OPTIMIZATION OF NICKEL ELECTRODEPOSITION SOLUTIONS FOR POWER USAGE.

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If electroplating processes are to be truly 'green' a number of issues must be addressed notably water and electrical power usage. Electricity is used both for the process itself and for the process conditions, eg. temperature, agitation etc. The study of solution conductivity for electroplating solutions shows how some electrical power saving can be achieved. In the case of nickel small gains can be made by optimising solution concentrations but greater gains attained by the use of air-free agitation.

INTRODUCTION.

The word *optimization,* whether spelt with a 'z' or an 's', has sometimes a spurious scientific aura about it. It implies that care has been taken to ensure that the design parameters are correct or at least well-considered. However, it cannot correctly exist without qualification as to its relevance or association. Typically, in electrodeposition a solution is optimized with respect to deposit brightness or levelling and such optimization may involve both solution and process parameters. Perhaps the most famous example of such optimization is the hexavalent chromic acid solution for decorative chromium deposition which involves:

1. its solution formulation and the classical 100:1 ratio of chromic and sulphuric acids respectively;
2. its temperature and current density ranges of 45-55°C and 10-30 A/dm^2 respectively;
3. its use of agitation to eliminate hydrogen from the deposit surface
4. the use of foam suppressants (but not brightening or levelling additives) to counteract the side effects of air agitation and hydrogen evolution.

The most frequent examples of optimization relate to the use of additives for brightening and fortunately the existence of the Hull Cell makes the procedure relatively straightforward, the search being for additives that cause brightness in the deposit, over an adequately practical range of current density, and without deterioration or other loss. However, other examples can be cited.

1. the design of gold solutions of low concentration to minimize monetary value losses through dragout, minimize substantial inventory cost and possibly discourage theft;
2. the design of high speed plating solutions using highly concentrated salts, typically sulfamate or fluoborate, together with high agitation;
3. the choice of ions to exploit low valency states requiring low electron discharge numbers ensuring Faradaic efficiency;
4. the design of solutions having high throwing power for even deposition in holes and vias;
5. the design of solutions to operate at low to moderate temperatures to minimize evaporative losses.
6. the design of solutions to exclude highly toxic constituents, typically cyanides which have long been known as the most versatile complexing agents for metals;

OPTIMIZATION FOR POWER USAGE.

In today's 'green' economy two commodities now raise their heads for possible optimization – water and electrical power. The problem of water has been on concern in the UK since the Water Act of 1974 caused substantial price increases to be instituted from artificially low levels typical of traditional nationalised utilities to a realistic level needed for future investment in expanded supply and maintenance of old infrastructure. In metal finishing companies electricity usage is defined and controlled by current or current densities but it is bought as power and the voltage parameter can be considered as the driving force to attain the currents required. This manifests itself as circuit resistance or conductivity some of whose deleterious characteristics are well-known. These include bad contacts and switching, busbar cleanliness, short power line distances etc. The solution itself has rarely been considered because its formulation has been driven by other considerations as already cited.

What opportunities exist? Some are quite minor and can be disregarded: for example,

the use of levelling agents such as gelatine which form viscous electrode layers not only lower the cathode efficiency by 3-10% but add to the voltage drop by 10-70mV. These are normally regarded as trivial. Two aspects will be considered briefly.

Firstly, the optimization of solutions for maximum conductivity and secondly the choice of agitation method.

Present-day solution formulations have usually been based on historical bases and not often questioned very critically. Thus the cyanide formulations for silver and gold can be easily traced back to those of 1840-1850 with modifications relating to use of additives and control of carbonate etc breakdown products. The 'Watts' nickel solution was designed by Professor Watts [1], at the request of the American Electroplating Society and industry, primarily to attain a stable solution of high efficiency (hence the use of boric acid and close pH control) and good anode dissolution (hence the inclusion of a low concentration of chloride).

Few solutions have been challenged for their power profligacy. One can be cited from the days when electroforming was a development challenge, and electroforming of iron foil was an especial challenge [2-3]. It was believed that the economic advantage of electroforming over rolling for foil production was so marginal that a saving of 2V in the process made profit feasible hence a large study of conductivity salts and use of saturated chloride solutions at ~100°C was under development.

The use of Conductivity Salts has a long but not very active history so the principles are clear but not widely considered [4]. More important is the understanding that most solutions have an optimum concentration for maximum conductivity due to the dissociation of the salts in solution: up to the critical value the salts are fully ionised but above that value incomplete dissociation occurs and conductivity falls. This principle has long been worth exploring.

CONSIDERATION of SOME NICKEL SOLUTIONS.

Electrodeposition solutions for nickel have a long and honourable history. Three can be cited:

- Watts nickel, based on sulphate-chloride-borate invented in 1916 [1]
- Wesley all-chloride 'strike' solution used from 1939 [5]
- Kendrick sulfamate solution invented in the 1960s [6]

These were all developed for functional use and not for power efficiency. If the question is asked, *are they optimal for power efficiency?* the data is not readily available but can be obtained relatively easily

The variation of conductivity with concentration shows a maximum in each case as anticipated (fig.1) due to increasing ion concentration and then decreasing ion dissociation. The concentrations for maximum conductivity offer small ranges not too far from those for general practice.

SOLUTION	USUAL RANGE, g/l	MAX. CONDUCTIVITY, g/l
Watts	300-350	300-400
All-chloride	230-260	500-700
Sulfamate	600-900	450-550

The most interesting case is the sulfamate solution which was much heralded on invention for its very high solubility, and hence potential for high speed plating at ~1000g/l, but which in practice was recommended at ~600g/l. The reason for the recommendation is not clear from the literature but could be related to its optimal conductivity.

Increased temperature (fig.2) has a small effect, Change of pH (fig.3) also has a small effect but is dominated by the need to maximise current efficiency (pH>2) and minimise hydroxide precipitation (pH<6). However, modification of the Watts solution by adding chloride or replacing sulphate has clear advantages for conductivity (fig.4). Its use in this way, however, will add to costs and is therefore not attractive.

It is widely believed that most electroplating processes are optimal at ~30°C but these grounds are based primarily on the need to heat the solution for better performance compared to the inevitable losses due to heat transfer. It is convenient however that the lowest resistive heating cost due to the solution itself tends to leave the solution in well-insulated tanks at 25-30°C so for once coincidence is convenient.

Agitation for such solutions is traditionally by air agitation. It is now well-established that air is insulative in the two-phased solution and when distributed as small bubbles causes a typical loss of conductivity of 20-40% [7]. A small scale laboratory testing showed this to be true (fig.5) but omitted detailed measurements for varying cathode position in the small tank. A number of air-free agitation methods exist – cathode reciprocation, vibratory agitation, eductor jetting etc; the most appropriate technique should be adopted. However, the environmental bonus of eductor agitation is the virtual absence of spray-mist which carries with it hidden costs of extraction and scrubbing.

The conclusion is, therefore, that some scope for improved power efficiency in nickel plating exists by changing the solution concentrations but the largest opportunity exists for the use of air-free agitation. Eductors offer the obvious type of air-free agitation when their use is technically feasible.

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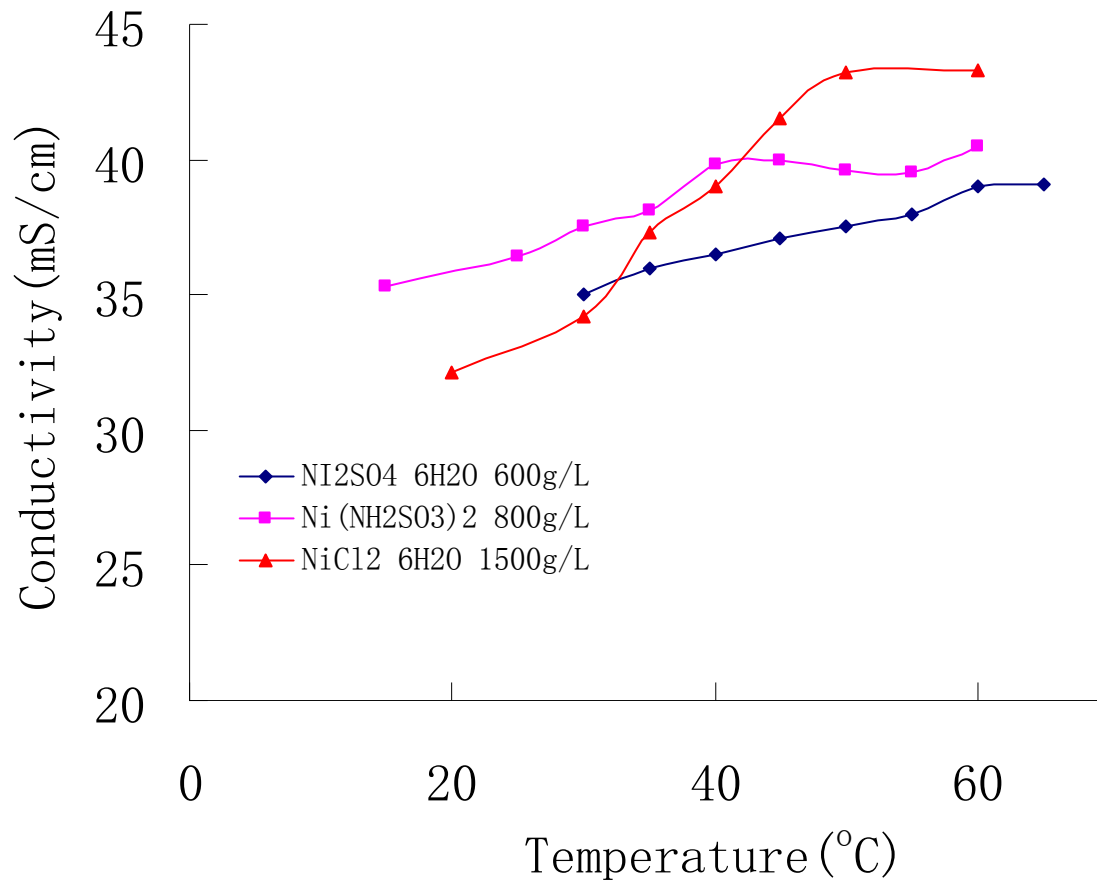7. J.Parker, M.Ward and D.R.Gabe. Russ. J.Electrochem. 2001, **37**, 677-683.
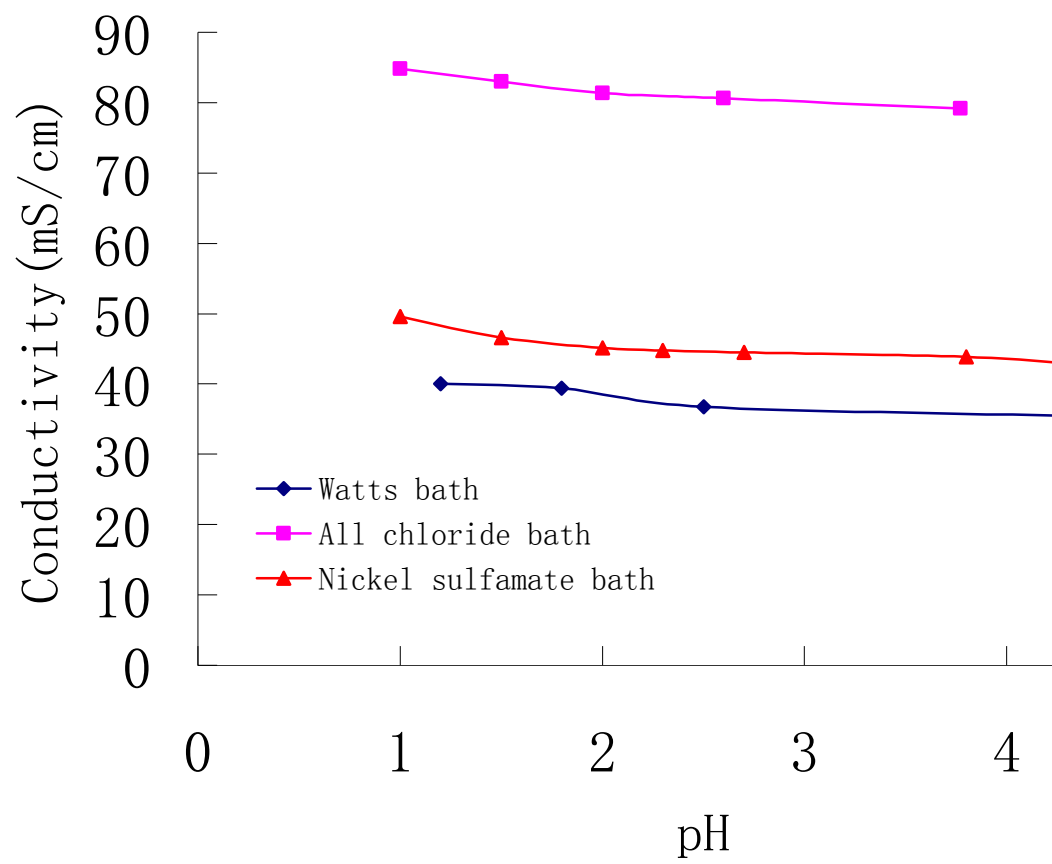
FIGURES.

Fig 1 Conductivity of different nickel solutions at room temperature

Fig 2 Conductivity of high concentrated nickel solutions at different temperature
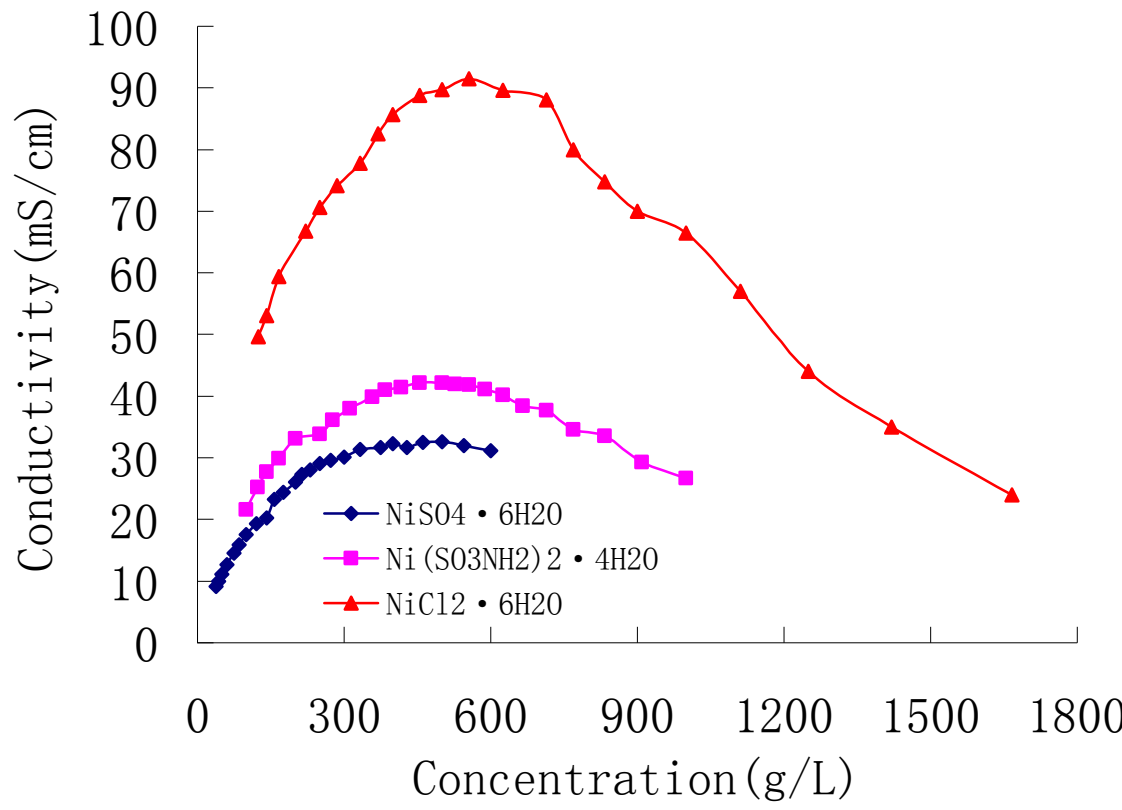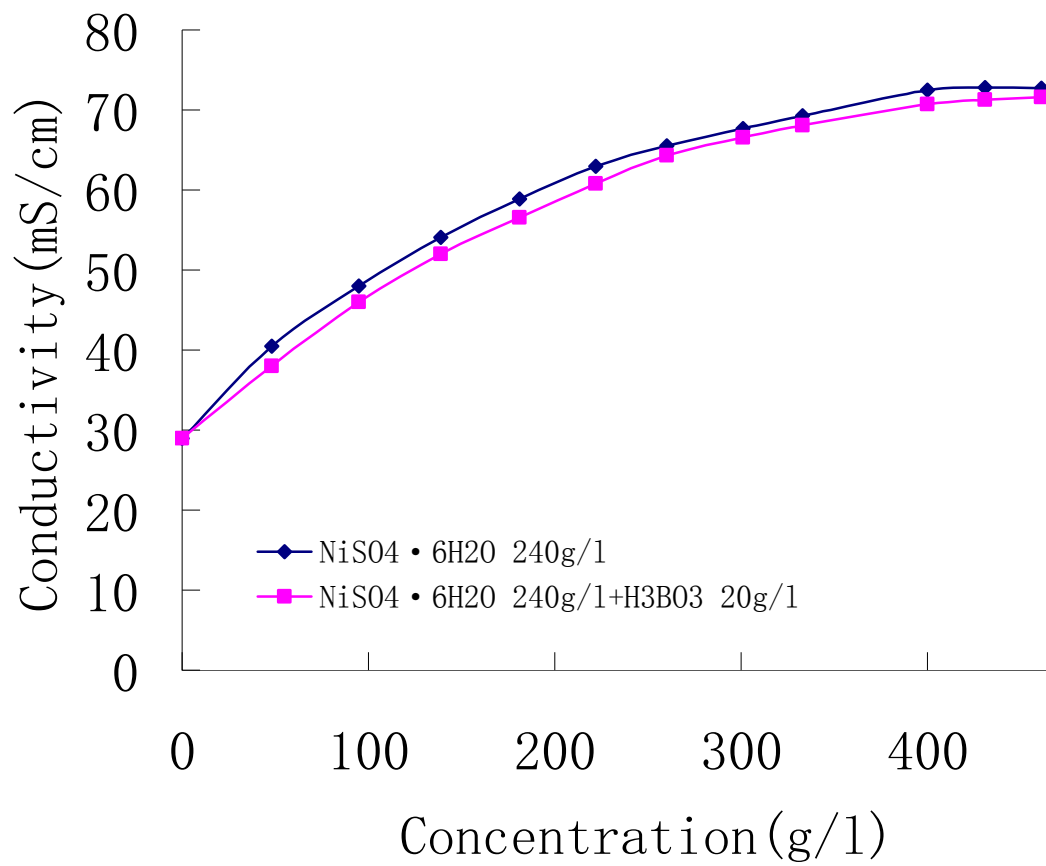

Fig 2 Conductivity of high concentrated nickel solutions at different temperature

Fig 3 Conductivity of different nickel solutions at different pH

Fig 4 the effect of addition of NiCl2 to NiSO4 solution

Fig 5 Air agitation rate Vs conductivity in an all chloride bath