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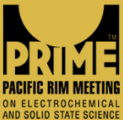
Reducing the risks of water and territory pollution by toxic metal-containing effluents of machine-building industry

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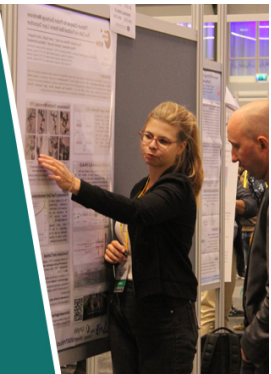
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Reducing the risks of water and territory pollution by toxic metal-containing effluents of machine-building industry

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Abstract: The article is devoted to the baromembrane method for cleaning washing waters of degreasing sites and for the bright nickel plating of galvanic productions. The authors analyzed specific features of technologies for part metallization in terms of the formation and separation of washing wastewater flows for their separate cleaning. Studies were carried out on the membrane extraction of nickel sulfate and sodium phosphate compounds on two types of membranes: nanofiltration OPMN-P and reverse osmosis Hydranautics ESPA-1. High selectivity (98-99,9%) and specific productivity of OPMN-P membranes (25 l/m² per hour) were proved during the extraction of nickel sulfate and sodium phosphate at concentration ranging from 50 to 200 mg/l specific to washing water of the processes of degreasing and bright nickel plating. The advantage of using nanofiltration membranes OPMN-P over reverse osmosis Hydranautics ESPA-1 membranes was substantiated. A technological scheme to create a closed water supply system at these sites was developed.

1. Introduction

Machine-building industry, the most important technological stage of which is the processing of metal products by applying various kinds of metal coatings, can be considered a critical infrastructure as it is extremely water-intensive and environmentally hazardous.

Technological lines of part metallization are linked to chemical and electrochemical treatment of metal surfaces in a water medium. Therefore, the formed wastewater contains toxic compounds of surfactants, acids, alkalis and transition metals ranging from tens of milligrams to hundreds of grams per 1 dm³ [1, 2]. Soluble complex compounds of heavy non-ferrous metals (copper, nickel, chromium, cadmium) are especially dangerous, since they are difficult to neutralize in traditional treatment facilities and pose a threat to the pollution of water bodies [3]. These toxic substances can cause diseases of the central nervous system, blood vessels, heart, liver and other organs in humans. In addition, they have a mutagenic effect, both for humans and aquatic biota.

To this end, the task of improving the technology of purification of metal-containing wastewater in order to create closed technological cycles and reduce the discharge of polluted effluents into bodies of water is highly relevant.

2. Specific features of the part metallization technologies

The process of applying metal coatings usually consists of two stages that is preparation of the product surface for coating (mechanically or chemically) and application of coating [4, 5]. Because of these processes, two main types of effluents like waste electrolytes and various washing waters are formed.



As a rule, concentrated effluents are regenerated and processed individually in each specific metallization line.

After each of the preparatory and basic technological operations the product is washed in cold or hot water. Washing products after the electrolyte bath helps to maintain the chemical composition and purity of the solution in a subsequent processing bath. The washing is usually carried out in the flow-through baths.

This method of washing uses a large amount of water (up to $2 \text{ m}^3/\text{m}^2$ of coating), and a significant amount of electrolyte enters the wastewater. Reduction of the amount of washing water and decrease in the loss of metals can be achieved through the installation of recovery baths, the use of advanced washing methods, etc. [4, 6].

All waste waters from the chemical and electrochemical metal processing are divided into three main groups based on the content of contaminants: cyanide-containing (contain highly toxic hydrocyanic acid compounds); chromium-containing (contain highly toxic compounds of chromium (VI)); acid-alkaline (contain free mineral acids and alkalis, salts of heavy, alkali metals and ammonium, organic compounds, etc.) [5].

The joint disposal of cyanide-containing and acid-alkaline or chromium-containing wastewater is unacceptable because of the possibility of formation and emission of highly toxic gas - hydrogen cyanide - into the production facilities. The joint disposal of chromium-containing and acid-alkaline wastewater and their subsequent neutralization inevitably results in a significant overexpenditure of reagents.

Therefore, cyanide-containing and chromium-containing effluents are processed separately and the solutions of the recovery baths and washing waters in the areas of nickel plating, copper plating, galvanizing, degreasing and other operations are mixed in acid-alkaline waste and sent to a neutralization station. Neutralization of ions of heavy non-ferrous metals is carried out through adding water-soluble alkaline reagents to wastewater. As a result, metal ions are converted into sparingly soluble hydroxides that precipitate. Flocculant polyacrylamide is used for better and more complete and rapid coagulation of hydroxides. The clarification time of neutralized water is 40 - 60 minutes; the sediment volume is up to 10% of the total volume of the liquid [1, 7].

The reagent method is the most widespread in the Russian practice of neutralizing the wastewaters of galvanic productions. Its main advantage is an extremely low sensitivity to the initial content of contaminants. The main disadvantages are high residual salinity of purified water and high humidity of the sediment. This calls for additional purification of clarified water, as well as construction of facilities for sediment dewatering [8].

The amount of many components in the treated wastewater exceeds the maximum permissible discharge values for both urban sewerage and water bodies. The existing approach - neutralization of the general wastewater - leads to a presence of sediment with a high content of heavy metals, which cannot be extracted due to its complexity. The sediment is currently subject to landfill. The amount of sediments is constantly increasing. Today, they are the main pollutants of the environment on the territory of cities with machine-building industries.

3. Experimental results

To solve this problem, the authors conducted research at one of the machine-building enterprises in Ekaterinburg. The research focused on the possibility of processing the nickel sulfate and sodium phosphate electrolytes using membrane plants equipped with the OPMN-P nanofiltration membrane.

The choice of this type of membrane is due to the effective parameters of membrane separation, i.e. high specific permeate productivity and selectivity in many components (including various electrolytes in a soluble form). In addition, affordability and availability of domestic production of these membranes make them extremely attractive for use in treating wastewaters from ions of heavy non-ferrous metals.

The authors carried out experimental studies on membrane purification of washing waters of the bright nickel-plating process with a concentration of nickel sulfate in the 10-50 mg/l range, as well as

of washing waters of the degreasing process with a concentration of sodium phosphate in the 5-100 mg/l range. Moreover, in order to study the membrane characteristics at various concentrations of electrolytes, the authors conducted experiments on the concentration of washing waters to 10 g/l for nickel sulfate and sodium phosphate respectively.

The experiments were carried out on a roll-type laboratory membrane installation using various types of membranes: nanofiltration OPMN-P and reverse osmosis Hydranautics ESPA-1.

The aggregated results of the experiments are shown in Figures 1 and 2.

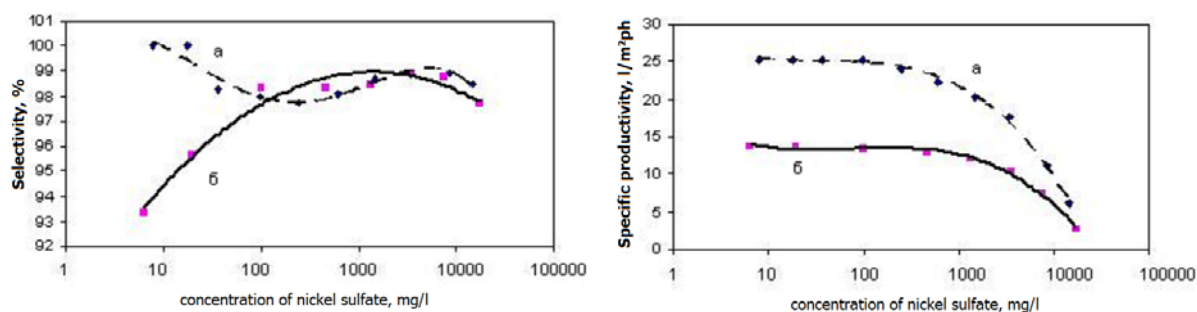


Figure 1. Dependence of selectivity and specific productivity of membranes on the concentration of nickel sulfate; operating pressure 0,4 mPa, solution temperature 22°C
membranes: a – OPMN-P, b – Hydranautics ESPA-1.

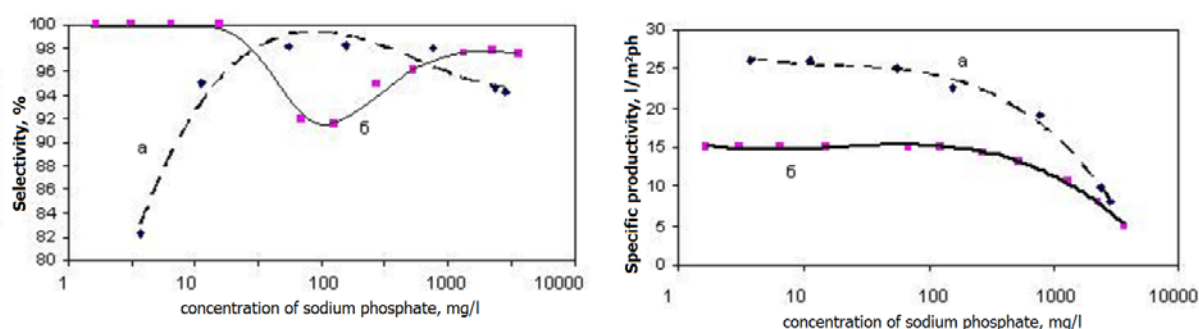


Figure 2. Dependence of selectivity and specific productivity of membranes on the concentration of sodium phosphate; operating pressure 1,0 mPa, solution temperature 22°C
membranes: a – OPMN-P, b – Hydranautics ESPA-1.

Figure 1 shows that the nickel sulfate selectivity of the OPMN-P membrane at the concentrations typical for the washing waters of the nickel-plating process (ranging from 10 to 50 mg/l) has a maximum value of about 99.9%. A further increase in the concentration to 1000 mg/l leads to a slight decrease in selectivity to a level of 97.5–98%. High selectivity of this type of membrane is due to the presence of a negative charge on its surface. In this case, even the ions, which are smaller than the diameter of the membrane pores, are electrostatically repelled from its surface and remain in the concentrate stream.

In this concentration range, the specific productivity of the OPMN-P membrane remains stable – 25 l/m² per hour. However, further concentration leads to a sharp decrease in the specific productivity of the membrane, which is unacceptable.

In contrast, the membrane separation parameters of the reverse osmosis membrane Hydranautics ESPA-1 are much lower in given concentration range: selectivity is only 93-95% and specific productivity is 15 l/m² per hour, which is 1.7 times lower than that of the OPMN-P membrane.

A series of experiments on the membrane extraction of sodium phosphate, the results of which are shown in Figure 2, demonstrate that specific productivity of Hydranautics ESPA-1 membrane is significantly lower than that of the nanofiltration membrane at close values of sodium phosphate membrane selectivity at a concentration of 50 to 80 mg/l (approximately 98.4–99.9%), and it decreases with increasing solution concentrations.

Thus, the possibility of use and effectiveness of Russian nanofiltration membranes OPMN-P in the development of technologies for cleaning washing wastewater from galvanic productions has been proved.

Based on the research results, the technologies of separate processing of individual solutions of galvanic lines have been developed. The basis of the implemented technological schemes is the membrane concentration of the recovery baths solutions in degreasing and bright nickel-plating sites. These technologies made it possible to reduce significantly the removal of nickel and phosphate ions to general wastewater treatment plants. However, they did not solve the problem of a large consumption of washing water, which is irrationally discharged into the city sewage system.

Thus, a new technological scheme has been developed (Figure 3) that allows comprehensively processing washing solutions of degreasing and bright nickel-plating sites, preventing their discharge into acid-alkaline wastewater.

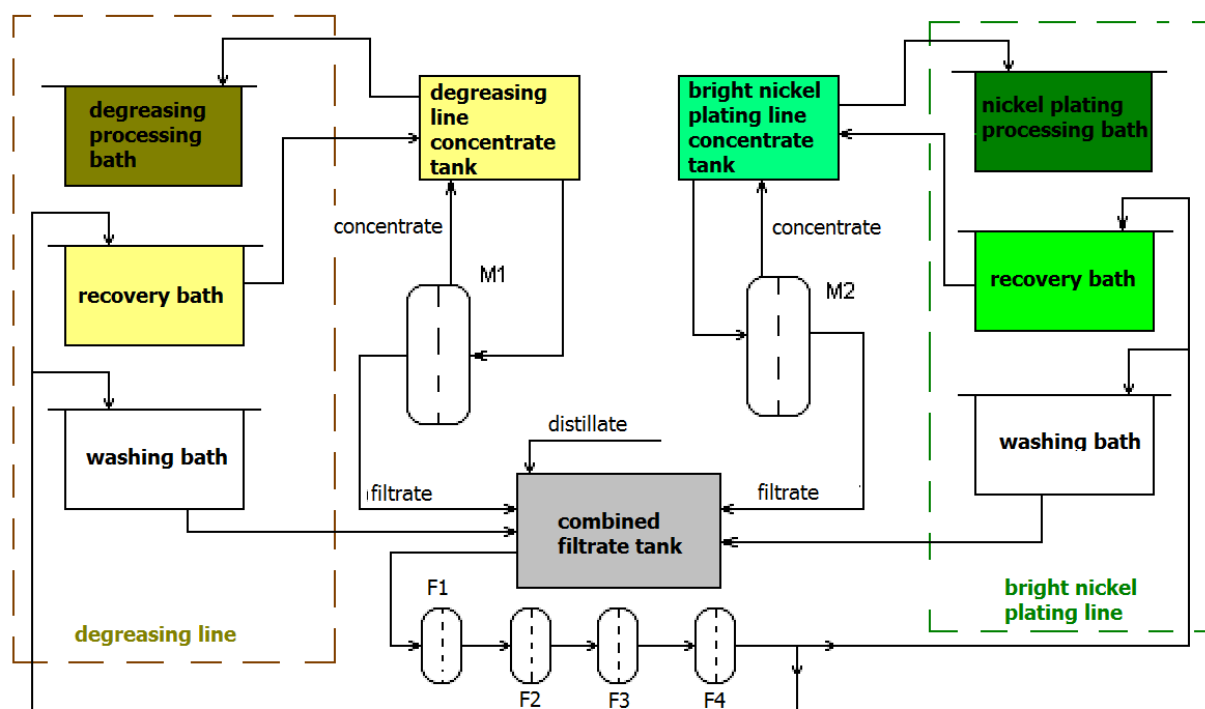


Figure 3. Technological scheme of the installation for complex processing of solutions of recovery baths and washing baths in the degreasing and bright nickel plating sites; M1 – degreasing line membrane unit; M2 – bright nickel plating line membrane unit; F1 – mechanical cleaning filter; F2 – sorption filter; F3 – H-cation filter; F4 – OH-anion filter.

Basic components of the degreasing solution are sodium phosphate and caustic soda. The salt composition of the technological solution of bright nickel plating is determined by nickel sulfate.

According to the technological scheme, the solution of the degreasing line recovery bath is periodically discharged into the concentrate tank of the degreasing line. This solution is concentrated

as follows: the solution from the concentrate tank of the degreasing line is directed to the membrane unit. Two streams are formed at the exit from the membrane unit:

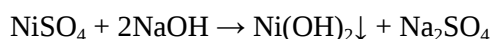
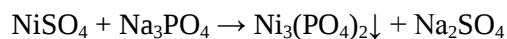
- concentrate (with increased salt content);
- filtrate (permeate with low salt content).

Concentrate is returned to the concentrate tank of the degreasing line, and permeate is returned to the combined filtrate tank. Thus, a solution with a low salt content leaves the concentrate tank and the concentration occurs. The concentrated solution, if necessary, is sent to compensate for the losses in the processing bath of the degreasing line.

The solution of the recovery bath of bright nickel-plating line is pumped to the concentrate tank of the bright nickel-plating line. This solution is concentrated similarly to the concentrate of the degreasing line.

The filtrate is sent to the combined filtrate tank, and the concentrated solution is sent to compensate for the losses in the processing bath of the bright nickel-plating line.

The filtrates are mixed in a combined filtrate tank, in which the following reactions occur:



The formed sediment of nickel phosphate is retained on the mechanical filter (F1). Sulfate ion, chloride ion and excess phosphate ion are retained on the anion exchange filter (F4). Sodium ion is retained on the cation exchange filter (F3). Organic substances and surfactants, which could have entered washing baths on the surface of the parts, are retained on the sorption filter (F2). The resulting desalted water is sent to the recovery and flow-through washing baths.

The scheme implements the circulation of water from the flow-through washing baths through a combined filtrate tank.

It should be noted that for continuous operation of ion-exchange filters, it is necessary to adjust the technological process in such a way that the solutions of both recovery baths are treated simultaneously.

The issue of regeneration of ion-exchange filters was not considered, since the salt content of the combined filtrate is less than 20 mg/l, and simple replacement of ion-exchange resins or cartridges is the most rational option.

4. Conclusions

Based on the results of the experiment, OPMN-P nanofiltration membrane having higher productivity compared to reverse osmosis membranes was chosen for complex solutions processing of recovery and washing baths in the degreasing and bright nickel-plating sites. Thus, during the concentration of a nickel sulfate solution on the OCMN-P membrane from 0.5 g/dm³ to 1 g/dm³, electricity consumption is 34% lower than during a similar process on the Hydranautics ESPA-1 membrane.

The developed technological scheme allows to:

- return valuable components to processing baths;
- completely stop the discharge of solutions of the recovery baths and washing water into the acid-alkaline stream;
- create a circulating water supply system in the degreasing and bright nickel plating sites.
- In the future, the introduction of this technology will reduce the pollution of water bodies with metal-containing wastewater and improve the ecological situation in Ekaterinburg.

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