

PROCESS AGITATION: FROM AIR BUBBLING TO EDUCTOR JETTING.

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SYNOPSIS

Agitation has always been recognised as a necessary parameter for electrodeposition. However since its inception in 1840 the purpose has changed from avoiding stagnation to increasing production rates and quality properties of the deposit. Consequently the mode of agitation has changed substantially.

The methods and purposes of agitation are discussed and related to the enhanced characteristics achieved and the disadvantages which may arise.

INTRODUCTION

When electroforming and electrodeposition were invented in 1839-1840 the chemical and physical principles involved were only superficially understood. The main consideration was in fact to find a soluble form of gold and silver which was solved in the UK by a medical advisor to Elkingtons recommending cyanides. But within a very short time some enhancement took place: chemically by using higher concentrations of metal, alkali as pH stabiliser and excess cyanide to dissolve the anode; physically by increasing temperature a little and stirring to avoid stagnation and disperse evolved gases. The stirring was not electrically driven (motors not yet invented!) but mechanical and human. Once a motor was available – from about 1857 – the rotary stirrer became possible and soon after a motor driven cam to offer reciprocating motion in solution including beaters or of the cathode busbar itself. Air bubbling or sparging was a much later method and required some type of pump or piston. Textbooks of that time made a number of suggestions including striking the busbars occasionally in order to remove stratification of solution and maintain homogeneous solution; doubt existed as to whether it need be constant, regular or frequent. This position remained until well into the 20th century although some optimisation was attempted for air bubbling, eg. air flow and pressure, pipe holes etc.

In the period 1915-1930 the expansion of first nickel and then chromium plating was accompanied by the use of air agitation but the next major step was with tin and zinc plating of steel wire and sheet/strip. At first operated as a batch process, continuous movement as multiple wire or single strip strands in the bath became standard by 1935-8

with the obvious bonus of movement allowing much higher current densities to be employed. Furthermore, use of flow baffles created turbulence and a new realm of agitation had arrived. By 1950 other developments in for example electronics production led to reel-to-reel plating, selective plating by brush or jet, and electroforming as a regular production technology had caused agitation to be a major consideration. Perhaps the peak came in the 1970s when world record deposition rates were claimed, to be disproved after a notorious series of papers and patents were exposed and a more serious aspect of composite deposition developed out of apparently sordid 'dirty plating'.

A recent lecture and demonstration [1], which discussed agitation as an under-exploited degree of freedom in surface finishing, created considerable interest and this fuller more practical review has been written in response to that interest.

THEORY FOR AGITATION.

Agitation needs to be defined or at least characterised at the outset. For this reason it is important to distinguish between **solution mixing** and **interface agitation**. Mixing relates to the bulk solution and is particularly appropriate to ensuring homogeneity in solution, dispersing gases and perhaps mixing in additions to the electrolyte. Mechanical stirring and air bubbling are effective in this context. Interface agitation is directed at the electrode/electrolyte interface to reduce diffusion layer thickness and deliver or remove reactants and products from the reaction zones of both cathodes and anodes. Cathode motion and jetting are most effective in this category. If possible the stirring or agitation should be quantified to make systematic or standard practice possible.

It is now well-known that there are five reasons why agitation is vital in electrodeposition.

- To avoid stagnation and to disperse products and reactants, ie. avoid stratification. This arises firstly because as metal is deposited from solution to the cathode surface solution is depleted and unless it is replenished deposition will slow up and become granular. It is known that the change in density will promote natural convection but this is slow and upwards and insufficient to promote fast replenishment.
- To increase deposition rates. At higher currents the deposition is limited by a surface diffusion layer through which ions have to diffuse from bulk solution to the electrode surface for discharge by electrons. While increased temperature will increase diffusion rates the effect is relatively small. Agitation which thins that layer is much more effective and turbulence can reduce it by 10-100x giving a corresponding increase in deposition rate.
- To dissipate heat from the electrode/electrolyte interface. The energy of deposition overpotential is manifest as interfacial heating. Thus the deposit forms at a temperature above that of the bulk solution which is what can be controlled. Good stirring helps to maintain equilibrium and uniformity. In the case of anodising, the anodic film acts as a resistive thin film heater and great amounts of heat are generated making agitation much more vital.
- To incorporate particles in the coating – composite plating. In this case turbulence is counterproductive because it discourages particle incorporation in the deposit.

Consequently, a different approach is needed to encourage particle buoyancy and suspension by using pulsed or vibratory agitation, and by making the solution more viscous by using slurries or viscous agents.

- To modify or control deposit properties. The mechanical properties include grain size, internal stress, hardness etc but may include also throwing power and deposit distribution.

Diffusion theory relates to the high current density techniques required for high speed electrodeposition and is based on Fick's Law of diffusion adapted for electrochemical usage by Nernst. It relates the maximum or limiting current density j_L to the Faradaic equivalence for ion discharge nF , where n is its ionic valency and F the Faraday constant, the concentration difference of discharging ions between the bulk solution and the interface which is effectively the bulk value C_b at its limit, D the ion diffusion coefficient, the transport number for that ion t_+ and the diffusion layer thickness δ .

$$j_L = (n F C_b D) / \delta (1 - t)$$

Clearly to maximise J_L each of n , F , C_b and D must be large, δ and $(1 - t)$ small.

The effect of agitation is expressed through δ which is minimised by its focussed or directed use. This immediately demonstrates that solution mixing is not the best approach but any movement designed to break-up the diffusion layer will be.

In some instances this simple equation is too simple; for example, if temperature is introduced as a parameter to increase D , or if C_b is increased the viscosity will change. In order to rationalise these additional variables dimensionless group analysis can be used whereby the velocity of agitation is described by a Reynolds Number Re and the limiting current density by a Mass Transport Sherwood Number Sh . It is for such reasons that J_L is only approximately proportional to C_b or D but the error is small enough for the equation to be used in many practical calculations.

Dimensionless analysis shows clearly that creation of turbulence offers much more effective agitation. This can be by either using very high agitation in which turbulence develops naturally or by inducing turbulence by use of turbulence promoters such as rough surfaces or flow baffles which break up smooth laminar flow and induce eddies to form at the electrode surface (fig.1). Thus process design can be critical in ensuring either laminar or turbulent flow according to the process needs.

The effect of agitation can be directly measured through a determination of δ which unfortunately is difficult. A number of techniques exist from layer freezing and analysis to optical interferometry none of which is easy. Consequently an indirect comparison technique is desirable. The simplest one is to measure the limiting current density attained or the current density for a given deposit property or characteristic: brightness/roughness/hardness. By assuming that an unagitated solution is 1 ratio of currents will give an agitation enhancement factor EF which gives a good practical comparison. Typical ranges of values are as below.

No agitation	$EF =$	1
Cathode reciprocation		2
Mechanical stirring		2-10
Air sparging		2-6
Cathode motion (wire/strip plating)		4-20

Vibratory agitation	3-25
Jetting and eductor impingement	5-30

Clearly most electrodeposition processes are driven by a market need to produce good quality finishes and consequently limiting current values are not employed in practice because of the tendency to produce rough dendritic or powdery deposits. Good deposits are produced at a specific current density ratio i/i_L which is constant for a given metal, solution concentration, temperature etc. As agitation is increased, i_L increases and so does the value of i the practical deposition current density. As it is possible to determine the critical i/i_L ratio for any process solution the effect of agitation can be quantified – hence the credence of EF values..

CATHODE BAR RECIPROCATION

Perhaps the simplest of all mechanical agitation is reciprocating movement of the cathode busbar. Its use today has hardly changed since 1860 and consists of slow movement through 5-50cm of the bar in the direction of its length with a cycle time of 5-20sec. Any faster movement causes the jigs to swing too much, thereby affecting throwing power, and the movement is achieved with a small motor and offset cam device (fig.2). Such a cam can also raise and lower a hinged baffle plate at the bottom of the tank and this causes solution waves to form and turns out to be useful for composite plating. Similarly, reciprocating paddles have been used and have curiously been most investigated. The resulting agitation is small and invariably laminar so it is consequently the least effective (EF = 1.5-3) method although it is simple and still used for low technology decorative applications and operations where throughput is necessarily slow representing 1-2% of all installations [2]. The agitation attained is not easily increased because of the risk of electrical shorting if jugged work swings too much in solution.

MECHANICAL STIRRING

Although referred to as mechanical stirring it is invariably driven by electric motors of variable speed, this being usually regarded as the convenient main variable for control. However, other important parameters include stirrer propeller design, and position and angle of the propeller blades. For this reason the best performance is often not achieved from such agitation methods.

It is important to make a distinction with rotating electrodes, eg. rotating discs, rotating cylinders etc., which are important but different concepts [3]. Here the rotation is indirectly stirring because the main purpose is to promote shear motion at the electrode surface/solution interface thereby attaining thin diffusion layers and high current passage. Because it is usually quite impractical to rotate work being electroplated on jigs there is no general application in finishing technology except for laboratory electroanalysis instrumentation, process simulation and metal recovery from dilute effluents where commercial devices have been successful.

In recent years a large number of propeller designs have emerged (fig.3), often derived from propulsion considerations, in which the blades are set to drive solution motion in the tank and to create turbulence by shear action [4]. The importance of this requirement can

be seen by a simple experiment in which a central vertical stirrer shaft is placed in a cylindrical tank and rotated. Solution will tend to swirl around the tank with little or no internal mixing, the flow is laminar, and the best interfacial agitation is at the tank wall. However, if jiggled work is placed in the tank it acts as a baffle and immediately increases the general agitation. Further, if the shaft is placed at an angle, or better still two shafts placed at opposing angles the rotational flows interact with each other and the work and tank wall with marked improvement in general agitation. Such shear action is especially effective in mixing slurries and pigment suspensions, hence its standard use in paint production where particles may have spontaneously agglomerated; any application in preparing composite plating solutions is obvious. Thus mechanical stirring should not be dismissed but observed carefully and adjusted before deposition is attempted to maximise observed turbulence: such an approach can at least double the agitation achieved. The other recent advance is in propeller design. While such stirring is usually thought to be essentially solution mixing by use of shear blades the turbulence can extend or be directed towards the electrode with significant increase in electrode agitation (see fig.3). This has been particularly effective in some anodising installations where heat removal is vital for consistent hard anodising. It has also been claimed that because its energy requirement is not high it may be more energy efficient than eductor jetting but no good quantitative data has been published.

AIR BUBBLING

The origin of air bubbling or sparging in electrodeposition is not readily found but one possibility is that it came from electrowinning operations where froth flotation technology has long been practiced. However, nowadays this is where it is not where it is used because of the obvious tendency to disperse sludges and oxidise solution constituents. It is true that gases can be evolved at both cathodes and anodes (usually hydrogen and oxygen respectively) but the amount of agitation created is trivial for reasons that will be discussed later.

The attraction of air for agitation is obvious – it is free! However, the first rule is that it must be oil-free thus setting the first and most important requirement in pump selection. The common use of anode bags has minimised sludge problems in functional electrodeposition, in contrast to electrowinning and electrorefining where the sludge can be voluminous and is a vital economic product containing as it usually does valuable impurities such as the precious metals silver, gold or platinum. The disadvantages of air agitation are that it raises the electrical resistance of the solution – this will be discussed later – and can oxidise solution constituents which may well increase the sludge production. One or two notable examples exist for such deleterious oxidation: transition metals having several valency states such as tin in its lower stannous state which often demands no air agitation, or cyanides which are slowly lost from solution forming carbonates for which a subsidiary processing schedule for their removal has been devised (ie. use of sodium rather than potassium salts, exploiting the relative insolubility of carbonates by freezing them out of solution).

The air pressure and flow rate are related to the length of pipework and the tank size; they must be sufficient to maintain a good flow of bubbles from the perforated pipe at the bottom of the tank. Much more critical is the hole size in the pipe. A typical air supply specification might be:

Pipe material	PVC or polypropylene
Pipe diameter	18-32 mm (3/4 -1 1/2 in)
Hole diameter	~3mm (1/8 in)
Hole spacings	10-15 cm (4-6 in)
Compressed air	0.15 - 0.2 kg/cm ² (2.5 psi)
Air volume	0.2 – 0.45 m ³ per m ² of tank surface

The air ring, placed 2 cm above the tank bottom and ~5 cm in from the tank walls, should ideally be fed from two points and for a big tank two pumps supplying oil-free air may be used (fig.4). The holes should not be placed on the top of the pipework but on the side otherwise the air may stream directly upwards. These parameters can be expressed graphically.

The motion of the air has been studied using high speed photography and clear solutions. The bubble emerges from the hole and grows to a size which depends on the hole size, air flow and pressure, and the surface tension of the solution. It rises still attached by a stem, then breaks away as a hemi-spherical cap and rises up growing as the hydrostatic pressure decreases and as it may unite with colliding bubbles (fig.5). If it is too big it may emerge 'explosively' and rise without causing large agitation; if it is too small it forms a fine stream; if it is ejected from the sides of the pipe it has lateral motion as well as upward motion and cause agitation in a larger volume of solution: this has been studied by using a single hole and observing the effect of a single bubble stream. The large surface area ensures that it is saturated with moisture and contains dissolved ions, hence the eventual polluting mist. Agitation is produced by turbulent eddies in its wake and by low velocity eddying in the tank (fig.6). When the bubble reaches the meniscus surface it first merges with any foam layer but more usually its upward velocity/momentum causes it to break through the meniscus and explode into the air above the solution surface releasing the solution it is carrying to form the polluting spray (fig.7).

As a general rule then, small bubbles produce more agitation than large bubbles but very fine bubbles are less successful. However, there is little definitive research evidence for this observation.

If the air bubble motion is carefully watched the pattern of agitation can be seen [5,6]. It is recommended that after installation and before any electrodeposition is attempted this behaviour is studied and adjustments made to try to ensure the uniformity of agitation in the tank in relation to the jugged work positions. It should also be noted that as local agitation varies throughout the tank, notably on a wall-centre-wall and bottom-middle-top basis (this can be seen in thickness distributions for analogous positions on big jigs or on a printed circuit board) there are production implications which need to be corrected at the time of installation (fig.8). Anecdotal evidence suggests that this procedure is rarely carried out!

When air is bubbled through a solution it creates a two-phased fluid which can be termed a foam. In this fluid the air content is usually 20-30% by volume and the solution is the continuous phase. The consequence is that because air is essentially insulative the conductivity of the solution is reduced by an amount similar to the volume fraction (7-9). Thus a 30% volume fraction reduces conductivity by **about** 30% (fig.9). The

approximation is important to note because the exact amount depends upon several factors notably the agglomeration of bubbles forming double or triple bubbles and the tendency of bubbles to expand as they rise in the tank and the hydrostatic head diminishes thus changing the volume fraction from bottom to top. Several theoretical models have been proposed to define this effect; each is different but approximates to the proportionality given which is therefore an adequate practical relationship.

Although this effect of bubbles has long been known and was first discussed in electrochemical research papers in the 1970s, its importance has been re-emphasised in practical terms only in the last 7 years [9,10]. The loss of conductivity has economic implications, not from the cost of air bubbling but from the need to use increased power to electrodeposit. Typically, in a batch jigged tank installation an air-agitated solution may require a tank voltage of say 8 volts to drive the required current for electrodeposition. In the absence of the agitation air only about 6 volts (ie. corresponding to a drop in solution resistivity of 25%) is needed to achieve that current. However, a tendency to granulation will increase and lower currents may have to be used. The dilemma is thus: use air agitation to gain faster production but at the expense of power consumption. The alternative is clearly to find air-free agitation techniques. Some solutions are known to be prone to foaming. This is primarily associated with surface tension values for the solution concerned – lower surface tension promotes foams to be stable. Thus hexavalent chromium (chromic acid) is notorious for its foaming which is such that anti-foaming suppressants are regularly added to the solution. This foaming tendency is often attributed to the hydrogen generated by this highly inefficient cathodic deposition reaction. However, recent work has shown that the amount of hydrogen contributes much less than 1% towards the gas phase composition and the foam is due primarily to air agitation [10]. (The temptation to blame hydrogen arises because the decomposing surface raft of foam is often known to gently ‘pop’ as a spark ignites the hydrogen – if the hydrogen formed a substantial proportion of the foam gas a genuine hydrogen bomb might explode as has happened recently in a poorly vented non-air agitated anodising tank in another country). Similarity with the anode production of oxygen should be noted: its volume is <1% of the total air being used and both contribute little to the loss of conductivity and the generation of bath agitation.

An unfortunate downside of air agitation has recently been highlighted and may well mark the steady demise of air agitation. The air necessarily rises in the tank and breaks through the tank’s surface foam layers entering the air environment above the tank (fig.10). From here it is vented away but inevitably carries away traces of the process solution – water and constituents which have a number of effects:

- Loss of process raw material
- Increased corrosion to the infrastructures and condensing plant
- Environmental hazard to the operatives and the surrounding area.

The surface foam does nothing to reduce emissions because the bubbles usually break through dynamically and are ejected into the air. A blanket of polymer balls or truffles helps but does not eliminate the effect. The answer to the environmental hazard is first class venting and scrubbing, or elimination of the air as carrier phase. The answer is generally economic not technical, hence the interest in non-air agitation.

In summary the characteristics of air agitation are as follows.

- Air agitation is a simple technique requiring little control
- It is a cheap operation but heat losses with the fume are significant
- It can provide a relatively low degree of relatively even mass transport
- The air may oxidise solution ions and organic additives
- Air raises the solution resistance thereby increasing the power required for electrodeposition typically by 20-30%.

CATHODE MOTION – WIRE AND STRIP PLATING.

The development of continuous wire and strip plating can be traced to the 1920s. The market was initially zinc coated wire from the steel industry for fencing and later reinforcements which was originally met by hot-dip coating. The drive for thinner more economic coatings led to electrodeposition being preferred firstly for bundled wire coils in a batch tank process and later for multiple strand continuous processing. In the 1930s steel sheet coating with zinc and tin was being similarly challenged and by 1936 the first electrolytic tinplate line was operating. Difficulties of operation were many but the advantage of higher current densities resulting from the rapid strip motion were obvious and by 1950 hot dipping was in decline. For tinplate it disappeared in the UK in 1964 but for zinc it still has an important niche for thick coating used for long service life industrial building etc.

Plant design was a controversial topic and was confused by patents which defined not only an electrolyte but the type of strip motion (fig. 11) – horizontal skimming or vertical serpentine motion in the tanks (the former gives more laminar motion, the latter more turbulent motion with consequent difference in path lengths). This motion has established that additional agitation is generally superfluous and with strip speeds of 200 m/min for zinc galvanizing and 700 m/min for electroplating these represent the highest speed processes. One of the major difficulties has been laboratory control and simulation of such processes and comparing a static Hull Cell test with a production line inevitably introduces a factor of 20 or 25 in the current density values, this being in effect the EF value for the process.

With the introduction of reel to reel processes in the electrical connector and PCB industry a number of differences were inevitable. Firstly the production rates required were substantially less, and secondly because selective plating was often needed (eg. one edge only being coated) vertical strip with sideways motion was developed with strip speeds of 0.1-5 m/min. being common. At this low speed little agitation is generated and solution pumped flow and jetting were introduced and have proved to be adequate. If gold cyanide solutions were involved it is highly convenient not to use air agitation of course and so the alternatives suffice.

VIBRATORY AGITATION.

The use of vibratory agitation is not primarily to increase deposition rates but to enable other actions to take place mainly related to particles suspended in solution. The oldest technique utilises ultrasonics which is applied through a transducer on the wall of the tank which detaches particles from surfaces and each other (eg. removal of soil, de-agglomeration of particles) without significantly changing deposition rates. Vibratory motors usually operate at alternating current mains frequency (50Hz); it is not known at present whether this is optimal. They are used to maintain particle buoyancy in solution as a vital requirement in composite electrodeposition (ie, co-deposition of metal and particles). The motor does not vibrate the cathode but the solution by means of a perforated plate (fig.12) vibrating vertically with an amplitude of 3-15mm. Although a Reynolds Number can be defined its meaning is not appropriate because at low amplitude or pseudo-laminar agitation little effect is achieved while at higher amplitudes pseudo-turbulence sets in and particles become buoyant (fig.13).

Successful vibratory action is achieved only by using a perforated plate at the bottom of the tank (fig.14). Without perforations the plate acts as a lift pump or piston with little useful outcome. With perforations in the plate upward jetstreams cause particles to become buoyant with an accompanying drop of motor power and thoroughly mixed fluid within seconds. Thus this technique is primarily one of two-phase mixing and is found to be very successful at homogenising traditional paints.

Relatively little research has been reported [11-13] but the practical advantages are fairly obvious and analogy with potato mashing commonly noted. Thus the jet streams must be generated by holes of 2-4mm diameter and the plate must leave space around it for circulating eddies to descend to the bottom of the tank. Components should occupy a central position in the tank be small in relation to the tank volume otherwise uneven coating thickness may occur. Thus the technique is not for agitation *per se* but for the specialist needs of a composite deposition process.

In summary, vibratory agitation has the following characteristics.

- No oxidative air is employed and the solution is unaffected chemically.
- No insulative air is employed and the solution conductivity is unaffected.
- The technique is simple and not markedly energy-intensive.
- Particles can be made buoyant in solution thereby facilitating particle co-deposition.
- Deposition rates are generally higher than with air agitation.
- Agitation uniformity is generally poorer than for air agitation but better than for stirring; it is very effective at dislodging electrode-generated bubbles.

JETTING

Although jetting has long been used as a means of circulating solution and enhancing flow in local spots it has been used primarily for contact spot and line plating in association with the electrical connector industry. For this latter purpose jets have changed from the wide orifices, which may be considered as fore-runners of eductors, to narrow and focussed jets capable of giving fine definition to deposits. By generating substrate or jet motion line patterns can be produced hence the possibility of direct plating tracks for printed circuit purposes.

Solution is delivered to the jet reservoir using pumped flow which in principle can be laminar or turbulent although the jet design to be converging or diverging is more important. Clearly the jet flow creates agitation thereby raising mass transport but the pattern of jet flow can give rise to three jet-stream profiles (see fig.15) depending on the flow rate and the solution viscosity. For a classical Newtonian fluid (ie. dilute plating solutions) the pattern is defined by the Reynolds Number $Re = U_d j/v$; for $Re < 1$ jet convergence occurs while for $Re > 1$ divergence occurs with contraction of ~63% and expansion of ~15% respectively. For a non-Newtonian fluid (ie. one having viscous nature through high concentration or addition of drag agents such as glycerol) considerable divergence can occur due to compression in the tube and energy release after the jet orifice.

Jets used in electroplating are usually converging and are now well-understood [14-19]. They yield a deposit having four possible zones (fig.16) due to high central deposition rates, a moat and possible secondary ridge: this must be carefully controlled in relation to the resulting spot profile.

Zone I	core zone where flow changes from pipe to free jet flow
Zone II	mixing zone where the forward velocity falls and fluid expansion occurs
Zone III	stagnation zone in which the forward velocity is zero and radial flow develops
Zone IV	wall jet zone where radial possibly laminar flow occurs – a maximum turbulence may occur at the boundary of zones III and IV.

The theoretical challenge of describing this behaviour is now reasonably well-understood. The resulting spot geometry depends upon the flow/agitation and can be controlled for the main specialist applications of silver/gold electrical contacts. The use of focussed lasers to enhance local deposition rates has been much researched as a competitor but little exploited commercially.

EDUCTOR AGITATION

Solution re-circulation has been practiced for many years usually in the context of solution filtration for which the flow rates are slow in order not to overload, damage or block up the filters. Similarly jetting has been practiced but primarily as a means of enhancing local deposition either for 'spot' plating or at regions of low throwing power. The possibility of combining these is therefore obvious. However, the flow rates are not often compatible and the pump is inefficient.

With the introduction of designer jets especially of the *Venturi* type the option has become viable. The Venturi jet was invented in Italy in the late 1700s and has been adopted in a number of devices notably the Bunsen Burner. It exploits a jet entry to a tube whose primary flow creates a pressure drop which draws in a secondary flow such that the total exit flow can be 2-5x the primary pumped flow (fig. 17). In the Bunsen burner the primary fluid is fuel gas and the secondary flow air; by varying the secondary flow volume using a rotating sleeve shield for the entry hole the flame can be varied from reductive blue/black to oxidative luminous. In its Eductor format for agitation, the secondary flow is maximised and rated at 4x the jet volume thus creating an efficient jet agitation device (further details can be found elsewhere [1,20]). In the 1980s commercial

eductors were marketed and in the 1990s their virtues were appreciated. In the 2000s they are being widely used not only for electroplating but for anodising, cleaning and pickling and rinsing in the surface finishing industries (one eductor generating convective mixing as in fig. 18) and are known by several commercial registered names such as Serductors, Floductors etc.

The main process parameters of importance are the Solution characteristics of density and viscosity, and the input volume flow rate with its expansive character at the jet which controls the pressure drop induced.

The eductor design parameters are:

- Pipe inlet diameter
- Pipe outlet diameter
- Throat diameter
- Diffuser cone divergence angle

In practice the last parameter is a fixed design factor (at 11°) as a consequence of several standard specifications (eg. ISO 4006, ISO 5167, ASTM D2458-69) which are not directly related. The other parameters are incorporated in eductor sizing from small to very large, one commercial range consisting of five sizes. To feed those eductors large pumps with high flow rates are needed well beyond those used for filtration (fig. 19). The energy required has been regarded as a disadvantage although there are energy savings to offset this as will become apparent. Typically a small 100-400l tank may require 1-2 KW while a 20,000l tank may require 5-10KW.

A flow ring must be installed at the bottom of the tank, ideally just above the bottom, with the pipework able to swivel in its unions and have screw threaded holes prepared for eductor placing. Not all holes may be used at any one time and the pipe can be rotated in order to change the angle of eductor jetting towards the jugged work. The eductors emit a plume of solution and the divergent angle ensures that at a range of 50-80cm they will disperse over a work area of 1-3m. It is strongly advised that, because the plume is invisible during use, before they are actually used modelling experiments are carried out in the tank containing water in which fine glass beads or an air feed are used in the pump line to define the plume size and shape and adjustments carried out with the work in jugged position. For a conventional oblong tank 2-4 eductors per side would suffice but for a deep tank a midway in depth ring may be needed for supplementary agitation.

Previous investigations have used this methodology together with measurements of local degrees of agitation to characterise the agitation pattern using computer spreadsheet graphics [20-24] – see fig. 20. Much of the detailed work was carried out for printed circuit board production with acid copper solutions but later work has been reported for anodising of aluminium [25-26], a practical study for nickel plating has been reported [27] and many trade reports can be found for all the common metal processes [28-30]. That particular nickel installation [27] is the only fully documented system in the public domain and its specification is worth summarising.

- Tank size 1.8x1.8x1.8m with a working volume of 6000 L
- Agitation rate 40 turnovers per hr., ie. 4000L/min or *pumped* volume of 800L/min
- Pump size 800L/min. using 2.2kW three-phase pump at 415V
- Eductor size 3/8in eductors at 10.7m total head and nozzle flow of

41.8L/min

- Eductor number total number is $800/41.8 = 19.14$
- Eductor arrangement 20 total in four banks of five

The pipework was designed to be submerged using a support frame inside the tank walls independent of the existing air pipes so that a comparison could be made. It is vital, however, that the tank be thoroughly cleaned because the eductor action is erosive and tends to dislodge all residual scale and consolidated sludge.

The system costing involves an initial capital cost which is modest and a running cost which is significant but which must be offset by process savings of lower plating (Faradaic/resistive) power, less heating and air pumping, less sludge for disposal, lower fume extraction and scrubbing. The operational advantages claimed included better agitation, 36% increased deposition rate, reduction of nickel thickness variability of 92%.

The advantages and disadvantages can be summarised quite clearly. The advantages are:

- Good agitation, several times better than air, which can be work-focussed
- The absence of air means no loss of solution conductivity (typically ~25% energy loss)
- Little or no fume from the tank thereby reducing fume extraction needed and fume chemical scrubbing. Heat losses in such fume is consequently zero.
- A reduction in sludge production by oxidation, hence reduced filtration
- A reduction in plating additive consumption by oxidation
- A saving of solution heating energy due to lower losses

The disadvantages naturally include the installation costs and are limited to the increased pumping costs which are sometimes regarded as unacceptably high without adequate costing of the advantages.

The use of eductors in Anodizing is analogous [25-26] but their purpose is not to enhance mass transfer but to enhance heat transfer. This is because the anodic film forms by solid state diffusion through the film, not by solution diffusion at the electrode diffusion layer. The heat arises because the film acts as a thin film heater accounting for a voltage drop of 10-20V which is entirely absent in electroplating: the consequence is that unless the heat is removed rapidly the film formed becomes characteristic of some higher temperature, not that set by the bulk solution temperature, and the film will be thinner and softer than planned.

OTHER RELATED TOPICS.

Some other electrochemical processes make use of agitation as part of the essential technology of the operation but are not easily applicable for general use. These will be mentioned for the sake of completion.

Jet Plating's anodic counterpart is **Electrochemical Machining** and this has been the inspiration for some developments. It is used primarily for metals and alloys which are difficult to machine and where the remaining surface needs to be left in a stress-free condition. The *Nimonic* range of nickel alloys used in aero engines are the most successful category of metals. Selection of a suitable electrolyte and its re-generation

after use by means of heat exchange and precipitation are an integral part of the process besides the use of a jet to localise dissolution.

Barrel Plating is a long-standing technique for coating large numbers of small articles such as nails, screws, washers and coins, contacts etc. The Barrel is rotated relatively slowly primarily to tumble the work and produce evenly coated product. The tumbling necessarily causes agitation of the solution but the degree of agitation is low (eg. $EF = 4$) and the practical restriction is usually replenishment of solution. Consequently, if increased deposition rates are required it is more effective not to increase barrel rotation rates but to pump solution (jetting?) into the mouth of the barrel. Air agitation is usual for general mixing but trapped air in the barrel attached to individual components can be counter-productive.

Brush Plating necessarily has a certain amount of agitation in the act of brushing but this is incidental to the process which is essentially one of local deposition for high-lighting or repair on surfaces. Any attempt to increase rates of deposition has been achieved by design of the solution constitution and increased temperature.

Electroforming can take several forms, in some of which agitation is merely a case of solution mixing because for deposit integrity reasons the whole process is necessarily slow. In the special case of electroformed foil and mesh pumped flow in a channel surrounding the drum former is usual and high rates of deposition are important and are widely achieved.

CONCLUSIONS.

The range of agitation techniques in use is substantial and still growing almost 200 years after the invention of electrodeposition. The choice of technique for a specific application can depend on many factors including past personal experience. But the need to increase production rates and optimise a process for specific objectives is now common and well-established.

However, in the last ten years some new considerations have been introduced into the factors affecting selection and these have been discussed.

- Energy economy by maintaining solutions as conductive as possible.
- Reducing unnecessary oxidative reactions in solution from the agitative air.
- Reduction of sludge production, and hence the cost of its disposal.
- Reducing process fume for environmental and cost reasons.

It is likely that future driving forces are likely to be more environmental and economic than purely technical.

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FIGURES.

1. Agitation system design for maximum agitation
 - a. high critical Re , eg. Rotating disc electrode (RDE)
 - b. moderate critical Re showing effect of wall roughness for a pipe as a turbulence promoter
 - c. low critical Re , eg. Superior turbulence promoters or a rotating cylinder electrode (RCE)
2. Traditional cathode bar reciprocation using offset cam motor
 - a, b sliding frame busbar
 - c. baffle or paddle
3. A classification of rotary stirrer designs (after Zlokarnik) for mixing and agitation.
4. Schematic for an air supply ring submerged near a tank bottom.
5. Stages in the generation of spherical-cap bubbles from a sparge hole.
6. Flow pattern around a rising spherical-cap bubble.
7. Bubble pattern during air agitation of an electrodeposition tank.
8. Relative levels of agitation attained in an air-agitated tank.
9. Reduction of fluid conductivity with air void fraction in the fluid. A typical air-agitated tank has $\varepsilon = 0.2-0.3$ and a loss of conductivity of $\sim 35\%$ (after Sigrist et al).
10. Rising air bubbles from a single sparge hole increase their size/volume and disperse their zone of influence but not the degree of agitation attained.
11. Cathode strip or wire motion in a continuous process:
 - a. vertical serpentine tank
 - b. horizontal strip motion
 - c. reel-to-reel process
12. Design of a vibratory plate showing chamfering.
13. The vibratory flow mass transfer transition
14. Agitation pattern in a vibratory agitated tank for three configurations: small plate in a large tank, medium plate in a large tank, and a large unperforated plate in a large tank.
15. Profile of jet flow:
 - a. Newtonian flow, $Re < 1$
 - b. Newtonian flow, $Re > 1$
 - c. Non-Newtonian visco-elastic flow
16. An impinging jet electrode showing four zones of flow pattern (after Chin and Tsang).
17. Design principles of the agitation eductor showing the primary pressurised input, the secondary induced input, the throat and diffuser zones.
18. A plating arrangement with one eductor's emerging flow generating convective mixing.
19. Schematic installation showing four eductors fed by one pump; a small air input is employed to make the exit plume visible.
20. An agitation map showing the zone of high agitation and thence limiting current using the installation as in fig.19.

APPENDIX. TEXTBOOK (19th century) ADVICE ON AGITATION.

Motion of the plated article is very advantageous
Motion permits faster deposition
Agitation improves uniformity of deposit
Mechanical agitation reduces solution resistance

Gore 1877

Homogeneous solutions are necessary, hence need of agitation
Gentle stirring or cathode shaking are recommended
Slow agitation is desirable to allow anode inclusions to sink

McMillan 1890

Agitation is needed to:

- Remove hydrogen bubbles
- Eliminate solution stratification

Mechanical stirring is normal. Striking the busbars occasionally
Or operators removing the work frequently may be sufficient.

Langbein 1891

Fig.1. Agitation system design for maximum agitation
a. high critical Re , eg. Rotating disc electrode (RDE)
b. moderate critical Re showing effect of wall roughness for a pipe as a turbulence promoter
c. low critical Re , eg. Superior turbulence promoters or a rotating cylinder electrode (RCE)

Fig.2. Traditional cathode bar reciprocation using offset cam motor
a, b sliding frame busbar
c. baffle or paddle

Fig.3. A classification of rotary stirrer designs (after Zlokarnik) for mixing and agitation.

Fig. 4. Schematic for an air supply ring submerged near a tank bottom.

Fig.5. Stages in the generation of spherical-cap bubbles from a sparge hole.

Fig.6. Flow pattern around a rising spherical-cap bubble.

Fig.7. Bubble pattern during air agitation of an electrodeposition tank.

Fig.8. Relative levels of agitation attained in an air-agitated tank.

Fig.9. Reduction of fluid conductivity with air void fraction in the fluid.
A typical air-agitated tank has $\epsilon = 0.2-0.3$ and a loss of conductivity of $\sim 35\%$ (after Sigrist et al).

Fig.10. Rising air bubbles from a single sparge hole increase their size/volume and disperse their zone of influence but not the degree of agitation attained.

Fig.11. Cathode strip or wire motion in a continuous process:
a. vertical serpentine tank
b. horizontal strip motion
c. reel-to-reel process

Fig.12. Design of a vibratory plate showing pattern of holes and chamfering

Fig.13. The vibratory flow mass transfer transition for a perforated plate.

Fig.14. Agitation pattern in a vibratory agitated tank for three configurations: small plate in a large tank, medium plate in a large tank, and a large unperforated plate in a large tank.

Fig.15. Profile of jet flow:
a. Newtonian flow, $Re < 1$
b. Newtonian flow, $Re > 1$
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Fig. 16. An impinging jet electrode showing four zones of flow pattern (after Chin and Tsang).

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Fig.19. Schematic installation showing four eductors fed by one pump; a small air input is employed to make the exit plume visible.

Fig.20. An agitation map showing the zone of high agitation and thence limiting current using the installation as in fig.19.

