DEVELOPMENT OF A PORTABLE PILOT LINE FOR PURIFICATION OF SPENT PLATING BATHS FROM THE SURFACE TREATMENT INDUSTRY

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ABSTRACT
Electroplating is a flexible low-cost method of manufacturing metallic coatings via the application of electric current through an electrolytic bath, resulting in the reduction of metal cations to their metallic state and subsequent deposition on metal surfaces. This surface treatment can significantly enhance the properties (mechanical strength, chemical resistance) and improve the appearance of various metallic objects and components used in a variety of industries such as aerospace, automotive, medical, electronics, batteries. However, lower than ideal current efficiency during the electroplating process results in the accumulation of metal cations within the electrolyte bath. The gradual increase in the concentration of metal cations reaches a threshold beyond which the electrodeposition yield is dramatically decreased, and the bath is characterized as ``spent``. The spent baths should then be removed and transferred to dedicated recycling centers [1]. The electroplating industry produces a total amount of 300.000 tons of hazardous wastes per year in the EU area [2], which is addressed as a hazard problem.
Creative Nano (Cnano), as a partner in the H2020 EU funded PureNano project, has developed a low cost, sustainable by design method for the purification of spent Ni-based electroplating baths which can significantly extend their operational lifetime and decrease their environmental impact. Purification is carried out by capturing excess Ni species on the surface of Fe_3O_4-based magnetic nanoparticles (MNPs) which are then removed from the plating bath via magnetic filters [3,4]. In house lab scale experiments verified that approximately 10% of Ni(II) cations can be captured from an aqueous solution containing dissolved Ni(II) salts within 5 min after the addition of MNPs at the required Ni/MNP ratio. Creative nano has already installed in its premises and is currently testing a pilot line, capable of purifying and regenerating spent Ni-based electrolyte baths up to 120 L. The purification pilot line consists of two tanks with integrated motor stirrers, two magnetic filters for removing MNPs and an air diaphragm pump for recirculation of the electrolyte. All parts of the remote pilot line are interconnected with flexible PVC pipes. Operation of the pilot line and preliminary results will be presented hereby.

KEYWORDS: Purification, pilot line, spent electrolytic bath, MNPs

1. INTRODUCTION
Electroplating is a low-cost method to produce metallic coatings for several applications. Coatings produced through electroplating method can be used in jewellery, electronics or other industrial applications. A serious challenge encountered during electroplating is the increase of metal concentration in the electrolyte bath that leads to the gradual deterioration of the whole electrolyte. After a specific threshold, the electroplating bath is characterized as ``spent`` and has to be replaced. This produces a significant amount of waste that must be recycled. Therefore, it is of utmost importance to find a way to purify or regenerate the spent baths and ether extend their life cycle to reuse them.

The PureNano project proposes a way to purify Ni-based electrolytic baths using functionalized magnetic nanoparticles (MNPs) that can capture the excess nickel species and restore the electrolyte composition. A specific amount of functionalized MNPs is added in the spent bath and the mixture is stirred for a certain time period to capture excess Ni species. Afterwards, the MNPs-nickel aggregates are removed with the aid of magnetic traps. Important part of the PureNano project is the development of two diverse pilot lines. The first one is used to purify baths coming from electrolytic processes while the second one is used to purify baths coming from electroless plating processes. The portable electrolytic pilot line was designed, manufactured and installed in Cnano`s premises. Herein, the purification method and the various system components are presented. Moreover, the manufacturing process and the integration of the system are discussed, and preliminary results are reported.

2. METHODOLOGY

The scope of the process is based on mixing the MNPs with the spent bath in a given ratio, this allows capturing the excess nickel and finally removing the MNPs-nickel aggregates from the bath. The Fe_3O_4-based MNPs have a ferromagnetic core and an outer customizable coating to capture Ni ions with a removal capacity of approximately 200-250 mg MNPs/ g Ni [3,4]. The ferromagnetic core allows an easy and faster method of separation by applying an external magnetic field.

The simplest way for the removal of aggregates is a standard nanoporous filter, however some of the baths used by Creative Nano, contain reinforcing nanoparticles to produce nano-composite coatings, which makes the process even more complex. In these cases, the use of a filter is less advisable, and this is attributed to the fact that the reinforcing nanoparticles will be removed together with the MNPs. For that reason, it was crucial to design a process that includes a filter which will only remove the MNPs-nickel aggregates. In order to overcome the latter issue, magnetic filters (traps) were used to only trap the magnetic species.

Following that, the type of magnetic traps had to be selected. Nevertheless, the commercially available magnetic traps present significant drawbacks related to the handling of the electrolytes. All commercial products are based on a single inlet and outlet configuration. Accordingly, in this case the risk of having residuals from the electrolyte in the bottom of the trap was faced. Moreover, the commercial traps come with only one or two magnetic bars. In order to remove more efficiently the MNPs, traps more magnetic bars should be utilized. Hence, Cnano designed and manufactured customized traps to accommodate its electroplating process requirements, instead of purchasing any commercially available solutions. The customized traps have more magnets to “catch” more MNPs and two outlets, one in the upper side, and one in the bottom for drainage. The customized magnetic traps are made of two parts, the cap where the magnets are attached and the container where the spent electrolyte passes through and exposed to the magnets. The cap can be easily removed to clean the attached magnets.

The type of the pump used for recirculation is also important. For apparent reasons, the presence of MNPs eliminated the option of using a simple magnetic pump, thus, air diaphragm pumps were used. Diaphragm pumps are air-operated, positive-displacement, self-priming pumps. They have an air inlet that moves the diaphragms that are installed in the center of the pump and create a pressure difference that drives the liquid transfer. The main disadvantage of the diaphragm pumps is that they generate pulse flow. To overcome this problem and obtain a smooth flow that is necessary for effectively trapping the MNPs, a dampener was used. Diaphragm pulsation dampeners consist of a pneumatic actuator connected to the diaphragm. The sturdy outer body forms the actuator’s compressed-air chamber for suppressing pressure surges on one side of the diaphragm and the chamber through which the fluid flows on the other. The ability of the dampener to minimize pulsation, vibration, and hydraulic shock (water hammer) enabled excellent protection and smooth system flow.

Concernig the purification process, the spent bath is mixed with the MNPs with the aid of a motor stirrer in the main tank which has an outlet at the bottom. The amount of MNPs added is selected based on the Ni species concentration of the spent bath. After 20 – 30 min of stirring [3], the mixture is transferred to the two magnetic traps with the aid of a diaphragm pump. A system of valves directs the mixture to one of the two traps. In this way, one trap can be opened and cleaned to collect the captured MNPs while the other is still working. Once the mixture passes through the magnetic traps, it is circulated back into the main tank. The recirculation of the spent bath and the periodic cleaning of each trap during the process while the other one is working ensures that all MNPs-nickel aggregates are captured and removed from the electrolyte. Once the purification process has finished, the electrolyte is transferred to the second tank (right). Importantly, an exhaust system has been installed at a lower level to avoid leakages when one trap is opened for cleaning. The whole purification system is "portable" and can be transferred to different locations of Cnano's plating facilities with the aid of a platform. The main parts of the pilot line are presented below.

2.1. Main parts

A. Reactors/tanks

Two main tanks were designed. They are made of stainless steel AISI 316, they have a motor stirrer in the middle to mix the electrolyte and the MNPs, a cone-like bottom in order to achieve drainage, an opening cap that enables the recirculation of the electrolyte, and finally four wheels that enable easy transfer.

B. Magnetic traps

Magnetic traps are built from two parts that were manufactured by two different companies. The first part is the cap of the trap that was manufactured by a magnet-specialized company. The second part is the container of trap that was manufactured by an iron-specialized company. All parts are made from AISI 316 stainless steel to prevent corrosion.

C. Pumps and compress air device

Air diaphragm pumps had to be used, since magnetic pumps would capture MNPs. Therefore, a 7.5 hp air compressor was installed in Cnano`s premises with an air capacity of 100 L/min, as well as air regulator to control the electrolyte flow rates in the process. The air diaphragm pumps have a maximum flow rate of 72 L/min.

D. Dampener

A dampener was purchased to achieve smooth flow in the process and avoid cavitation. The dampener has an air inlet of 4/6 in order to achieve smooth flow. A small air inlet was used for this reason.

E. Piping system

In order to achieve flexibility in the portable system, reinforced PVC flexible pipes were selected, as they present excellent acidic resistance. Additionally, HDPE pipes were used in some points of the portable pilot line. HDPE also presents excellent acidic resistance.

Figure 1: PVC reinforced pipe.

Figure 2: HDPE pipe.

F. Platform

To enable portability of the whole system, a stainless-steel platform with 4 wheels was designed and manufactured. The dampener with its base, the pumps and the magnetic traps can be placed on the platform and transferred to different locations within Cnano's plating farcicalities.

3. RESULTS & DISCUSSION

3.1. Manufacturing and integration

Following the designing and dimensioning process, all the parts were manufactured and installed in Cnano premises. Furthermore, stainless steel 316 ball valves were purchased and installed in the portable system to control the flows. The final portable system can be seen in Fig.3.

Figure 3: Final purification system.

An inox ball valve was installed in the tank to control the flow right after the tank. After that, a flexible PVC pipe was connected with the diaphragm pump. A HDPE pipe was chosen as the outlet of the pump to achieve stability in the connection between the pump and the dampener. After the dampener a ball valve was installed to further control the flow. Subsequently, the first separator was installed to separate the flow to the two magnetic traps and have the ability to clean the traps separately without interrupting the process.

3.2. Initial tests of the purification system

After the remote purification system was installed, first runs were performed using reversed osmosis (RO) water. After the first run, three problems were identified: cleaning process of the magnetic traps, remnants in the piping system, and a welding issue. The optimization of the cleaning process was achieved by adding three extra exhaust valves. These valves were integrated in the lower level of the line. They are opened when the traps are cleaned to prevent leakages due to fluid returns. In this way, the returns are collected through the exhaust valves and added back into the main tank. Moreover, the remnants at the end of the process are also removed and collected via the exhaust valves. The welding problem was solved through cold welding. After the final integration, runs with nickel salts and MNPs in water with or without SiC nanoparticles were performed.

3.3. Pilot scale experiments

Subsequently, pilot scale experiments were performed to check the operation of the line and evaluate the proposed method in a simulated semi-industrial environment. A water solution containing the nickel salts, the surfactants and the SiC nanoparticles at the concentration of a standard Ni-P/SiC electrolyte was prepared according to Table .

Table 1: Composition of nickel salts and nickel salts solution with SiC

Component	Concentration (V = 10 L)
$NiSO_4$	260 g/L
$NiCl_2$	48 g/L
SDS	2.5 g/L
SiC	10 g/L
MNPs	8.8 g/L

The solution (10 L) was mixed with MNPs in the main tank and the mixture was stirred for 20 minutes before the start of the process. The air pressure supply of the pump was set to 1 bar, corresponding to flow of 10-20 L/min (Figure 1). The flow was periodically switched between the two magnetic traps as described above. The entire purification process lasted 2 hours. Samples of the solution were collected before (t=0) and after the 2 h treatment and analysed with ICP. A second experiment was run in the absence of SiC NPs. The Ni concentrations are listed in Table . For the solution containing SiC NPs, a 12.0% removal of Ni species was observed after 2 h of purification. Likewise, for the solution without SiC NPs, 10.3% removal of Ni species was observed. Importantly, ICP did not detect and Fe or Si species, suggesting that SiC and MNPs remained intact during the process.

Table 2: Nickel concentration before and after purification

Time (h)	Ni (g / L)	Removal (%)
0	7.00	
2 (with SiC NPs)	6.16	12.0
2 (without SiC NPs)	6.28	10.3

In conclusion, a portable purification pilot line was designed, manufactured and integrated in Cnano's premises. Cnano designed a part of the equipment to meet some of its needs. First trials led us to identify leakages and operational problems. After the final integration the proposed purification method ran with solutions of nickel salts with or without SiC nanoparticles. Preliminary results suggested that approximately 10% of nickel ions was successfully captured and removed. Future work within PureNano involves the synthesis of MNPs that are stable at lower pH and optimization of the pilot line parameters with respect to time, loading and removal of nickel species.

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