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## NEUTRALIZATION OF FLUOROBORATE WASTES FROM ELECTRICAL INDUSTRY

One of technological operations in electrical industry is the electrolytic plating of metal parts with alloy Pb-Sn in fluoroborate baths. Considerable amounts of noxious wastewaters containing mainly  $Pb^{+2}$  and  $BF_4^-$  ions are formed in this process. The wastewaters can be divided into two groups: concentrated ones containing the exhausted baths and the dilute ones, i.e. rinsing waters.

The aim of research has been to work out a complex solution for the problem of neutralization of both the wastes with simultaneous recovery of deionized water.

The process of precipitation of  $BF_4^-$  and  $Pb^{+2}$  ions from the concentrated wastewaters has been investigated using different precipitants and its optimum conditions have been determined.

In order to neutralize the dilute wastewaters the following ion-exchange resins have been applied: strongly acidic cation-exchange resin, Wofatit KPS, and weakly basic anion-exchange resin, Wofatit AD 41. It has been found that removal of fluoroborates and lead from the wastewaters on ion-exchange bed is complete and the recovered water can be reused. Regeneration of ion-exchange bed runs properly. Post-regeneration wastewater containing  $Pb^{+2}$  and  $BF_4^-$  ions can be with good effects treated in the same way as the concentrated exhausted baths.

### 1. INTRODUCTION

Fluoroborate baths are, with great advantage, used for electroplating of metal surface. They are applied in production of rolling bearings, printed elements, electric parts working in strongly corrosive environments etc [1]. Other advantages of this method besides high deposition rate and high quality of coating are its efficiency, easy control of the process, and stability of the bath.

The shortcomings of this method are the tendency to form dendrites and high cost of the bath. The process of coating metals with Sb-Pb alloy is worth noticing. Beside other advantages, coats of this alloy have excellent soldering properties, and therefore are used to cover electronic elements requiring automatic soldering.

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Treatment of wastewaters from metal electroplating in fluoroborate baths required appropriate methods because of high toxicity of the bath ingredients and good solubility of most metal fluoroborates.

Treatment by means of precipitation of heavy metals in form of hydroxides does not result in removal of either boron or fluorine.

The electroplating wastewater generation is due to the processes of metal surface pre-treatment, coat formation, and rinsing.

Physicochemical characteristics of the separate wastewater stream justifies their segregation into two groups:

1. Concentrated wastewaters, i.e. the exhausted baths and post-regeneration solution; this group is characterized by high concentrations of metal fluoroborates, low frequency of disposal, and small volumes.

2. Dilute wastewaters, i.e. rinsing wastewaters containing the components at low concentrations; they are discharged continuously in considerable amounts.

Fluoroborate baths are rarely used in Poland. The dilute wastes are mixed with other industrial wastewaters and the exhausted baths are treated by heavy metals precipitation and multiple dilution.

The problem of fluoroborate wastewater treatment has become actual in Poland in connection with production of colour TV sets, since to this end a technology of new transistor production had to be designed and applied in one of electronic plants. One of the unit processes within this technology is a galvanic coating formation where Sn-Pb alloy is placed on a basic element of a transistor, first by high-temperature treatment and next electrolytically from fluoroborate bath. The wastewaters generated in this process are of a quite different type and — as it follows from preliminary investigations — they should be treated individually. Thus, it was necessary to design a technology of fluoroborate wastewater treatment both from the exhausted baths and the rinse waters.

In case of the concentrated wastewaters the main idea was to utilize the relatively low solubility of potassium fluoroborate, whereas the ion-exchange seemed to be the most recommended process for dilute wastewater treatment. The ion-exchange should simultaneously enable the deionized water recovery for rinsing operation. The exhausted solutions from ion-exchanger regenerations can be treated in the same way as the concentrated wastewaters. The precipitates formed in the process can be treated together with other plant precipitates.

## 2. MATERIALS AND METHODS

In order to prepare the model wastewaters both concentrated and the dilute ones a licenced bath for electroplating the elements with tin-lead alloy was used. The bath contained lead and tin fluoroborates (at total concentration of the metals equal to  $35 \text{ g/dm}^3$ ), free fluoroboric acid ( $70 \text{ g/dm}^3$ ), and some special additives (LA-1 and LA-2 at concentration of  $20 \text{ g/dm}^3$ ). Qualitative compositions of the latter, imported components are not known pre-

cisely, since their technology is licenced. It is assumed that the special additives contain reducers, surfactants, and colloids.

In investigations on concentrated wastewater treatment the bath was applied directly, whereas the composition of the rinse waters was modelled by diluting the bath with deionized water. Basic analytic control of the investigations included determination of fluoroborates and lead. Concentration of fluoroborates was determined by extraction-colorimetric method using brilliant green [2], lead being determined polarographically [3, 4].

Investigations on concentrated wastewater treatment were carried out in a glass apparatus at a laboratory scale, its scheme and description being presented in figure.

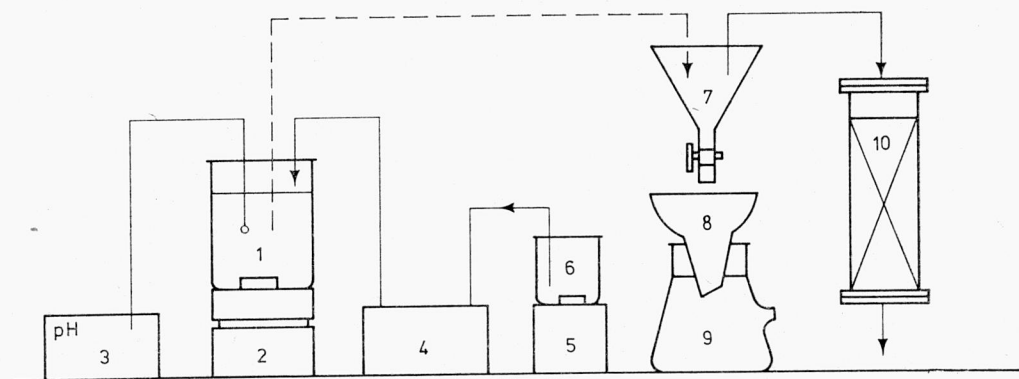


Figure. Scheme of the apparatus for concentrated wastewater treatment

1 — reactor, 2, 5 — magnetic stirrer, 3 — pH-meter, 4 — peristaltic pump, 6 — dosing tank, 7 — settling tank, 8 — Büchner's funnel, 9 — suction flask, 10 — rapid sand filter

Rysunek. Schemat aparatury do oczyszczania stężonych ścieków

1 — reaktor, 2, 5 — mieszkadło magnetyczne, 3 — pehametr, 4 — pompa perystaltyczna, 6 — zbiornik dawkujący, 7 — osadnik, 8 — lejek Büchnera, 9 — kolba próżniowa, 10 — filtr żwirowy

A defined volume of wastes was placed in reactor (1) into which the reactant solution was dosed by peristaltic pump (4) from the tank (6). After precipitation reaction the content of the reactor was transferred into a settling tank. The precipitate was dewatered in the dewatering set (8, 9), dried, and analysed. The supernatant was filtered through the sand filter (10) and analysed.

The dilute wastewater treatment was performed in the apparatus consisting of cation-exchange and anion-exchange glass columns connected in series. In most investigations the columns used were of a diameter of 18 mm and contained 15 cm<sup>3</sup> of cation-exchange resin and 15 cm<sup>3</sup> of anion-exchange resin. Glass columns containing 100 cm<sup>3</sup> of the ion-exchange resins were also applied in large laboratory scale experiments.

In order to remove lead and tin Wofatit KPS, a strongly acidic cation-exchanger produced in GDR was applied, as it is recommended by the producer for metal regeneration because of its good thermal, mechanical, and chemical properties. As the anion-exchange

resin was applied to remove fluoroborate ions, it should be also effective in the presence of organic compounds, small amounts of which can be found in rinsing waters. The selected anion-exchange resin, weakly basic Wofatit AD-41 of GDR, is particularly recommended for demineralization of waters containing organics.

Dilute wastewater was let through the column with strongly acidic cation exchanger in hydrogen form and weakly basic anion exchanger in hydroxide form. In the effluent electric conductivity, pH, lead, and fluoroborate concentrations were controlled; in case of large-scale experiments the surfactants concentrations were also determined.

### 3. RESULTS

#### 3.1. CONCENTRATED WASTEWATER

In the investigations on the exhausted bath treatment two precipitation agents: potassium carbonate and potassium sulphate were applied. These investigations were preceded by the test in which optimum pH range for lead and fluoroborate precipitation were to be determined. The tests consisted in the treatment of 100 cm<sup>3</sup> portions of the exhausted bath using different volumes of potassium carbonate solution (concentration of 500 g/dm<sup>3</sup>) to reach pH of the mixture equal to 5, 6, 7, 8, 9, and 10. The results are presented in tab. 1. Solution of potassium sulphate at the concentration of 60 g/dm<sup>3</sup> was also applied as a precipitant together with 5% milk of lime for pH adjustment. Results of investigations on concentrated wastewater treatment are presented in tabs. 2 and 3.

Table 1

Supernatant resulting from tests of concentrated wastes treatment with solution of potassium carbonate at concentration of 500 g/dm<sup>3</sup>

Skład roztworu otrzymanego po wstępnym oczyszczaniu stężonych ścieków roztworem węglanu potasowego o stężeniu 500 g/dm<sup>3</sup>

Super-natant from run No.	pH	Volume of K <sub>2</sub> CO <sub>3</sub> solution cm <sup>3</sup>	Conductivity mS/cm	Volume of precipitate after neutralization cm <sup>3</sup>	Concentration of BF <sub>4</sub> g/dm <sup>3</sup>	Concentration of B g/dm <sup>3</sup>	Concentration of Pb g/dm <sup>3</sup>	Sum of cations eq/dm <sup>3</sup>
1	5	12.2	19.8	23	2.4	0.295	0	0.236
2	6	12.9	23.1	23	1.7	0.209	0	0.230
3	7	14.5	38.0	22	1.6	0.197	0	0.246
4	8	17.4	> 500	29	1.2	0.148	0	0.284
5	9	19.4	> 500	35	1.4	0.172	0	0.280
6	10	24.8	> 500	33	1.2	0.148	0	0.292
Raw wastes	1.55	—	> 500	—	99.6	12.4	33	1.08

Table 2

Average results of the concentrated wastewater treatment

Średnie wyniki oczyszczania stężonych ścieków

Parameter	Neutralization with solution of $K_2CO_3$ , 500 g/dm <sup>3</sup>	Neutralization with solution of $K_2SO_4$ , 60 g/dm <sup>3</sup> and 5% $Ca(OH)_2$
Volume of wastewaters taken for investigation, dm <sup>3</sup>	2.0	0.5
Wastewater after treatment		
final volume, dm <sup>3</sup>	1.98	1.2
pH	8.0	7.97
colour	yellow-brown	light yellow
Pb, g/dm <sup>3</sup>	0	0
BF <sub>4</sub> , g/dm <sup>3</sup>	3.2	2.47
Precipitate from sedimentation		
volume, dm <sup>3</sup>	0.86	0.29
H <sub>2</sub> O contents, %	77.5	58.6
Precipitate after filtration		
mass, g	304	82.2
H <sub>2</sub> O contents, %	28.3	2.73
Precipitate after air drying		
mass, g	220	79.8
Pb contents, %	19	21

### 3.2. DILUTE WASTEWATER

In the experiments on ion-exchange treatment of rinse waters the following essential process parameters were investigated: quality of filtrate till column breakthrough, the bed capacity, and the effect of hydraulic and ionic load on a column work. The results are presented in tabs. 4 and 5.

The ion-exchange method of the dilute wastes treatment can be applied only when the effective regeneration of beds is possible. As a result of investigations on regeneration of cation-exchange resin it has been found out that the optimum regeneration agent is 2-normal solution of nitric acid. In laboratory conditions the excess of the acid necessary to complete regeneration of the cation-exchange resin is 800%. Regeneration of the anion-exchange bed can be easily accomplished with 1-normal solution of sodium hydroxide. The organics adsorbed on the anion-exchange bed are also removed during regeneration. At first stage of the process the loose, gelatinous organic precipitates are formed.

As it was expected, the mixture of post-regeneration solutions can be treated in the same way as the concentrated wastewater metals and fluoroborates being removed by potassium carbonate or potassium sulphate.

Table 3

Treatment of the bath with potassium carbonate and potassium sulphate  
 The values refer to 1 dm<sup>3</sup> of the bath  
 Oczyszczanie kąpeli za pomocą węglanu potasowego i siarczanu potasowego  
 Wartości odnoszą się do 1 dm<sup>3</sup> kąpeli

Parameter	Neutralization with solution of K <sub>2</sub> CO <sub>3</sub> (500 g/dm <sup>3</sup> )	Neutralization with solution of K <sub>2</sub> SO <sub>4</sub> (60 g/dm <sup>3</sup> and 5% Ca(OH) <sub>2</sub> )
Precipitation agent demand, dm <sup>3</sup>	0.140	2.0
Precipitation agent dry weight demand, g	70	120
Final volume of the wastewater, dm <sup>3</sup>	1.0	2.4
Concentration of Pb in wastes after neutralization, g/dm <sup>3</sup>	0	0
Concentration of BF <sub>4</sub> in wastes after neutralization, g/dm <sup>3</sup>	3.2	2.5
Load of BF <sub>4</sub> in wastes being discharged, g	3.2	6.0
Mass of air-dried precipitate, g	110	160
Time of precipitate sedimentation until clarification of supernatant, h	24	16

#### 4. DISCUSSION

As it follows from tab. 1 the optimum pH for precipitation of potassium fluoroborate from the concentrated wastes ranges between 7.5 and 8.5. In supernatant no lead was found within the whole controlled pH range. Data presented in tab. 3 show that both the investigated methods can be applied to concentrated wastewater treatment. It seems, however, that the use of potassium carbonate as a precipitant is more convenient due to the possibility of working with smaller volumes of solutions (smaller dimensions of dosing devices), because of precipitation and neutralization of the bath during one operation with no necessity to apply the milk of lime and for smaller mass of precipitate and load of the fluoroborates being discharged.

Disadvantage of this precipitant is the intensive foaming due to addition of potassium carbonate to acidic bath. This effect may be limited by a suitable construction of the reactor, the use of antifoaming agents and low dosing rate of potassium carbonate.

Table 4

Results of investigations on dilute wastewater treatment by ion-exchange method  
 Column diameter 18 mm, volume of ion-exchange resin in column 15 cm<sup>3</sup>  
 Wyniki badań nad oczyszczaniem rozcieńczonych ścieków metodą jonowymienną  
 Średnica kolumny 18 mm, objętość jonitu w kolumnie 15 cm<sup>3</sup>

Composition of wastes being neutralized mg/dm <sup>3</sup>	Exhaustion flow rate m <sup>3</sup> /m <sup>3</sup> h	Breakthrough volume		Effluent characteristics (mean values to the breakthrough point)			
		dm <sup>3</sup>	dm <sup>3</sup> /dm <sup>3</sup> of bed	pH	Conductivity μS/cm	Pb mg/dm <sup>3</sup>	BF <sub>4</sub> mg/dm <sup>3</sup>
Pb — 38 Sn — 1.9 BF <sub>4</sub> — 114	9.2	13.5	900	5.56	2.48	0	0
as above	27.5	7.0	467	5.70	1.19	0	0
as above	40.0	5.0	333	5.53	0.67	0	0
Pb — 38 Sn — 1.9 BF <sub>4</sub> — 214	10.8	6.0	400	5.74	0.94	0	0
Pb — 38 Sn — 1.9 BF <sub>4</sub> — 414	11.2	4.0	266	5.82	1.24	trace amounts	trace amounts
Pb — 153 Sn — 1.9 BF <sub>4</sub> — 46	11.2	3.5	233	6.13	2.42	0	0

Table 5

Results of investigations on dilute wastewater treatment by ion-exchange method  
 Column diameter 44 mm, volume of ion-exchange resin in column 100 cm<sup>3</sup>  
 Wyniki badań nad oczyszczaniem rozcieńczonych ścieków metodą jonowymienną  
 Średnica kolumny 44 mm, objętość jonitu w kolumnie 100 cm<sup>3</sup>

Composition of wastes being neutralized	Exhaustion flow rate m <sup>3</sup> /m <sup>3</sup> h	Breakthrough volume		Effluent characteristics (mean values to the breakthrough point)				Contents of surface active substances mg/dm <sup>3</sup>
		dm <sup>3</sup>	dm <sup>3</sup> /dm <sup>3</sup> of bed	pH	Coductivity μS/cm	Pb mg/dm <sup>3</sup>	BF <sub>4</sub> mg/dm <sup>3</sup>	
Pb — 90 mg/dm <sup>3</sup> Sn — 4.5 mg/dm <sup>3</sup> BF <sub>4</sub> — 270 mg/dm <sup>3</sup> Conductivity — 705 μS/cm	10.0	22.0	220	7.5	0.75	0	0	0

Investigations on neutralization of dilute wastes by ion-exchange have shown that the parameters of the effluent allow the recycling of rinse waters (tab. 5).

The most sensitive indicator of the breakthrough of columns is electric conductivity. Under suitable operating conditions anion-exchange column is first exhausted and free fluoroboric acid present in the effluent gives clear conductometric signal. pH is also a good indicator.

As it follows from tab. 4 the influence of hydraulic load on the ion-exchange operation system is significant. It is due to the sensitivity of weakly basic anion-exchange bed to the hydraulic loading.

With the increasing concentration of free fluoroboric acid in the wastes the concentration of  $Pb^{+2}$  ions in the column effluent (tab. 4) also increases.

High excess of nitric acid necessary for regeneration of cation-exchange bed is among others, due to the classification of ion-exchange resin particles, taking place while backwashing the bed. Particles containing  $Pb^{+2}$  cations have greater density and during the water upflow they precipitate on the bottom of the column. This creates disadvantageous conditions of regeneration and increases the necessary excess of regeneration agent.

## 5. CONCLUSIONS

From the investigations performed the following conclusions can be formulated:

1. Treatment of concentrated fluoroborate wastewaters by precipitation of metals and potassium fluoroborate proceeds at high efficiency.
2. Removal of fluoroborates and lead from the dilute wastewaters on ion-exchange beds is complete, thus the water obtained in the process can be reused.
3. Two normal nitric acid for cation-exchange resin and one normal sodium hydroxide for anion-exchange bed can be used as the regeneration agents. Treatment of the post-regeneration solutions proceeds with as good results as that of concentrated wastewaters.

## REFERENCES

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## UNIESZKODLIWIANIE ŚCIEKÓW FLUOROBORANOWYCH POCHODZĄCYCH Z PRZEMYSŁU ELEKTROTECHNICZNEGO

Elektrolityczne powlekanie metalowych części stopem ołowiowo-cynowym w kąpielach fluoroboranych jest jedną z operacji technologicznych w przemyśle elektrotechnicznym. Podczas tego procesu powstają duże ilości szkodliwych ścieków, które zawierają przede wszystkim jony  $Pb^{+2}$  i  $BF_4^-$ . Ścieki można podzielić na dwie grupy: na ścieki stężone zawierające zużytą kąpiel i ścieki rozcieńczone, czyli popłuczyny.



Celem badań było opracowanie kompleksowego rozwiązania problemu unieszkodliwiania obu rodzajów ścieków, z równoczesnym odzyskiem zdemineralizowanej wody.

Zbadano wytrącanie jonów  $\text{BF}_4^-$  i  $\text{Pb}^{+2}$  ze stężonych ścieków przy użyciu różnych środków strącających i określono optymalne warunki tego procesu.

W celu unieszkodliwienia rozcieńczonych ścieków zastosowano następujące wymiennicze jonowe: silnie kwaśną żywicę kationitową, Wofatit KPS, i słabo zasadową żywicę anionitową, Wofatit AD 41. Stwierdzono, że wymiennicz jonowy całkowicie usuwa fluoroborany i ołów ze ścieków i że zregenerowana woda może być ponownie użyta. Regeneracja wymiennicza jonowego jest całkowita, zaś woda poregeneracyjna zawierająca jony  $\text{Pb}^{+2}$  i  $\text{BF}_4^-$  może być oczyszczona w ten sam sposób, co stężona zużyta kąpiel.

### REINIGUNG VON FLUOBORAT-HALTIGEN ABWÄSSER DER ELEKTROTECHNISCHEN INDUSTRIE

Elektrolytische Stabilisierung von Metalloberflächen mit einer Blei-Zinnlegierung im Fluoboratbad ist ein typisches, technologisches Verfahren der elektrotechnischen Industrie. Es entstehen dabei große Mengen von schädlichen Abwässern die u.a. Ionen von  $\text{Pb}^{+2}$  und  $\text{BF}_4^-$  beinhalten. Zwei Abwasserarten fallen an: die konzentrierten Bäder und die verdünnten Spülwässer.

Ziel der Arbeit war, beide Abwasserarten zu reinigen und das Wasser rückzugewinnen. Untersucht wurde die Ausfällung der  $\text{BF}_4^-$  und  $\text{Pb}^{+2}$  Ionen aus den Konzentraten bei Anwendung verschiedener Fällungsmittel.

Zwecks Rückgewinnung der Spülwässer, kamen folgende Ionenaustauscher zur Anwendung: der stark saure Kationenaustauscher Wofatit KPS und der schwach alkalische Anionenaustauscher Wofatit AD 41. Durch den Ionenaustausch werden Fluoborate und Blei völlig aus den Spülwässern beseitigt, diese können in den Spülprozeß wieder eingesetzt werden. Die Regeneration der Harze ist voll durchführbar und das  $\text{Pb}^{+2}$  und  $\text{BF}_4^-$  haltige Regenerat kann man genauso behandeln wie die Konzentrate selbst.

### ОБЕЗВРЕЖИВАНИЕ ФТОРОБОРАТНЫХ СТОЧНЫХ ВОД ЭЛЕКТРОТЕХНИЧЕСКОЙ ПРОМЫШЛЕННОСТИ

Электролитическое покрытие металлической части свинцово-оловянным сплавом во фтороборатных ваннах является одной из технологических операций в электротехнической промышленности. Во время этого процесса образуются большие количества вредных сточных вод, которые содержат прежде всего ионы  $\text{Pb}^{+2}$  и  $\text{BF}_4^-$ . Сточные воды можно подразделить на две группы, а именно, на концентрированные сточные воды, содержащие отработанную ванну, и разбавленные сточные воды, т. е. промывные воды.

Целью исследований являлась разработка комплексного решения проблемы обезвреживания обих видов сточных вод с одновременной регенерацией деминерализованной воды.

Исследовано осаждение ионов  $\text{BF}_4^-$  и  $\text{Pb}^{+2}$  из концентрированных сточных вод при использовании различных осаждающих веществ и определены оптимальные условия этого процесса.

Для обезвреживания разбавленных сточных вод были применены следующие иониты: сильнокислая катионообменная смола, вофатит KPS и слабощелочная анионообменная смола, вофатит AD 41. Выявлено, что ионит полностью удаляет фторобориты и свинец из сточных вод и что регенерированная вода может быть повторно использована. Ионит полностью регенерируется, послерегенерационная же вода, содержащая ионы  $\text{Pb}^{+2}$  и  $\text{BF}_4^-$ , может быть очищена таким же образом, как концентрированная отработанная ванна.