ELECTROLYTE MAINTENANCE BY ADSORBER POLYMER AND LIQUID-LIQUID EXTRACTION

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ABSTRACT

Extended use of electrolytes in plating processes show increasing amounts of organic impurities. These impurities often result from decomposition of organic brighteners and/or wetting agents. If the concentration of impurities in electrolytes exceed certain limits, plating errors occur. A complete regeneration is necessary (e.g. activated charcoal). In order to lower the freight of unwanted substances and to extend solution lifetime, electrolytes can be cleaned by certain technologies in a by-pass system: The adsorber polymer technology and the concept of liquid/liquid extraction.

In this paper the two different concepts are discussed by laboratory and technical scale results.

INTRODUCTION

Processing baths used by the electroplating industry are subjected to constant changes in their composition caused by the intended material turnover, by water and impurities which are dragged into the solutions, by electrolyte drag-out, and other affects such as evaporation, anodic and cathodic ancillary reactions, absorption of components from the air (e.g. absorption of carbon dioxide in alkaline baths, dust, micro-organism) and even false dosing. This means, that the electrolytes must be constantly or at certain intervals regenerated, in order to avoid the eventual necessity of a new make-up and disposal of the spent solution. To avoid the latter and to improve the cleanliness of the electrolytes several different types of processes are available.

The extraction of particles (metallic flitter, dust particles, colloids, micro-organism, various metal compounds, anode sludge, etc.) is without doubt the first and most important method of bath maintenance. Without filtering, the deposits would be rough. The majority of filters can be operated with filter aids such as celite or active carbon (with back-washing). However, filtering in this manner cannot be performed while the electrolyte is working/1/.

Another process, which has proved itself under practical working conditions, is UV-H_2O_2 Oxidation. In this case part of the bath volume, of a bright nickel bath for example, will be treated with UV/H_2O_2. Oxidation is to be carried out discontinuously outside the tank. All organic compounds, decomposition products as well as the effective brightening additives and the wetting agent will be completely broken down. This treatment leads to a Watt's Basic Make-Up, which can be mixed into the bath again. /3,4/. But again, this system does not work in a by-pass system and a UV-H_2O_2 units are quite expensive.

This paper will discuss two technology (one new and one improved) for electrolyte maintenance that perform in by-pass: Liquid-liquid extraction and adsorber polymer technology.

ELECTROLYTE MAINTENANCE BY ADSORBER POLYMERS

Adsorber polymers, which can be regenerated, will meet the foregoing requirements. Divinyl benzol co-polymer resins, which belong to no functional group and thereby have no ion exchange function, have proved themselves in this respect. Polarity, and more specifically the inner surface areas as well as the diameters of pores can be determined with the help of the manufacturing technology employed for adsorber polymers. These resins are able to remove most of the organic components presently used as well as the accompanying decomposition products, operating conditions such as pH, the strength of the ions, the type and concentration of the organics used, and the flow-rate in the adsorber columns, all affect the efficiency of the adsorber polymers.

But not all resins can be used for every application. Results in the lab have shown that in several cases combination of two or more polymers show the best performance in electrolyte purification. After purification the adsorber polymer has to be regenerated.

Regeneration is accomplished by an oxidation with 1-3% strong hydrogen peroxide by desorption of the adsorbate with 3-6% sodium lye. Corresponding rinsing water will then occur, and one should ensure that no surplus hydrogen peroxide be allowed to enter the wastewater treatment plant. The sodium lye used in regeneration and the alkaline rinsing water contain all organic substances used, which increases the concentration of TOC in the waste water /2.3/. For balancing the pH an acidic post treatment is required.

Both the oxidative pre-treatment and the sodium lye used will gradually attack the resin. For this reason, the resins will have to be renewed after about 2 years.

But not only organic impurities have to be considered. Related to the facilities for example bright nickel plating solutions are contaminated by copper and chromium ions. Therefore, it is also useful to stabilize these concentrations by ion exchanger.

Using different polymers and ion exchanger the regeneration procedure has to be considered individually because there is no universal applicable regeneration procedure.

An "easy to handle system" that takes all into account is shown in Figure 1.

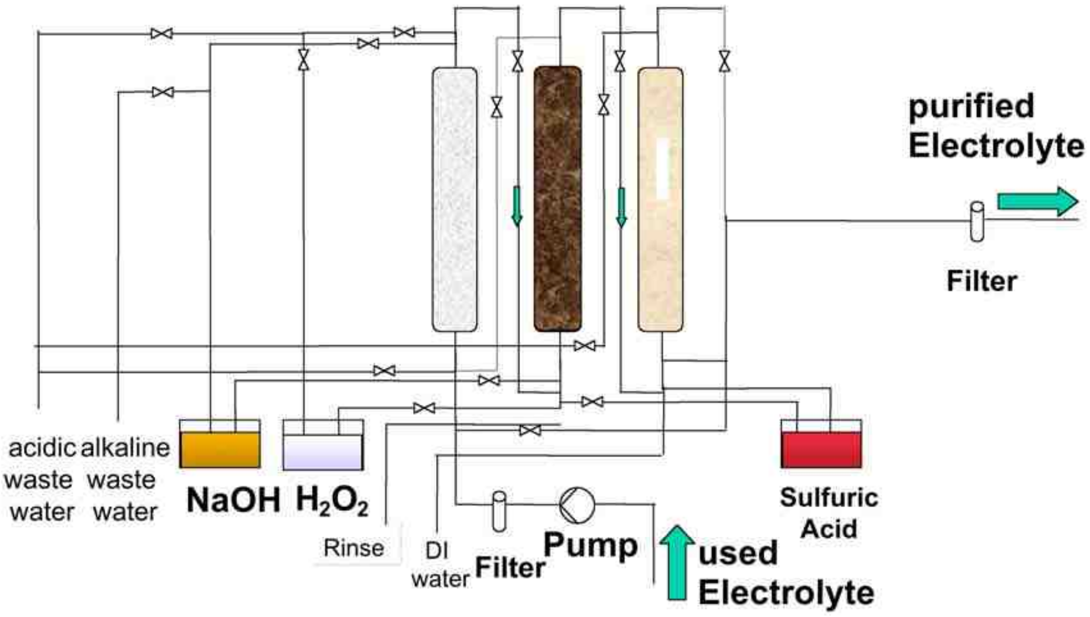

Fig.: 1 Schematic sketch of an plating electrolyte purification unit

The unit consists of several columns that are filled with different adsorber polymers and ion exchangers that can purify plating electrolytes. The adsorber columns can be regenerated separately related to the requirements and the best performance. Figure 2 shows qualitatively the performance comparison of HPLC before and after passing the adsorber system.

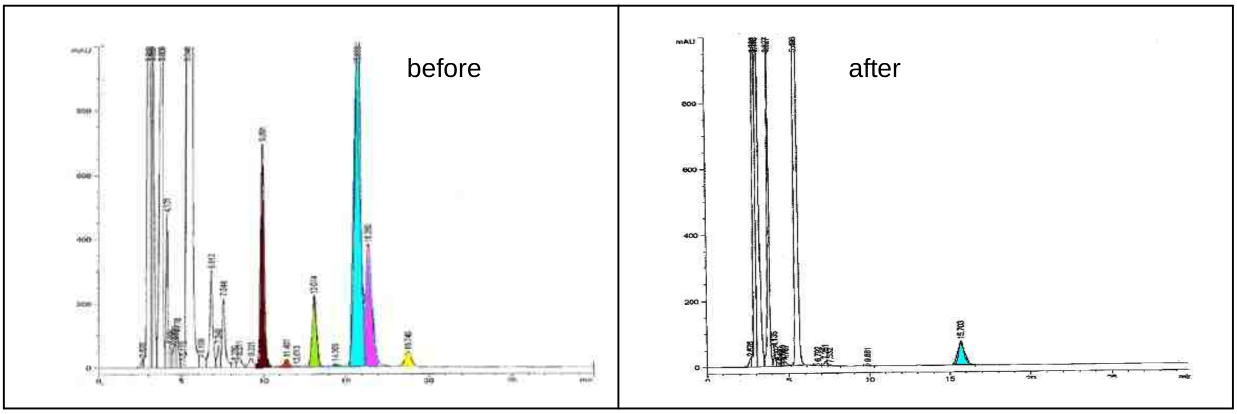

Figure 2: HPL Chromatogram for bright nickel plating before (left) and after (right) passing the adsorber system (the non colorized peaks belong to the additive package for bright nickel plating).

Depending on the size of the unit and the plating solution the amount of impurities, unwanted drag-ins and breakdown products can be lowered up to 50 % in the plating tank by just one treatment. The performance of the adsorber polymer is dependent on the runtime. The cleaning performance related to time is shown in Figure 3.

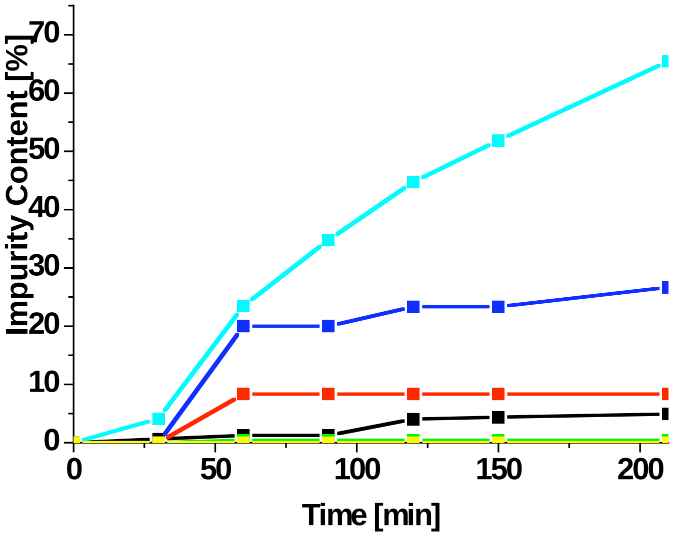

Figure 3: Organic **i**mpurity concentration related to start condition after passing the adsorber polymers.

After a while the adsorber columns are saturated with organics and lose cleaning performance. Additionally, after 200 minutes some of the impurities are released from the columns in a higher concentration compared to the now existing concentration in the plating tank (e.g. the blue lines). The reason for this is the chromatography effect. The adsorption is not static as it shows a certain mobility. Impurities are located throughout the column. This results in a high outgoing impurity concentration. Therefore, the adsorber treatment has to be stopped and the resins have to be regenerated.

Besides the removal of the "bad organic", significant amounts of "good organics" are removed. Brighteners such as saccharine also adsorb at the adsorber. Therefore, a replenishment is needed that can be performed by recharging the adsorber polymer.

As mentioned previously, an inorganic purification component may be added to a adsorber system. With the assistance of ion exchange ions, such as Zn^{2+}, Cr^{3+}, Al^{3+}, Cu^{2+}, $Fe^{2+/3+}$ impurities can easily be reduced up to 60%.

PLATING ELECTROLYTE CLEANING BY LIQUID-LIQUID EXTRACTION

When cleaning with Liquid-Liquid Extraction, impurities can be removed from the carrier liquid – in this case the electrolyte to be cleaned–with the help of a liquid extraction medium.
The substance transportation from one liquid to another, which thereby takes place, results by virtue of the different solubility of the two liquids, and their different concentrations.
Extraction medium and carrier liquid should be insoluble, so that good separation is ensured, and at the same time as little solvent as possible is dragged out.
Generally, one of these liquids will be aqueous, the other an organic solvent, i.e. the solution from the extraction medium in an organic solvent.

The solvent must meet following requirements:

- High solubility of the material to be extracted
- High selectivity
- Great density difference to the carrier liquid, to ensure good separation
- There must be no prevention of emulsification
- Good regeneration characteristics
- Favourable price

Since with this extraction method a distribution takes place between two media that cannot mix with each other, replacement and the establishment of equilibrium takes place via the phase interface. A high phase interface will accelerate the establishment of equilibrium.
Large technical extraction applications work in accordance with the Mixer-Settler Principle (Abb. 3). Here, the extraction medium and the carrier liquid will be mixed with each other in the first chamber (Mixer). This mixture goes into the so-called Settler over a weir. Here the phases can separate again. The separate phases can then be removed separately from the chamber. If the extraction results do not meet the set requirements, several so Mixer-Settler-Units can be connected one behind the other.

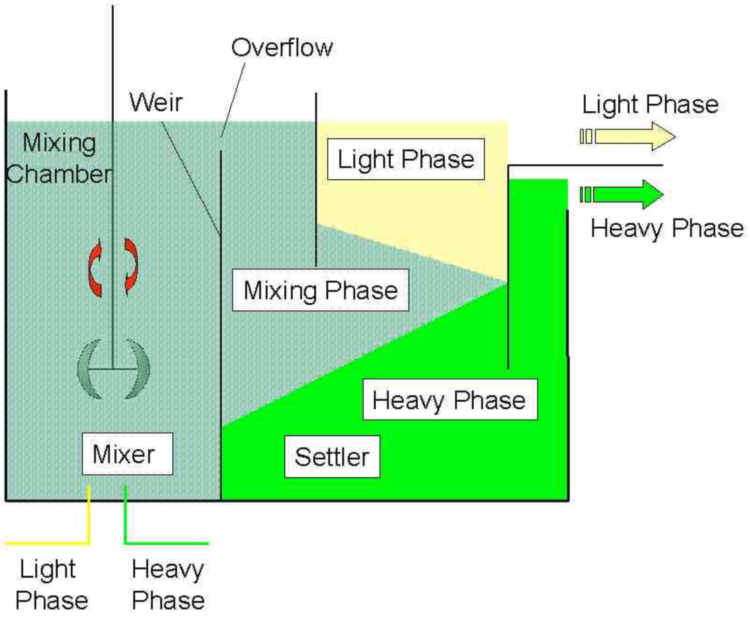

Figure 3: Liquid-Extraction According to the Mixer-Settler Principle

A prerequisite for the successful use of the Liquid-Liquid Extraction in electroplating systems is that a solvent is found that: a) will selectively dissolves impurities; b) is easy to separate, and; c) leaves very little residue in the electrolytes, so that no plating faults occur.
Acetic acid butyl ester has proved to be a likely candidate to meet these requirements. In Screening-Experiments it was possible to remove impurities from bright nickel electrolytes to such an extent that they were no longer detectable by HPLC, whilst additives, such as brightening additives like saccharine for example still remained in the aqueous electrolyte solution. Tests with the regenerated electrolytes also showed that the extraction medium had no negative affect on the deposits. However, a problem was the extended time they had to remain in the Settler. In some cases, it took several

minutes until the aqueous, salt electrolyte phase had separated itself from the butyl acetate phase. Here the decisive factor is the affect of the tenside charge, which sometimes generates very stable emulsions.
In order to ensure that a continuous bath cleaning processing is achieved other techniques; based on the Liquid-Liquid-Extraction principle, need to be applied.

Centrifugal Extractors

A special design in accordance with the Mixer-Settler-Principle constitutes the Centrifugal Extractors. In this case, the carrier fluid and the extraction medium are mixed by the shear rate, and separated again by making use of the centrifugal force. In the turbo-separator unit (Diagram 4). The difference in density between that of the solvent and that of the electrolyte are hereby made use of. In this manner, the emulsion with the higher density will be thrown outwards by the rotation action, the other part with the lower density remains in the centre of the separator. A density ratio specific weir can then separate the light and the heavy phases from each other.

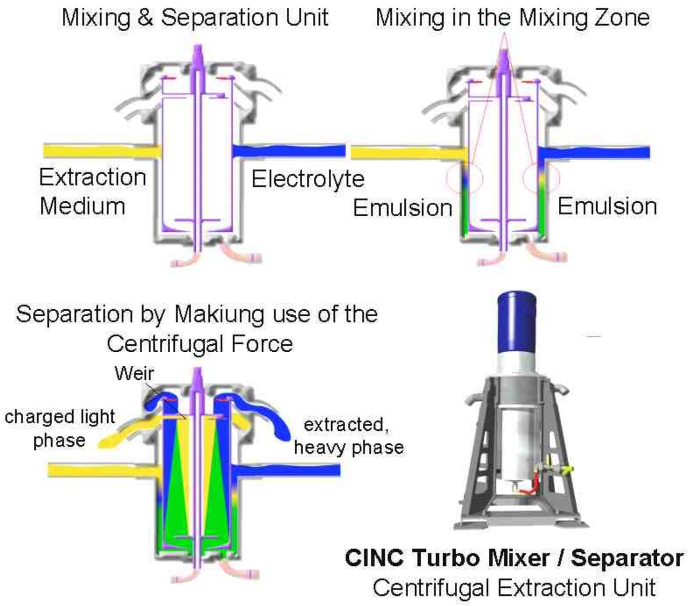

Figure 4: Principle of Centrifugal Extraction: Schematic Diagram of the Turbomix and Separation Unit [6]

By way of example, we have here depicted the cleaning results achieved in a bright nickel electrolyte, which is currently in operation in a production line being used by a fittings manufacturer (Diagram. 5). For these tests a centrifugal extraction unit manufactured by **CINC Deutschland GmbH & Co. KG** was used. From the HPL-Chromatogram one can clearly see, that it was possible to considerably reduce the share of impurities with all parameters. Impurities of the Type A were lowered by 90%, those of Type B by 60 – 80 % and Type C by 60%, whilst important additives like saccharin (brightener) were not extracted.

The best parameter set was a combination of shear rate (low rotation frequency) whilst mixing, and short exposure time (6 seconds). This is most remarkable, since the parameter set is particularly interesting, as regards efficiency and material care. Short exposure times with good extraction results mean high throughput quantities, and low rotation frequencies mean material care of the extraction unit.

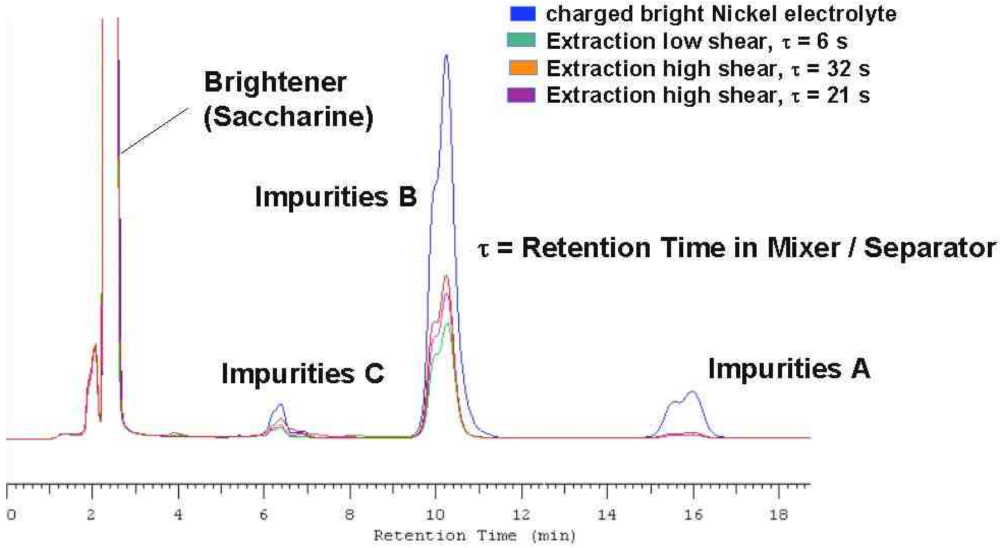

Figure 5: HPL- Chromatogram of a spent and by single-step centrifugal extraction then cleaned bright nickel electrolyte.

When a row of centrifugal extraction units are employed, it is possible to lower the burden the electrolyte is subjected to even further. However, of even more interest is the fact, that this system makes low-price bypass operation possible, which in comparison to diaphragm and absorber resins does not suffer from loss of efficiency.

Diaphragm Supported Liquid-Liquid Extraction with the Help of Hollow Fibre Modules

The Liquid-Liquid Extraction processes thus far described are based on the formation of an emulsion, and the phase separation, which then follows, which can cause quite a problem. A different approach is Diaphragm Supported Liquid-Liquid Extraction. In this case, the organic extraction medium and the carrier (electrolyte) are separated by a porous diaphragm. With a microporous, hydrophobic diaphragm the organic phase will spontaneously moisten the diaphragm and endeavour to get to the other side through the pores of the diaphragm. A slight over-pressure can avoid such penetration on the electrolyte phase. The interface point between the aqueous and the organic phases can in this manner be immobilised in the mouth of the pores. (Diagram. 6). The driving force for the exchange of material is the concentrate gradient. The liquids are simply led passed both sides of the diaphragm. It is possible to adjust the flow rate of both phases over a wide range, without fear of any penetration problems occurring. Furthermore, systems with a tendency to form emulsions can also be treated in this manner. Contrary to the systems described above, no moving particles will be found in the extraction unit.

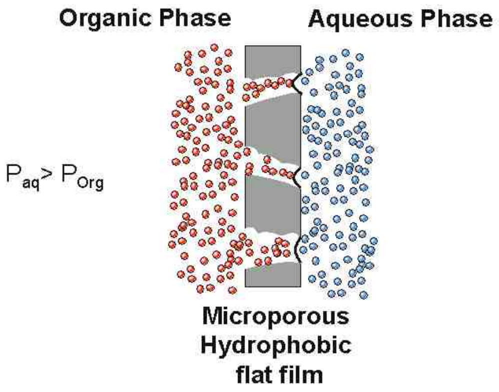

Figure 6: The Principle of Diaphragm Supported Liquid-Liquid Extraction

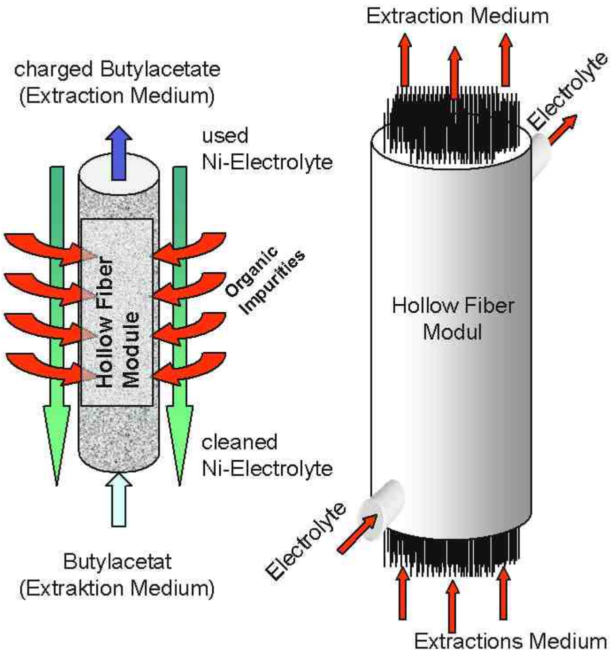

Figure 7: Hollow Fibre Module for Liquid-Liquid Extraction

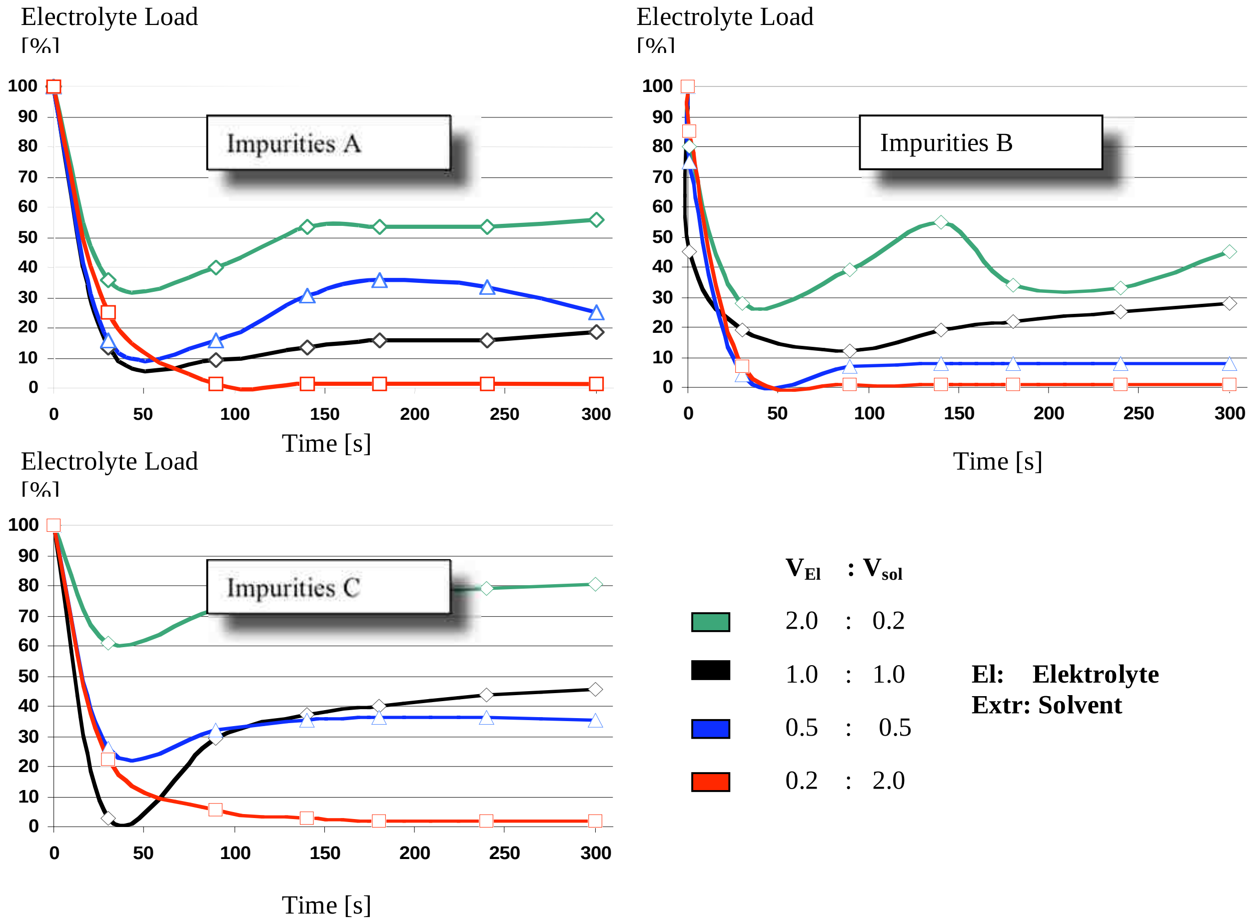

Figure 8: Electrolyte Cleaning Success Dependency on the Flow Rates of Extraction Medium and Electrolyte (V_{El} and $V_{Extr.}$)

A special case of the diaphragm process is the use of so-called hollow fibre modules. These consist of a large number of porous capillaries, through which extraction medium and electrolyte flow. (Figure 7). The tests illustrated here were carried out with hollow fibre capillaries with an inner diameter of about 1.8 mm, wall strength of 0.45 mm and a microscopically small pore diameter of about 200 µm. The Diagram 8 shows the influence the workload has on the cleaning results.

As expected, the success of cleaning will be better the longer the electrolyte stays in the system, and the more extraction medium butyl acetate is passed through the hollow fibre. All can be reduced up to 95%, so that a notable quality improvement is achievable. Even when the worst parameters possible were chosen, impurities were reduced by 20-50%. With by-pass operation this system can also considerably increase the operational life of an electroplating bath. Technical use is made difficult by virtue of the smell and the low ignition point of the butyl acetate.

SUMMARY AND CONCLUSION

Plating electrolytes in plating processes show increasing amounts of organic impurities. These impurities result from decomposition of organic additives, wetting agents and drag-ins. If the concentration of impurities in electrolytes exceed certain limits, plating errors occur. To avoid plating errors, two types of technologies were discussed in this paper: the adsorber polymer and the liquid-liquid extraction technology.

The adsorber technology is already used in several facilities. It is well known, user friendly and safe. Impurities can be removed from plating electrolyte in a “semi by-pass process” as regeneration of the adsorber polymer is necessary.

If the right adsorber system is chosen for a process the purification properties will show good results and increase the performance and stability of plating electrolytes. Impurities can be lowered significantly after passing the adsorber unit. Two points that have to be addressed are the investments and the higher cost for replenishments.

The liquid-liquid extraction, however, shows significantly higher selectivity concerning the removal of the breakdown products. Plating additives such as saccharine are not removed from the plating solutions while the extraction of impurities is highly efficient. The liquid-liquid extraction therefore is an operable by-pass process and will considerably increase the operational life of an electroplating bath. However, other problems may occur. Using the mixer settler principle (e.g. the turbo mixer and separator), the phase separation takes a long time. Although the best-in-class solvent Butylacetate does not affect the plating, the resulting vapour will cause exhaust and smell concerns.

To avoid these issues, the membrane system seems to be the best choice. Porous pipes allow the exchange of impurities without mixing. The phases will be kept separately. However, using this type of liquid-liquid extraction the pressure has to be kept stable on both sides of the membranes because of possible breakthrough. Additionally, technical use is made difficult by virtue of the smell and the low ignition point of the butyl acetate.

Plating facilities have to choose which technology they want to use: the established adsorber polymer technology or the more selective but more difficult liquid-liquid extraction technology. The first one is easy to handle, whereas the liquid-liquid extraction is highly selective but more expensive in regard of the special equipment beside. There are some risks that have to be considered (flammable extraction medium, smell and possible break through the hollow fiber modules).

Literature: will delivered later on