COMMUNICATION

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THE RECOVERY OF NICKEL
COPPER, CHROMIUM AND ZINC
FROM PLATING SOLUTIONS**

1. INTRODUCTION

The most fashionable word in the metal finishing industry these days is "recovery". There are plenty of recovery schemes offered in the trade journals. All of them claim to recover significant amounts of valuable materials lost in the drag-out. In addition to recovery of these chemicals, it is also claimed that recovery will help to approach zero discharge schemes which are supposedly being required by EPA in the 1980's. It is very difficult for the metal finisher to determine which of these systems can be beneficial in his particular process. This paper will make an attempt to guide the reader through the existing recovery systems and discuss the merits of each of them. Before discussing each system in greater detail, it seems appropriate to mention a few general points about recovery.

First of all, recovery should always be based on sound economics. This means that the value of the recovered material should result in a reasonable payback period on the required capital investment. The recovery method under consideration should be compared with simpler systems already in use for a long time. For example, a drag-out recovery station following nickel baths have been employed almost since the beginning of commercial high-production electroplating. An interesting fact, which is seldom fully appreciated is that this type of drag-out recovery rinse can return 40–50% of the nickel carried out of the plating bath. When the economics of sophisticated recovery schemes are considered, the calculated returned values should really be reduced by about 50% since that amount could be recovered with no investment in special equipment. By making special provisions in other plating systems, it is possible in a similar way to recover significant amounts of drag-out.

Another point that should be taken into consideration when evaluating recovery systems is that no recovery scheme will completely eliminate the requirement for waste treatment facilities. For example, a chromium recovery system will not eliminate the need for treatment facilities for hexavalent chromium. Most of the chromium will be recovered with the particular recovery system, but still, significant amounts of hexavalent chromium can enter the rinse water stream after rack stripping and by stripping of rejected parts. Also the racks themselves will carry hexavalent chromium in the crevices into subsequent process steps and rinse stations. The same reasoning applies to cyanide-containing plating baths. The effluent limits on cyanide are so strict that it will be very hard to meet these limits without any facilities for cyanide destruction.

Another general comment on recovery applies to the optimum percentage of the drag-out to be recovered. One should try to avoid the accumulation of impurities in the bath. For example, a recovery system

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aimed at 100 % recovery of the nickel drag-out would create serious problems in the plating bath after a while. The main concern tends to be with organic impurities, notably breakdown products of brighteners and leveling additives. Although removable by treatment with activated carbon, an increase in the frequency of this treatment is undesirable, both because it is costly in time, labor, and materials, but also because substantial volumes of nickel are often lost with the carbon sludge which can be recovered only by expensive filtration equipment. Also, in case of copper, chromium, and zinc plating, it is desirable to have a certain blowdown from the plating bath in order to reach an equilibrium for the impurities, rather than have a constant build-up.

2. RECOVERY METHODS

2.1. EVAPORATIVE RECOVERY

A very popular recovery method at this time is the removal of excess water from a recovery rinse stream so as to permit its return to the process bath. This can be accomplished in either a vacuum or atmospheric evaporation system. In general, the atmospheric evaporators have a lower initial capital investment. However, they do require the use of fairly high temperatures, such as 180°F, which eliminates them from use on applications where the process solution is sensitive to high temperature. A typical and very successful application for the atmospheric units is on recovery of chromium plating solution drag-out. A double benefit is gained in this case because the evaporating tower also serves as an excellent fume scrubber for the air exhausted from the plating tank.

There is also a wide variety of vacuum evaporators on the market. These units often require less space and are relatively easy to install. The optimum percentage recovery depends on the energy cost of the plant. Above a certain percentage recovery, the energy cost for the evaporation of the water will be higher than the value of the recovered material. Typically speaking, the optimum percentage recovery will be around 80–90%. Figure 1 shows a case for chromium recovery for which is calculated the return on investment versus the percentage of recovery. In this case, the optimum recovery is reached at around 90%. The calculations are based on the assumption of complete mixing in the rinse tank. Because in practice one will need more rinse water than calculated in this manner, the optimum recovery percentage will be somewhat lower.

In one plant, drag-out loss of chromic acid amounted to 700 lbs./day. The plant had installed an atmospheric evaporator which was supposed to recover 100% of this drag-out. The design flow to the evaporator was 15 GPM which resulted in prohibitively high energy cost for operation of the unit. By tolerating a daily loss of 30 lbs./day of chromic acid to the rinse waters, the flow to the evaporator could be reduced to 1.5 GPM. The savings in energy cost easily compensated for the minimal amount of chromic acid to be treated.

Another advantage of partial recovery is that, depending on the particular application of the plating bath, one might be able to eliminate the need for removal of impurities from the recovered drag-out if a blowdown of a few percent of the drag-out proves to be adequate for maintaining a low level of these contaminants.

2.2. REVERSE OSMOSIS

Reverse osmosis is another method of eliminating excess water from a recovery rinse stream. A number of commercial installations are operating successfully on the drag-out from nickel plating solutions. The overall effectiveness and efficiency of this application will depend on variables whose effect can only be evaluated over a long period of time. Some examples of these variables are:

a. The effect on plating solution balance and control of returning all of the dragged-out salts. A scheme designed for almost 100% recovery will increase the frequency of purification of the bath. In this way, one can lose significant amounts of chemicals. Again, a partial recovery system will prove to be advantageous.

b. The expense of cleaning or, more likely, replacing the membranes due to fouling.

In addition to the problem of membrane fouling, a wide application of reverse osmosis on process solutions is also limited by the chemical resistance of the membranes. Future development of membrane mate-

rial will undoubtedly improve the chemical resistance, but the overall cost effectiveness of the approach must always be compared to the available alternatives.

The application of reverse osmosis often is limited to plating baths with relatively high evaporation losses. The maximum practical attainable concentration of the rinse waters by applying reverse osmosis is around 2–3%. In most applications, this is not high enough for use as plating bath, and therefore further concentration is required by evaporation.

One will also have to realize that the membranes used in R. O. are not selective for all chemicals used in plating. For example, boric acid and coumarin are only rejected for a low percentage. This means that the chemical composition of the recovered drag-out will have to be adjusted before returning to the plating bath. In case the permeate is reused in the recovery rinse, one will notice an accumulation of these chemicals in the rinse water. This could cause problems in subsequent stations.

2.3. ION EXCHANGE

The ion exchange process will concentrate the cations or anions in a rinse water stream. Chemicals are required for regenerating the resin after it is loaded, so that the main advantage of the process is in concentrating materials which are removed from the rinse water. For example, a rinse water stream containing 50 ppm of nickel can be passed through an ion exchanger. When the unit is regenerated, the result will be a solution containing several ounces per gallon of nickel. However, this solution is generally not concentrated enough to return directly to the plating bath, so that further evaporation or some other recovery technique must still be applied. Furthermore, it should be remembered that approximately 50% excess regenerant chemicals are required so that the chemical expense frequently offsets a considerable portion of the recovery value.

The excess acidity in the recovered nickel salt might also prove to limit the reuse potential in the plating bath without proper treatment. Studies in our laboratory showed that in regeneration of a typical cation resin with 15 lbs./ft. [3] of sulphuric acid, only 85% of the nickel sorbed in the bed was recovered. The acid utilization was, in this case, around 50%. The maximum nickel concentration in the regenerant was $17 \, g/dm^3$.

Another application for ion exchange is the recovery of chromic acid. The ion exchange system will recover chromic acid plus excess regeneration chemicals. A barium treatment may be necessary to remove excess sulphate before return to the bath. A concentration step will often be required before reuse of the chemicals in the bath is possible because the product of the ion exchanger will contain only approximately 12 oz./gal. chromic acid.

Chemical consumption of a chromic acid recovery system is about 1–1.6 lbs, caustic and 2 lbs. sulphuric acid per pound of recovered chromic acid.

2.4. DRAG-OUT RECOVERY STATIONS

By far the cheapest recovery method is a drag-out recovery station after the plating tank. By making up evaporation losses from the plating tank with the recovered drag-out, one will be able to experience a significant decrease in the amount of plating chemicals lost in the rinse waters. In order to recover a high percentage of the drag-out, a few "tricks" might have to be employed.

First of all, evaporation losses can be increased by heating the bath during non-production hours. Secondly, one can obtain a difference in the volume of drag-in an drag-out of the plating bath by using air blowoffs after the rinse station before the plating bath. The difference can be made up by pumping out of the drag-out recovery tank.

Naturally, the higher the volume losses out of the plating tank the higher the percentage recovery. With the help of figures 2 and 3, the reader can estimate the potential for drag-out recovery in his particular application. With a minimal water flow in the drag-out station, it is possible to recover a significant portion of the drag-out. The figures provided are based on theory. One of the assumptions is that one will have complete mixing. This will be approached as closely as possible when one mixes the contents of the tank with air and moves the parts slowly.
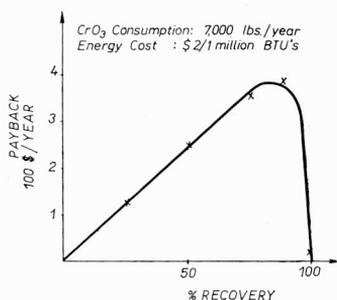
Fig. 1. Economics of evaporative recovery of chromic acid
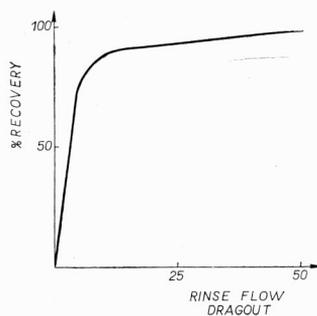
Fig. 2. Theoretical recovery potential for a drag-out recovery station
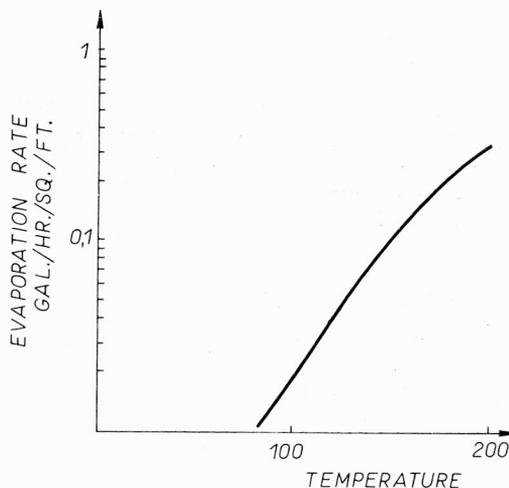
Fig. 3. Evaporation from water surfaces into stagnant air

In practice, it will be difficult to recover more than 50–70% of the drag-out chemicals because one has to keep the concentration of the plating bath chemicals relatively low in order to avoid passivation or staining of the parts on the one hand and, on the other hand, the evaporation and other losses of the bath are limited.

2.5. THE INTEGRATED RECOVERY SYSTEM

One of the oldest recovery systems in use is the integrated system after nickel, copper, and zinc plating. Figure 4 shows the general layout of such an integrated system. Normally, after the plating bath, one first has a drag-out recovery station in which a significant portion of the lost drag-out can be recovered as discussed in section 2.4. After the drag-out recovery station, the parts are immersed in the chemical rinse tank. An excess of treatment chemicals in this station removes practically all of the residual dragout from the film of the parts. The subsequent fast-flowing rinse will wash off the harmless salts from the parts. The integrated system will result in a dense metal hydroxide or carbonate sludge. In the case of copper and zinc cyanide plating, one destructs the cyanide and precipitates the copper and zinc in the oxide form. Due to the long retention time of the sludge in the reservoir of the Integrated System, the sludge will thicken
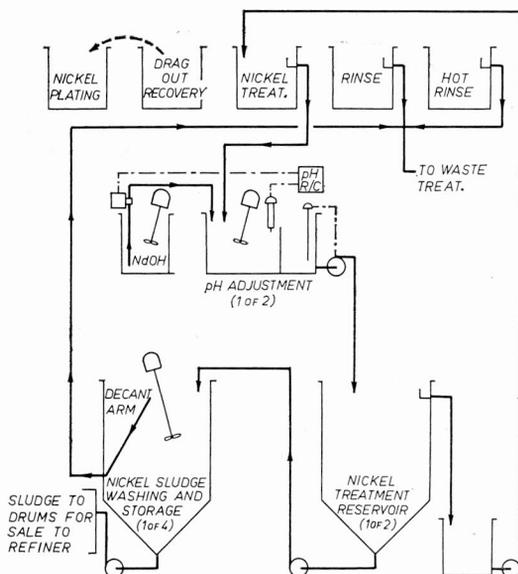
Fig. 4. Integrated nickel recovery system

to a high degree. Typically, the sludge blowdown of the reservoirs has a consistency of 5–10%. Depending on the quantities of sludge generated, one has the option to dispose of the sludge by sending it to a refiner, or to recover the metal value from the sludge at the site.

In the case of on-site recovery, one can recover the metal as a salt solution for use in the plating bath or as a metal by electrolytic recovery.

For example, nickel s`udge can be dissolved in sulphuric acid. In order to minimize the amount of impurities entering the plating bath, the sludge is first washed a few times before sulphuric acid is added. The nickel sulphate can be used as a make-up chemical in the bath. Also, the nickel lost with carbon treatment can be recovered in the same system.

The other recovery approach is to recirculate the dissolved metal salt through an electrolytic cell. The nickel, copper, or zinc will be collected in its metallic form with such a system.

When relatively small quantities of sludge are generated, it might be more economical to sell the sludge to a refiner or a chemical company. For example, we are able to sell the nickel containing sludges for $ 0,40 per lb. of nickel, which is 70% of its present market value.

2.6. ELECTRODIALYSIS

Electrodialysis should open up many opportunities to recover metals and plating solutions. Basically, the electrodialysis process uses an ion exchange membrane to separate two different electrolytes. If a process solution accumulating in metal is circulated through an anolyte compartment, which is separated from the catholyte compartment by a cation membrane, the metal ions can be passed into a catholyte solution. In case a valuable metal is involved, one can recover it by direct electrolytic recovery. The basic structure of an electrodialysis membrane is a non-conductive polymerized plastic film into which ion exchange polymers are cast in such a manner that the membrane will be selective for the passage of cations or anions. Figure 5 shows the regeneration of chromic acid etch solution by electrodialysis. The copper is transferred across the membrane to the catholyte. The copper is recovered in a small electrolytic cell. The trivalent chromium in the anolyte is oxidized to the hexavalent state. Another potential application for this process
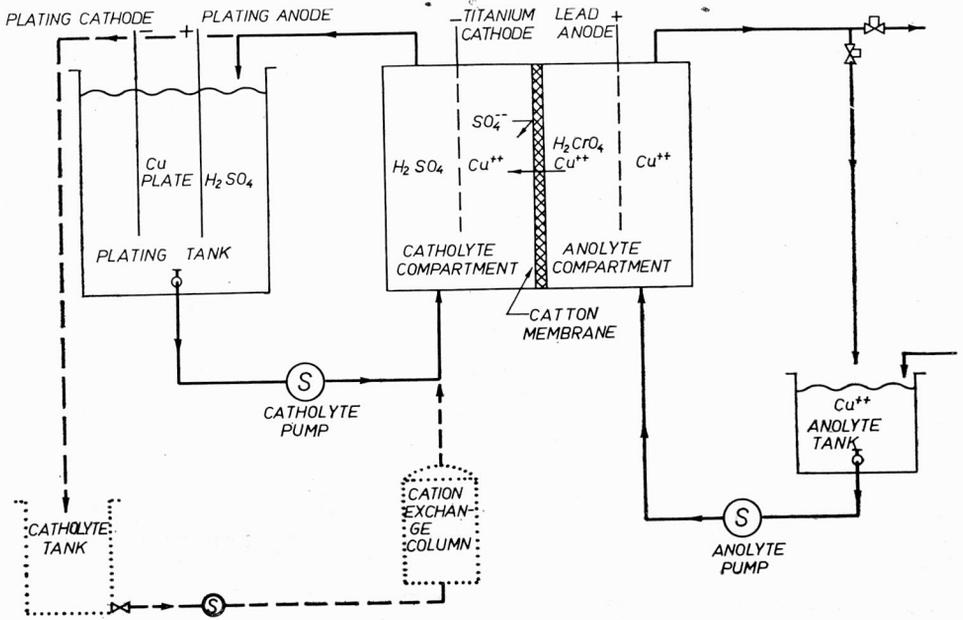
Fig. 5. Recovery of copper and regeneration of chromic acid with electrodialysis

si the continuous purification of chromium plating baths. This system is still in the pilot stage. The major porblem encountered in the development of the process is to find materials of construction that will guarantee long-term operation. We are confident, however, to be able to market such a system within the near future.