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TREATMENT OF ELECTROPLATING SHOP WASTEWATER AT ENTERPRISES OF THE REPUBLIC OF BELARUS

This paper presents an overview of galvanic production in the Republic of Belarus are considered employed in this production of water supply, as well as requirements on the quality of water for electroplating. Based on the analysis of treatment facilities plating plants (sites) of the enterprises of the Republic of Belarus. It was found that as the main wastewater treatment used elektrokoagulation, reagent treatment, including the use of ferroferrigidrozol and galvanokoagulation. The basic shortcomings of existing treatment systems and provides general recommendations on improving the efficiency of their operation.

Introduction. On the largest Belarusian enterprises of machine building, instrument making, metallurgy the processes of metal plating and surface treatment are used in order to give it the necessary properties. The electrochemical (galvanic) coating method is the most widespread and is used for metal plating, and also for obtaining of oxide films when anodic processing of the products. Its main advantage is considered to be able to obtain coverages of desired thickness - from a few to tens and even hundreds of micrometers. In the surface treatment processes in order to provide it with anticorrosive and decorative properties a variety of reagents containing heavy metals are used. They are part of the by-products of this production – solid and liquid wastes, wastewaters, air emissions.

As a result, enterprises in which electroplating shops (sites) operate are the main sources of toxic heavy metals discharge to the environment. At that the prescribed standards for allowable concentrations of heavy metals ions for wastewaters discharged into the sewer system are often not implemented, which complicates the work of municipal wastewater treatment plants. At wastewater treatment of electroplating plants on local treatment facilities the sediments are produced that relates to the wastes of 3–4 class hazard. In the process of technological solution application sludges are formed, which are practically not used but are stored at the sites of enterprises. That's why the aim of this work is to analyze the effectiveness of existing treatment facilities of electroplating enterprises in the RB and the development of general recommendations for their improvement.

Main part. In Belarus, galvanic production operates in more than 140 plants (Table 1) [1].

The largest among them are: RUE "Byelorussian Steel Works" (Zhlobin), RUE "Gomel casting and normal Plant ", JSC "Minsk Bearing Plant", RUE "GomSelmash "RUE" BelAZ "(Zhodino) PRUE" Minsk Automobile Plant " RUE "Minsk Tractor Plant", JSC "Atlant" (Minsk), RUEG "Vityaz" (Vitebsk), etc. The most widely used are zinc, chromium, nickel, copper and cadmium coatings.

The electroplating production impact on the environment depends largely on the organization of the water sector, the effectiveness of the treatment facilities and the use of sediments and sludge generated during the production.

General water quality requirements for galvanic production, ways of its rational management and the use of low-water and low-waste leaching circuits are established SS 9.314-90.

Table 1

Distribution of enterprises having electroplated production by regions of the Republic of Belarus

Region	The total number of enterprises	Number of enterprises in which sewage sludge and electroplating production sludge are formed			
		to 1 т	from 1.1 to 10 т	from10.1 to 100 т	more than 100.1 т
Brest region	19	10	7	2	–
Vitebsk region	13	9	3	1	–
Gomel region	23	13	4	3	3
Grodno region	18	10	8	–	–
Minsk region	16	8	6	2	–
Mogilev region	16	7	6	3	–
Minsk	37	14	12	9	2
Total	142	71	46	20	5

In the electroplating industry direct-, back- and combined-flow systems of water supply are used.

Direct-flow system of water supply provides a single water use with the following discharge into the sewer after appropriate purification. Reusable water system (reverse system) is focused on multiple water use in production after cleaning and can be centralized, local and mixed. Centralized system involves the collection and combined treatment of all wastewater types on single treatment plants and subsequent distribution of treated water according to the technological operations. The post-treatment of the purified water and its feeding in the rinse tanks, which require high water quality, is possible. Local water system suggests rinsing water cleaning after a single technological operation, and its return for washing after the same operation. Mixed water system provides rinsing water cleaning on local units after each technological operation with discharge of water treated at these facilities to centralized post treatment facilities and then further return to the wash.

Water in the electroplating industry depending on the application area, is divided into three categories (Table 2) [2].

Process water used for washing products, parts and preparation of electrolytes and solutions in the electroplating production, must be safe in the epidemiological relationship and chemically inert to the coating. Physico-chemical characteristics of the water used in the electroplating production, must meet the requirements given in Table 3 [2].

Water consumption in the coating processes largely depends on the allowable concentrations of the components of technological solutions in the rinsing waters, on the accepted washing scheme and on the availability of trapping bath. Using multistage schemes of washes and trapping baths allows reducing water consumption up to 4 times.

Creating a fully decentralized wastewater treatment of electroplating plants, as a drainage system of water economy of electroplating production is practically impossible, since even after repeated use of electrolytes in the process of their regeneration wastewaters requiring neutralization are produced, there are bath leaks and overflows, wastewaters from washing and cleaning equipment, etc., therefore the mandatory centralized treatment facilities are required.

Taking in consideration the potential hazards of pollutants contained in the wastewater normative requirements towards them are constantly tightened.

Normative requirements established for electroplating wastewater production in the EU significantly vary in different countries (Table 4) [3].

In the Republic of Belarus, the requirements for wastewater until recently have been regulated in terms which were established by local executive committees. The control was carried out by organizations that provide disposal and treatment of wastewater (water and wastewater treatment plants). For example, in accordance with the decision of the Minsk City Executive Committee "On the wastewater admission conditions to the Minsk municipal soil piping" the list of pollutants and their allowable concentrations at wastewater discharge to Minsk municipal soil piping from machine building, machine-tool and electrical industry are the following [4]: pH – 6.0–9.0; COD – 400 mg O_2/dm^3; suspended solids – 300 mg/dm^3; ammonia nitrogen – 10 mg/dm^3; phosphates – 5 mg/dm^3; solids – 1000 mg/dm^3; surfactants – 4 mg/dm^3, chromium (VI) – 0,1 mg/dm^3; chromium (III) – 0,4 mg/dm^3; iron – 2 mg/dm^3; copper – 1 mg/dm^3; phenols – 0.002 mg/dm^3; zinc – 2 mg/dm^3; nickel – 1 mg/dm^3, lead – 0.5 mg/dm^3; cadmium – 0.5 mg/dm^3; cobalt – 0.1 mg/dm^3; petroleum products – 0.9 mg/dm^3.

In comparison with regulations in other countries the requirements established in the Republic of Belarus are softer relative to such indicators as COD and suspended solids, but relative to other indicators they are in the concentration range established for different EU countries. Since January 1, 2013 in the Republic of Belarus there is enacted 17.06-08-2012 TAP (02120). In the Tables 5 and 6 there are presented allowable concentration values of polluting substances contained in industrial wastewater of metal processing enterprises discharged into water bodies and in soil piping of settlements in accordance with the named TAP [4].

Table 2

Fields of application of water in electroplating production

Water category	Field of application	Additional instructions
1	Washing of parts in operations of surface-to-cover preparing, except for the 2nd and 3rd categories	–
2	Preparation of electrolytes and washing in all cases except for those listed for water of the third category.	The water used for washing, can be applied repeatedly as a 1st category water
3	Preparation of electrolytes and washing before processing in electrolytes (solutions), compiled on the third category water, as well as at special requirements to quality and appearance, especially for critical parts.	The water used for washing, can be applied repeatedly as a 1st and 2nd category water

Table 3

Physico-chemical characteristics of the water used in the electroplating production

Value	Standart for the category		
	1	2	3
The pH value	6.0–9.0	6.5–8.5	5.4–6.6
Dry residue, mg/dm^3, not more	1000	400	5.0
Total hardness, mg-ekv/dm^3, not more	7.0	6.0	0.35
Turbidity on a standard scale, mg/dm^3, no more than	2.0	1.5	–
Sulfates (SO_4^{2-}), mg/dm^3, not more than	500	50	0.5
Chlorides (Cl^-), mg/dm^3, no more than	350	35	0.02
Nitrates (NO_3^-), mg/dm^3, no more than	45	15	0.2
Phosphate (PO_4^{3-}), mg/dm^3, not more than	30	3.5	1.0
Ammonia, mg/dm3, no more than	10	5.0	0.02
Petroleum products, total, mg/dm^3, no more	0.5	0.3	–
Chemical oxygen demand, mg/dm^3, not more than	150	50	–
Residual chlorine, mg/dm^3, not more than	1.7	1.7	–
Surface active agents (surfactants), mg/dm^3, no more than	5.0	1.0	–
Heavy metal ions, mg/dm^3, not more than:	15	5.0	0.4
– iron	0.3	0.1	0.05
– copper	1.0	0.3	0.02
– nickel	5.0	1.0	–
– zinc	5.0	1.5	0.2
– trivalent chromium	5.0	0.5	–
– specific conductivity, S/m	$2\cdot10^{-3}$	$1\cdot10^{-3}$	$5\cdot10^{-4}$

Table 4

Permissible concentrations of polluting substances in wastewaters of the EU countries

value	Belgium	France*	Germany	England and Wales **	Italy***	Holland	Spain	Portugal
Discharge into sewage (HA) or pond (PX)	–	PXB	–	ГК	PXB	–	–	–
Ag (silver)	0.1	–	0.1	0.1	–	0.1	–	–
Al (aluminum)	10	5	3	–	1	–	1–2	5
Cd (cadmium)	0.6	0.2	0.2	0.01	0.02	0.2	0.1–0.5	0.2
CN (free cyanide)	–	0.1	0.2	0.2	0.5	0.2	0.5–1.0	0.1
Cr (chromium (VI))	0.5	0.1	0.1	0.1	0.2	0.1	0.2–0.5	0.1
Cr (total chromium)	5	3	0.5	1	2	0.5	Cr (III) 2–4	Cr (III) 3
Cu (copper)	4	2	0.5	2	0.1	0.5	0.2–10.0	2
F (fluorine)	10	15	50	–	6	–	6–12	15
Fe (iron)	20	5	3	–	2	–	2–10	5
Hg (mercury)	–	0.1	–	–	0.005	0.05	0.05–0.1	0.05
Ni (nickel)	3	5	0.5	1	2	0.5	2–10	5
NO_2 (nitrite)	–	1	–	–	0.6	–	–	1
P (phosphate)	2	10	2	–	10	15	10–20	10
Pb (lead)	1	1	0.5	–	0.2	–	0.2–0.5	1
Sn (tin)	2	2	2	–	10	2	10	2
Zn (zinc)	7	5	2	–	0.5	0.5	3–20	5
COD (BOD)	300	150	400	–	160	–	–	150
EDTA	–	–	0	–	–	0	–	–
Petroleum products	–	5	0.1	0.1	5	0.1	20–40	–
VOC (volatile organic compound)	–	–	1	0.1	–	0.1	–	–
Suspended substances	–	–	–	50	–	–	–	60

* Water consumption: 8 l per 1 m^2 of the surface being treated for each washing stage.

** The Environmental agency of England and Wales.

*** The reduced MPC enacted in several regions (i. g., catchment area of the Venice lagoon).

As it can be seen from the tables, the allowable values of polluting substances contained in industrial wastewaters for metalworking enterprises, established by TAP, almost at all indicators are at the lower limit of concentrations established in EU countries, and in some cases are even more stringent. These wastewater requirements are periodically revised downwards permissible concentrations. This stipulates the requirement increase towards treatment facilities of industrial wastewater of given enterprises.

Based on the analysis of electroplating shop treatment facilities (plots) on Belarusian enterprises it has been found that as the main applied wastewater treatment methods are considered electro coagulation, reagent treatment, including using ferroferrihydrosol, static galvanic coagulation combined with electronic separation. The adsorption, ion exchange is applied for post treatment. In many enterprises, sewage treatment plants are in operation more than 15–20 years. The obsolete equipment does not allow to achieve high efficiency of wastewater treatment.

Analysis of treatment facilities work in electroplating enterprises of the Republic of Belarus shows that in most cases the used electrolytes are fed into the overall treatment system. This can lead to the instant increase of pollutant concentration; increase of loading on wastewater treatment plants and to the risk of exceeding the established standards in purified water. Studies in a number of enterprises of the Republic of Belarus indicate that in the case of joint disposal of washing water and used electrolytes to the neutralization station, the contribution of the latest to the total wastewater pollution is up to 20% at chromium, up to 70% – at cadmium. However, the neutralization of used electrolyte solutions on local units can only be used as temporary or forced solution in the absence of other technical capabilities, and should not be regarded as a technical solution, corresponding to the present level of electroplating development, because it causes a loss of nonferrous metals, being valuable and scarce raw materials. For most rational organization of electroplating production it is necessary to develop methods of technological solution regeneration. It also completely unacceptable to wash down the galvanic slimes in wastewaters which follow to the sewage treatment plant.

Currently, dehydration of these sediments to about 70% moisture is used at most enterprises. The sediments dehydration is carried out in vacuum filters, most of which are obsolete; it is characterized by high energy intensity and moisture content of the dehydrated sludge. In most cases, the resulting sediments are stored on the enterprises area. However, as shows the analysis of literature, sewage sludge of electroplating can be successfully used in various industries [5–7].

The main problems with the existing treatment facilities include:

1) lack of separate collection of waste electrolytes and other technological solutions;

2) periodic discharge of waste processing solutions into sewage treatment, which increases the load and reduces the efficiency of sewage neutralization;

3) in some plants when replacing technological solutions the baths are cleaned from sludge that are eroded and fed for overlapped processing with the wash waters;

4) enterprises do not prepare balances on individual components, so do not take into account the contribution of the periodic disposal of waste solutions in the overall load on the sewage treatment plants;

5) in most cases the regeneration of the used electrolytes is missed, which leads to the loss of valuable reagents contained therein;

6) the applied wastewater treatment schemes do not provide cleaning from anions;

7) the lack of equipment for sewage water dehydration or the use of inefficient mechanical methods;

8) In most cases, sewage sludge is not processed but stored on the enterprises area;

9) at individual enterprises there are no reagents dosage control devices, it results in periodic exceeding of established standards for pollutants.

When designing new technological lines and treatment facilities in accordance with the requirements of the Law of the RB "On Environmental Protection" from November 26, 1992 as amended in 2002 No. 1982-XII the best available techniques should be used.

Conclusion. The analysis of wastewater from electroplating facilities of Belarusian enterprises indicates their insufficient effectiveness. The efficiency growth of existing treatment facilities in electroplating can be achieved by:

– the separate treatment of wash waters and waste solutions;

– more efficient use of waste degreasing solution after separation of oils as neutralization reagents;

– selection and use of more effective flocculants;

– replacement of the vacuum filter for more efficient equipment;

– organization of the input and output streams control to assess the real effectiveness of the use of technological solution components;

– creation of demonstration objects at the expense of innovation funds;

– unification of measurement techniques used in the laboratories of enterprises with techniques applied by controlling entities.

Table 5

Permissible concentrations of polluting substances contained in industrial wastewaters discharged into water bodies for metalworking enterprises

Polluting substances	The Fields of wastewater											
	1	2	3	4	5	6	7	8	9	10	11	12
Aluminum, mg/dm^3	3	3	–	–	–	–	–	–	2	3	3	3
Ammonium-ion, mg N/dm^3	100	30	–	30	30	50	50	50	20	30	–	–
Nitrite-ion, mg N/dm^3	–	5	5	5	–	5	–	5	5	–	–	–
COD, мг O_2/dm^3	400	100	100	200	200	400	600	200	100	400	400	300
Total fluorine , mg/dm^3	2	2	2	2	2	2	2	2	2	2	2	2
Total iron, mg/dm^3	3	3	–	3	3	–	3	3	3	3	3	3
Fluorides, mg/dm^3	50	20	20	–	20	–	50	–	50	30	–	–

Note. 1 – electroplating, 2 – etching processes, 3 – anodizing, 4 – oxidation 5 Hot-dip galvanizing and hot tinning, 6 – metal hardening, 7 – manufacture of printed circuit boards, 8 – manufacture of batteries and accumulators, 9 – enameling, 10 – enterprises for mechanic metal processing, 11 Grinding and polishing treatment processes, 12 – varnishing of metal products

Table 6

Permissible concentrations of polluting substances contained in industrial wastewaters discharged into soil piping of settlements for metalworking enterprises mg/dm^3

Polluting substances	The Fields of wastewater											
	1	2	3	4	5	6	7	8	9	10	11	12
Arsenic	0.1	–	–	–	–	–	0.1	0.1	–	–	–	–
Barium	–	–	–	–	–	2	–	–	–	–	–	–
Iron	3	3	–	3	3	–	3	3	3	3	3	3
Lead	0.5	–	–	–	0.5	–	0.5	0.5	0.5	0.5	–	0.5
Cadmium	0.2	–	–	–	0.1	–	–	0.2	0.2	0.1	–	0.2
Free chlorine	0.5	0.5	–	0.5	–	0.5	–	–	–	0.5	–	–
Total chromium	0.5	0.5	0.5	0.5	–	–	0.5	–	0.5	0.5	0.5	0.5
Chromium (VI)	0.1	0.1	0.1	0.1	–	–	0.1	–	0.1	0.1	0.1	0.1
Cyanide ion	0.2	–	–	–	–	1.0	0.2	–	–	0.2	–	–
Cobalt	–	–	1.0	–	–	–	–	–	1.0	–	–	–
Copper	0.5	0.5	–	–	–	–	–	–	0.5	0.5	0.5	0.5
Nickel	0.5	0.5	–	0.5	–	–	–	–	0.5	0.5	0.5	0.5
Mercury	–	–	–	–	–	–	–	0.05	–	–	–	–
Selenium	–	–	–	–	–	–	–	–	1.0	–	–	–
Silver	–	–	–	–	–	–	0.1	0.1	–	–	–	–
Sulphide ion	1.0	1.0	–	1.0	–	–	1.0	1.0	1.0	–	–	–
Tin	2	–	2	–	2	–	2	–	–	–	–	–
Zinc	2	2	2	–	2	–	–	2	2	2	2	2

Note. 1 – electroplating, 2 – etching processes, 3 – anodizing, 4 – oxidation 5 Hot-dip galvanizing and hot tinning, 6 – metal hardening, 7 – manufacture of printed circuit boards, 8 – manufacture of batteries and accumulators, 9 – enameling, 10 – enterprises for mechanic metal processing, 11 Grinding and polishing treatment processes, 12 – varnishing of metal products

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