variations in pH. Fig 26 illustrates the effect of increases in pH upon cathode efficiency for both systems. From this, it can be seen that the efficiency of deposition of cobalt-tungsten and cobalt-molybdenum increases with increasing pH, an effect observed by Still(51) working on vat plated cobalt alloy deposits. The effect of pH upon the partial efficiencies of deposition of cobalt-tungsten and molybdenum have been calculated and presented in table XXVI. These results are shown graphically for the cobalt-molybdenum system Fig 59 and the cobalt-tungsten system Fig 60. From these figures, it can be seen that an increase in pH results in an increase in the partial efficiency of cobalt deposition for both alloy systems. This may be explained by the reduction in hydrogen ion concentration appropriate to high pH values, making hydrogen "liberation" less favourable. The efficiency of molybdenum deposition did not vary greatly with increasing pH, thus resulting in little change of the percentage molybdenum incorporated into the deposit.

## TABLE XXVI

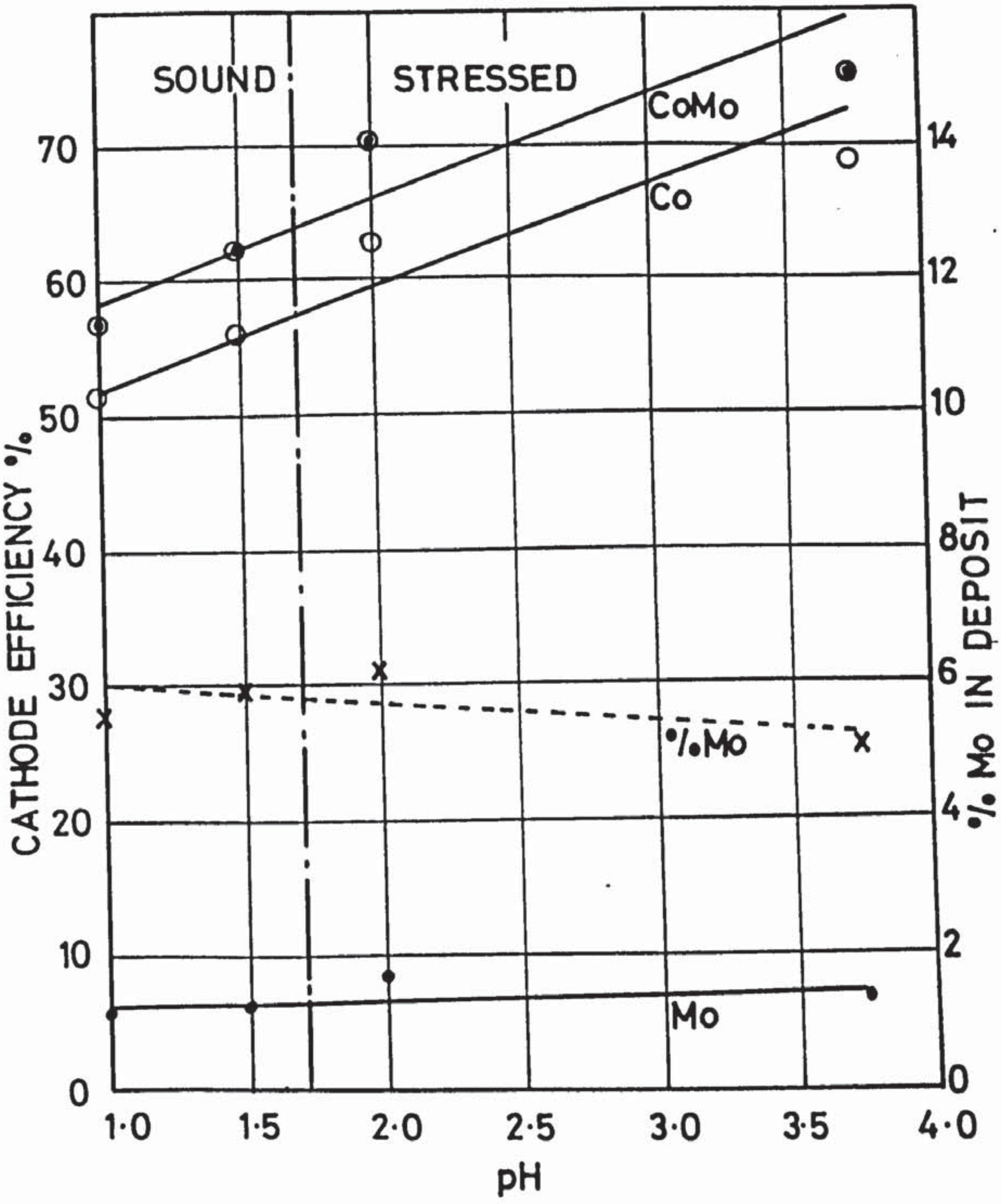
Effect of pH on the Partial Efficiency of Cobalt, Tungsten and Molybdenum.

| pH | Partial Cathode Efficiency % | | Combined Cathode Efficiency % |
|---|---|---|---|
| | Mo | Co | CoMo |
| 1.0 | 5.59 | 51.31 | 56.90 |
| 1.5 | 6.57 | 55.79 | 62.36 |
| 1.5 | | | |
| 2.0 | 7.83 | 62.76 | 70.59 |
| 3.75 | 6.71 | 68.54 | 75.26 |

| pH | Partial Cathode Efficiency % | | Combined Cathode Efficiency % |
|---|---|---|---|
| | W | Co | CoW |
| 1.0 | 6.70 | 59.77 | 66.48 |
| 1.5 | 6.21 | 62.08 | 68.30 |
| 2.31 | 2.07 | 79.57 | 81.65 |
| 3.02 | 1.79 | 81.75 | 83.54 |

Fig 59.

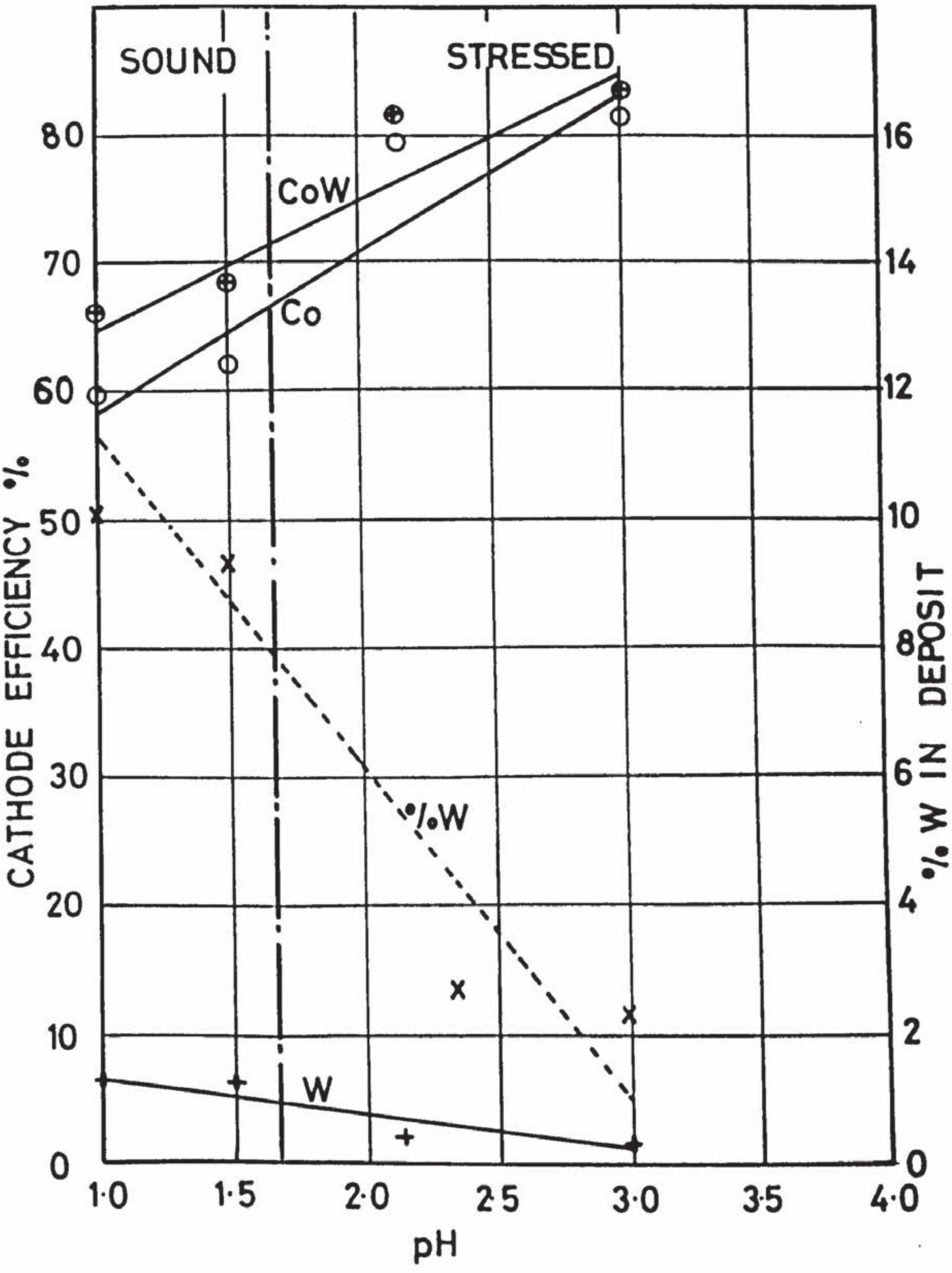
Effect of pH on the partial efficiencies of cobalt and molybdenum in the deposition of a cobalt molybdenum alloy.



——— Cathode efficiencies
- - - - - - % Mo in deposit

Fig 60.

Effect of pH on the partial efficiencies of cobalt and tungsten in the deposition of a cobalt tungsten alloy.



——— Cathode efficiencies

- - - - - - - % W in deposit

However, in the case of the cobalt tungsten system, the efficiency of tungsten deposition fell at pH values in excess of 1.5, and at this level of pH, the efficiency of cobalt deposition increased rapidly. The combined effect of this, is a rapid fall in the percentage of tungsten incorporated into the deposit on increasing pH. This difference in behaviour must in some way be associated with the difference in stability of the molybdenum and tungsten complexes at varying pH. Cobalt efficiency behaved as expected; it increased as the pH was increased.

In practice, pH values in excess of 1.5 were avoided as stressing of the deposits occured when using higher values.

The results of investigations into the effect of pressure upon deposition characteristics proved inconclusive. Variations in the pressure applied to the stylus during deposition appeared to have little effect on deposit composition or efficiency. However, the results of investigations into the effect of relative stylus speed showed a number of trends. Fig 27 illustrates the effect of relative speed upon deposit composition for the two systems. From this it can be seen that over the speed range chosen, the percentage of tungsten incorporated into cobalt tungsten deposits increased with increasing speed, whilst the percentage of molybdenum in equivalent deposits decreased. This again is evidence of a difference in fundamental deposition behaviour between the two systems. It is not clear why the effect of speed produces such differences, but it is considered that the lower operating voltage, and the range of speeds chosen are responsible for the relatively low levels of alloying element incorporated into these deposits. Over the range of speed chosen the cathode efficiency of deposition for both alloy systems increased with increasing speed. This appears reasonable, as increasing relative speed of stylus movement would increase the efficiency of disruption of the cathode film (section 3). It is assumed that the relatively low levels of cathode efficiency obtained in the "speed" trial was a characteristic of the speed range chosen, and increasing speed may improve cathode efficiency.

Hence by consideration of the various aspects of electrolyte development, table XXVII has been constructed to indicate optimum solution composition and operating conditions.

## 18.2 Coating Properties.

Comparison of the deposition characteristics of the developed cobalt tungsten electrolyte was made with a proprietary equivalent brush plating solution (Table XV). The developed solution was

# TABLE XXVII

## Optimum Composition and Operating Conditions of Brush Plating Cobalt Tungsten and Cobalt Molybdenum Electrolytes.

### Composition

| | |
|---|---|
| Cobalt Sulphate | 500 g/l |
| Sodium Heptonate | 200 g/l |
| Glacial Acetic Acid | 42.0 g/l |
| Sodium Molybdate (Tungstate) | 50.4 g/l |

### Operating Conditions.

pH 1.5

Applied Voltage 17 - 20V.

slightly more efficient than the conventional one and gave a higher tungsten content in the deposit. It was of more importance that the commercial solution had to be operated at 11v whilst the developed solution was used at 17v. This resulted in a particular thickness being deposited much more quickly by the latter solution. The use of a nickel flash was recommended by the supplies prior to deposition of the proprietary deposit but was not used in this instance. Both composition and cathode efficiency appeared to be dependent on the substrate; as the efficiency of the developed solution decreased, the tungsten content increased. The variation in results for identical plating tests was much greater in the case of the die steel substrate than for brass. The brass and steel substrates were much thinner than the die steel but there were no other deliberate differences in experimental conditions. However, this could have affected the temperature of the solution in contact with the workpiece; as under brush plating conditions, the electrolyte can boil.

This series of plating trials confirmed that precise control is difficult when using brush plating to obtain alloy deposits of the induced codeposition type. The variation in these results should be bourne in mind when considering other results of brush plating trials reported in this work. The transmission electron micrographs of the brush plated deposits (Figs 29 and 30) showed them to possess an extremely fine grain size. However bath electrolytes incorporating sodium heptonate as a complexing agent have been shown to produce cobalt molybdenum and cobalt tungsten deposits of a similar fine grain size (107). The high current densities involved in brush plating may also contribute to this situation, as considerable energy is available for the nucleation of a large number of small grains.

Surface topography of brush plated deposits appears to depend to a large extent on the topograpgy of the underlying substrate. Scanning electron micrographs of 13µm thick cobalt molybdenum and cobalt tungsten deposits on brass (Figs 33(a) and 33(b)) reveal that the deposit has retained the smooth surface of the brass substrate. Deposition of the same thickness on to a grit blasted die steel substrate resulted in nodular deposit. The sharp angular asperities of the grit blasted surface (Fig 32(a) and 32(b)) appears to provide high current density regions, resulting in the nodular form of the deposit. However, brush plating on to a grit blasted surface gives an overall "smoothing" of the surface resulting in the "silky" feel of the deposits noted in Section 16.5. This effect is apparent in the rest of results concerned with surface roughness of brush plated deposits shown in Table XVIII. Hence, it can be seen that the surface roughness of a 320 grit abraded substrate is slightly increased from 0.45 to 0.75µm C.L.A by the action of brush plating. This may be explained by the formation of a nodular deposit on the asperities produced by abrading the surface. These surface roughness determinations also reveal that on brush plating a grit blasted surface having an initial roughness of 1.1µm C.L.A, the surface is smoothed to 0.8µm C.L.A: but on further brush plating the surface roughness increased to 0.9µm C.L.A. Initial smoothing may be explained by the formation of a nodular deposit having a lower surface roughness than the substrate. The subsequent roughening upon further deposition may be explained by growth of the deposit perpendicular to the cathode as illustrated in Fig 2.

The majority of the scanning electron micrographs of the brush plated deposits all provide evidence that the deposits are cracked. However, it should be noted that even under the extremely arduous conditions of hot forging, there was no evidence to suggest exfoliation of the deposits caused by poor adhesion or high internal stress.

Fig 37(b) shows a scanning electron micrograph of one such severely abraded area, where some of the coating has been lost due to erosion and scoring, but adhesion has remained satisfactory.

Table XVII presents the effects of deposit composition upon microhardness for deposits from the develqped cobalt tungsten electrolyte; together with results on brass for deposits obtained from a proprietary cobalt tungsten electrolyte. There appeared little correlation between percentage of tungsten in the deposit and microhardness, for individual results, but the mean values indicated that microhardness increased with increasing tungsten content. The hardness of deposits obtained from the proprietary electrolyte was lower at 673 VPN compared with 777 VPN for deposits obtained from the developed electrolyte on equivalent brass substrates. Maximum hardness of 807VPN was exhibited by deposits from the developed cobalt-tungsten electrolyte on die steel substrates. This coincided with the maximum tungsten content of 12.03%.

## 18.3 Laboratory Scale Wear Tests.

The results of pin and disc wear measurements indicate that a marked reduction in wear rate of the pin may be brought about by the application of a brush plated cobalt alloy deposit (Table XIX). Tests on untreated H 13 wear pins resulted in a measured wear rate of $9.1\times10^{-7}$mm.cm$^{-1}$ compared with $3.8\times10^{-7}$mm cm$^{-1}$ for the cobalt-tungsten treated pin. All tests were carried out with pins running against EN31 steel discs. Dynamic coefficient of friction was also greatly reduced from 0.77 in the case of the untreated pin, to 0.38 and 0.39 for the cobalt-tungsten and cobalt-molybdenum deposits respectively. The wear performance and friction characteristics of C.P.H cobalt and F.C.C cobalt alloys have been studied by Huppman and Clegg(103) and Buckley(104). These workers have indicated that the wear and friction performance of C.P.H cobalt is superior to F.C.C cobalt and cobalt alloys. Coefficient of friction determinations carried out on cobalt and cobalt-iron alloys agree with the values determined for the brush plated cobalt molybdenum and cobalt tungsten deposits used in this work:-

| Material | Crystallographic Structure. | Coefficient of Friction. |
|---|---|---|
| Co | hcp | 0.38 * |
| Co 8% Fe | fcc | 0.80 * |
| Brushplated CoMo | - | 0.39 |
| Brushplated CoW | - | 0.38 |

* Results from Huppman and Clegg(103) (Rubbing against SAE 4620 steel 58-60Rc)

At higher applied loads and speeds, Buckley noted a rapid degradation in wear and friction performance of cobalt corresponding to the allotropic change from CPH to FCC. Testing a cobalt-25% molybdenum alloy under equivalent conditions resulted in little change in wear and friction behaviour, suggesting that the CPH structure had been stabilised at elevated temperature. Although little information was obtained from X-ray data on the structure of the brush plated cobalt alloys produced in this work, it would appear reasonable to assume that under the chosen load and speed conditions, these alloys exhibited C.P.H. wear and friction behaviour.

The results of the simulated hot forging tests indicate that considerable improvements may be obtained in wear performance, by the application of 13µm of the cobalt-molybdenum or cobalt-tungsten brush plated deposits developed in this work (Table XXI). Evaluation of an untreated No 5 die steel set resulted in a wear volume of $4.37 \times 10^{-3} cm^3$ being recorded, whilst equivalent figures for dies treated with 13µm of cobalt-molybdenum or cobalt-tungsten were 1.01 and $1.69 \times 10^{-3} cm^3$ respectively. These results compare favourably with those reported by Still for the same test upon 75µm thick cobalt-molybdenum and cobalt tungsten bath plated coatings. In this work, results were recorded in the range $0.55 \times 10^{-3} cm^3 - 5.27 \times 10^{-3} cm^3$ a marked lack of mill scale retention also being noted. The three die sets coated by brush plating from the proprietary electrolytes COW, NiW and NiCo all gave

disappointing wear results of 9.17, 9.57, and $5.98 \times 10^{-3}$ respectively.
However, the most unsatisfactory aspect of results observed for the commercial deposits was their ability to retain mill scale. Whether this was due to the surface properties of the deposits, or mechanical keying caused by breakthrough of the coating is not known.

The scanning electron micrographs of the die brush plated with 13µm of cobalt molybdenum illustrate the level of adhesion attained by this technique. There was little evidence of poor adhesion even on areas of the die which had experienced severe abrasion and metal movement.(Fig 37(b)). Examination of the central area of the worn die indicated that considerable flattening of the nodular deposit had occured during forging (Fig 35(a), Fig 37(a)). In this area of the die there is little relative movement between billet and die surface but high compressive load, and mechanical deformation of the nodular deposit can occur. Close examination of Fig 37(a) reveals that the high degree of scoring typical of the "wear ring" has not occured in the central plateau region.

## 18.4. Industrial Trials

The results obtained from the industrial trials outlined in sections 17.3 and 17.4 have shown that

the life of hot forging dies can be increased by 20-100% and that the down-time due to pick-up can be reduced significantly in the case of press-tools. It is also apparent that the coating system is capable of being used on a variety of substrates ranging from the various hot-work alloy steels used in the forging industry to the low-alloy steels and cast irons used for press tooling. In addition to this capability the system is also able to cope with the various weldments used for die repair.
This aspect is particularly important in the case of automobile press tools as these not only contain welded repairs but also include areas which have been built up by welding to accomodate design changes. Although only a small number of press tools have so far been tested each of the dies plated contained welded regions, including the cast iron die (Fig 5(a)), none of which caused any plating problems.

The exact mechanisms by which the coating extends the die life is not known. The cobalt alloy deposits have a lower erosion rate than No 5 die steel. However, even with a 75µm thick coating, the life of an industrial forging tool would only be increased by 10-15% by this means, instead of up to 100% as found in practice. The similarity between improvements in die life obtained with 75µm thick vat plated deposits and 12µm thick brush plated deposits suggest that erosion rate is not the main criteria governing die life. It seems likely that the film may act as a solid lubricant on the die surface. Pin and disc measurements show that the brush plated Co-Mo and Co-W deposits have a dynamic coefficient of friction of 0.38 and 0.39 when running against EN 31, as opposed to 0.77 for untreated H 13 tool steel. There have been reports of reduced sticking of the workpiece to the dies, and of plated dies having much less tendency to retain impacted scale from the workpiece. In one case, it was possible to reduce the forging temperature employed due to the ease of flow of the metal over the die surface.

Solid lubricating films tend to be very thin, of the order of 0.1 - 1μm(73), and so presumably the excess alloy deposit is eroded at the normal rate until an optimum minimum thickness is reached. This prevents further erosion until breakdown of the film occurs, at which point normal wear of the die steel commences. The delay in the onset of wear of the die steel may also allow the 'bedding in' of the die which would have a beneficial effect on the die life.

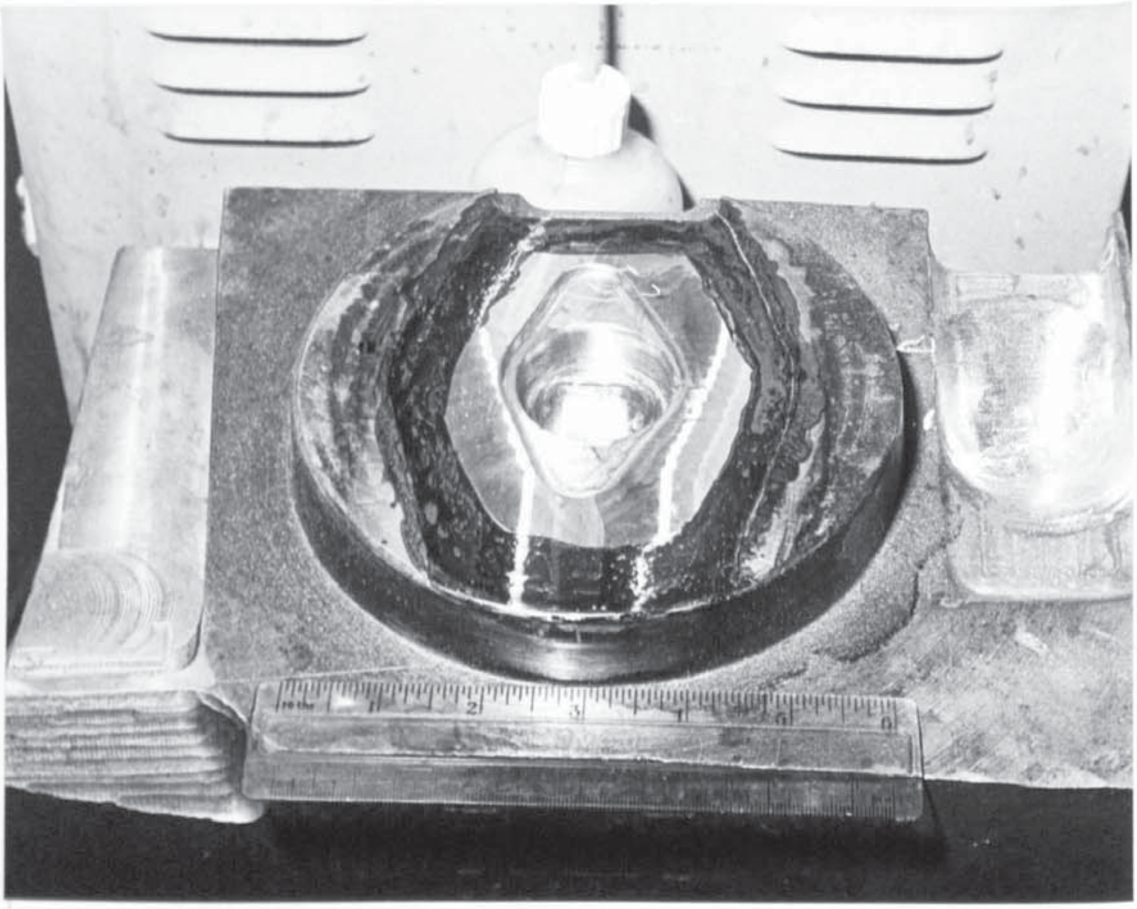
This lubrication effect should also be useful in the cold pressing of steel, but in this case a more important effect is the reduction in the tendancy for cold welding, which leads to pick-up on the die surface and scoring of components. Almost any coating will help to reduce the tendency of steel to weld against itself as it will reduce the mutual solid solubility of the workpiece and the die, but cobalt alloys are especially useful, as only 5% iron will dissolve in cobalt at 200°C(105). The addition of molybdenum to the cobalt will help to reduce pick-up still further, as it too has a low mutual solubility with iron(106).

The possible cost savings which can be obtained using this coating system are best illustrated by two specific examples. The forging die shown in Fig 61 normally produces approximately 2,000 forgings and might cost between £200 and £300 per pair, giving a direct die cost per forging of about 10-15 pence. The cost of brush plating these dies would be about £30-£40, and even if this increased the life of the die by only 30%, there would be a saving in the direct die cost per forging of 10%. If the die life is increased by more than 50%, as it was in this case, the saving may amount to 5% of the final selling price of the forging. This does not take into account any savings from the reduction in down time which may be achieved.

The cost savings obtained in the case of press tooling are much more difficult to assess as this involves an accurate costing of the 'down-time' saved. However, if we consider the die shown in Fig 48 the 'down time' saving on two production runs

Fig 61.

Drop forging die used for producing suspension and sockets for cars.



was reported to average $1\frac{1}{2}$ hours per die. It should be stressed that this figure represents time actually 'booked' for die repairs and does not include 'run-down' or 'start-up' time. The actual figure is therefore likely to be several times greater than this. If for the purposes of this excercise it is assumed that the cost of down time, including lost production, is of the order of £400 per hour then the minimum saving is equivalent to £600 per die.

The plating cost for this die was £150. There is therefore a direct cost saving of £450 per die plus the additional advantages to be gained from improved continuity of production.

From these examples it can be seen that significant savings can be made in both the forging and press tool industries, and it is considered that this coating system is a valuable addition to the growing number of surface treatments becoming available to die and mould users.

In addition to the industrial trials carried out on hot forging dies and cold pressing tools, there have been a number of requests for the application of brush plated deposits to solve specific problems. The most successful example of this being the cobalt alloy plating of dies used in the aircraft industry in an attempt to eliminate the nickel plating of the forging blanks.

Tools used for the industrial processing of molten glass have also been plated. This requirement for the application of brush plating for a wide variety of industrial uses endorses the potential of this on site technique of electrodeposition.

## 19. CONCLUSIONS

1. New brush plating electrolytes have been developed which enable cobalt alloys containing approximately 6% Mo or 8% W to be deposited at 17-20V. To the authors knowledge, there is no commercially available brush plating electrolyte for the deposition of cobalt molybdenum alloys; however the developed cobalt-tungsten electrolyte was compared with a proprietary equivalent. The performance of the developed cobalt-tungsten electrolyte (whose composition can be found in table XXVII) proved superior in many respects. Whilst capable of being used at higher operating voltages, the electrolyte developed in this work proved marginally more efficient, and the deposits produced were more highly alloyed and exhibited significantly greater wear resistances. Higher operating voltages resulted in a specific deposit thickness being attained over a much shorter period of time than possible at the 11V operation of the proprietary cobalt tungsten electrolyte.

2. The portability of the brush plating technique has been demonstrated. During industrial trials, almost all of the dies treated were plated in the tool-room or forge. Both extremely large forging dies and very small extrusion dies were plated, illustrating the versatility of the process. The

use of the polypropylene-nylon felt mixture for stylus covering proved an extremely important development, as covering materials used prior to this were not sufficiently durable to be used on die surfaces.

3. The cobalt deposits produced in this work possessed a mixed crystallographic structure of F.C.C and C.P.H at room temperature. X-ray diffraction techniques failed to positively identify the crystallographic structure of the alloy deposits produced, although their extreme wear resistance suggested a C.P.H structure. Brush plated cobalt alloy deposits exhibited a low coefficient of dynamic friction of 0.38 when running on tool steel, compared with a typical value for steel on steel of 0.8. The hardness of the brush plated cobalt tungsten deposits produced in this work had a mean value of 770 VPN compared with 670 VPN for the "proprietary" cobalt tungsten deposit.

4. Optimum wear performance of the brush plated cobalt alloy deposits was attained at coating thickness of 13µm. Hence there is some evidence to suggest that the coating may be acting as a solid lubricant under hot forging conditions.

5. Industrial trials have shown that considerable increases of between 20-100% in the life of hot forging dies may be obtained by the use of brush plated cobalt alloys. In the case of cold pressing tools, "down time" was significantly reduced due to the reduction in metal pick up on the die.

6. The application of brush plated cobalt-alloy coatings may give additional benefits in the case of hot forging. Lower forging temperatures, improved forging quality and lower retention of mill-scale have also been reported. The lubrication effect of the deposit has also been demonstrated in the pressing of "difficult" car body panels without lubricant.

7. A large commercial concern is using the electrolytes developed in this work to enable the forging of nimonic alloys to be performed without the need to nickel plate and subsequently strip each individual blank.

8. This work has been concerned with the brush plating of cobalt molybdenum and cobalt tungsten alloys. These systems being of the induced co-deposition type have complicated the understanding of the mechanisms involved in brush plating. It is a process that is difficult to control as boiling of

the electrolyte frequently occurs and current densities rapidly vary from 0-200A/dm$^2$. Hence variability of results is high, and an understanding of many aspects of brush plating cobalt alloy deposition is not complete. However sound deposits can be obtained which are sufficiently consistent for commercial use.

9. Variations of plating parameters illustrated significant differences in the behaviour of the cobalt-molybdenum and cobalt tungsten systems. This is almost certainly due to differences in the nature and stability of the molybdenum and tungsten complexes.

# 20. SUGGESTIONS FOR FUTURE WORK

The results of the industrial assessment of brush plated cobalt alloy coatings show the technique of brush plating to be a potentially valuable method of coating application. This investigation into the deposition of cobalt alloy coatings by brush plating arose due to the desire to coat large metal working tools "on site" with these alloys. Consequently the fundamental work carried out was complicated severely by the use of an induced codeposition system of an unpredictable nature. A most important aspect of future work would be to investigate the technique of brush plating whilst concentrating on single metal deposition. For example, the study of brush plated nickel with respect to variations in voltage, pH, electrolyte composition, current waveform, speed and pressure would yield fundamental information, as yet unavailable.

A fundamental study of molybdenum and tungsten complex formation with sodium heptonate and similar complexants such as gluconate is also desirable.

A further aspect concerns the use of the developed cobalt alloy deposits in wear environments other than hot forging or cold pressing. These are extremely arduous operations, and the use of cobalt alloy deposits in less demanding conditions for example upon "machine bearing surfaces" may prove worthwhile. Little work has been carried out upon heat treatment of these alloy coatings, and its effect upon wear resistance.

Brush plating in this work was concerned mainly with the application of wear resistant coatings, but electrolytes are commercially available suitable for the build up of worn components and decorative purposes. The degree of thickness control possible during brush plating allows build up of a worn component with little re-machining. An investigation into the use of appropriate electrolytes for metal build up, or decorative purposes would be advantageous.

# 21. ACKNOWLEDGEMENTS.

The author wishes to thank the Science Research Council for providing financial support for the work carried out. The author also wishes to thank the academic and technical staff for their constant support throughout the project.

In particular the author wishes to thank his supervisor Dr.J K Dennis for his guidance throughout the work, and Dr K Lodge and Dr. F Still who gave considerable guidance during the early stages of the project.

Finally, thanks must also go to the 40 or so collaboratory companies without whose assistance the industrial trials could not have been carried out.

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