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Project Summary

Removal and Recovery of Fluoborates and Metal Ions from Electroplating Wastewater

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The study conducted at the New Jersey Institute of Technology, Newark, New Jersey, was concerned with development of two separate methods for treatment of fluoborate-containing wastewater from electroplating of tin, solder, copper, and nickel stripping.

The first method was based on the specific ion flotation principle which involves removing specific ions from dilute wastewater through binding with a surfactant, followed by flotation or ultrafiltration. This part of the investigation involved the evaluation of structurally different commercially available surfactants to determine the type, structure, mechanism, and conditions which govern the formation of a fluoborate-surfactant complex. Also, air flotation and ultrafiltration were evaluated for removal of the complex from the wastewater. Methods for recovery of the surfactant were examined.

The fluoborate was found to bind with a commercially available alkylamine acetate type surfactant which reduces the fluoborate concentration in rinse wastewaters from 100 mg/l of fluoborate to 7-15 mg/l of fluoborate. Actual plating operation rinse wastewaters containing 100 mg/l of fluoborate were used in the study. Ultrafiltration followed by electrolysis provided the shortest treatment time with recovery of the surfactant.

The second method was electrodialysis. Here, the major effort was to find a suitable anode. Electrodialysis was found feasible for treatment of wastestreams containing plating chemical concentrations ≥ 1000 mg/l using a high density low porosity graphite anode. Electrodialysis can reduce the plating chemical concentrations in the wastestream to about 100 mg/l.

The specific ion flotation process either used separately or in the combination with electrodialysis can be useful and effective for closed-loop treatment of fluoborate-containing wastewaters from electroplating operations. Reagent recovery in specific ion flotation and fluoborate and metals recoveries in electrodialysis can be achieved in addition to pollution control. However, both methods need further development to make them commercially suitable for treatment of fluoborate-containing wastestreams.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A recognition of the detrimental effects of industrial pollution on our environment has surfaced in recent years. One of the industries contributing to this pollution is the metal finishing industry.

The wastewater produced in metal finishing operations contains toxic cation and anions. Concentrated wastestreams are generated by cleaning, stripping, passivating, and anodizing operations when the spent process solutions are discarded. The larger volume dilute streams come

from the rinsewaters that are contaminated with the process solution that has adhered to the surface or is entrapped in crevices due to the shape of the processed piece.

Presently, the most commonly used procedure for treating metal finishing wastestreams involves precipitation of the heavy metals and anions to form a sludge.

Problems arise mainly with the disposal of sludge because the precipitates present a potential leaching problem in landfills. Alternatives to the precipitation process are the recovery and recycle of plating chemicals from the wastestreams at their point of generation, or the substitution of toxic process chemicals with less objectional ones.

Substitution of process chemicals is practical only when the substitute does not compromise the quality of the finished product. One such substitution is the use of fluoborate to replace cyanides as a conducting salt in plating baths. Commercial fluoborate solutions are presently available for the plating of copper, indium, iron, lead, nickel, tin, and their alloys. Also, fluoboric acid is used in various pretreatment operations, such as stripping and cleaning. Fluoborate has been found to be an excellent carrier ion which gives uniform, bright, well-thrown covering. Also, fluoborate is much less toxic than cyanide, and therefore provides for a safer plating room.

There are presently no specific discharge limitations on fluoborate. However, when a wastestream is analyzed for fluoride by the approved method (Bellack Distillation), any fluoborate present will be hydrolyzed yielding inflated fluoride concentrations. For each fluoborate ion present in a sample the test will show four fluoride ions. This gives a false indication of fluoride concentration and can show a National Pollution Discharge Elimination System Permit (NPDES) violation where none exists.

Few processes are suitable for the removal of fluoborate from plating rinsewaters. It is a small ion and is not easily rejected by membrane processes such as reverse osmosis. Presently, there is no known ion exchange resin which will remove fluoborate from solution efficiently. Battelle Memorial Institute in their January 1974 Draft of the Development Document for Limitations for Electroplating Point Sources, suggested the hydrolysis of the fluoborate to fluoride followed by lime precipitation as a possible treatment. This, however, results in the production of a sludge that must be disposed in secure landfills.

Vacuum evaporation is currently being used as a means of recycling tin fluoborate rinsewaters back into the plating tank as a makeup solution. Although it provides closed-loop treatment, problems such as precipitation of stannic oxide which inhibits the evaporation are encountered during the evaporation process. It is also an energy intensive operation.

Since suitable technology for the treatment of rinsewater from fluoborate plating baths is lacking, this investigation was undertaken.

Two separate processes, ion flotation and electrodialysis, were investigated for the treatment of dilute and concentrated fluoborate wastestreams, respectively from the electroplating industry. Specific ion flotation has been investigated for the removal of metal cations and the anionic chromate from solutions, but it has not been explored for the removal of fluoborate ion from dilute wastestreams resulting from single tank rinsing.

The specific ion flotation investigation involved the identification of the type and structure of the surfactants that would provide maximum removal of the fluoborate ion, in dilute rinsewaters. This was followed by a series of studies to understand the mechanism involved in the removal of the fluoborate ion and the parameters that would influence its removal from the wastestream. Also, methods for recovering the surfactant and fluoborate anions for reuse were studied.

The second method involved the investigation of electrodialysis for the recovery and reuse of plating chemicals in concentrated rinse wastewater generated by multiple tank counter-current and series rinsing operations. Electrodialysis has been applied to the recovery of nickel and copper from plating rinsewaters and closed-loop control of cyanide rinsewaters. However, electrodialysis has not been employed in the treatment of fluoborate plating rinsewaters.

The use of electrodialysis treatment for the wastestreams containing copper fluoborate, tin fluoborate, and solder fluoborate required the development of a new anode that would resist the corrosive properties of the fluoboric acid electrolyte. Fluoboric acid which is extremely corrosive toward the commonly used platinized metal anodes was employed instead of sulfuric acid as the electrolyte to avoid contamination of the product with undesirable sulfate anions.

Results

Specific Ion Flotation

A number of different commercially available surfactants were examined. Only alkylamine acetate type surfactants provided significant removals of fluoborate ion from solution. The removal of the fluoborate ion was found to be dependent upon its binding to the surfactant through displacement of the acetate group on the surfactant. Kinetic studies of the displacement reaction revealed that optimum binding of the fluoborate ion to the surfactant occurred within one minute. Acidic conditions that favor the formation of the acetic acid from the displaced acetate ion improve the removal of the fluoborate ion by the surfactant. The presence of other anions in solution that form stronger acids than fluoboric acid tend to inhibit the removal of the fluoborate ion by the surfactant.

The molecular weight of the surfactant was observed to have a pronounced effect on the fluoborate ion removed. An increase in the size of the surfactant containing from 12-15 carbon atoms up to 18 carbon atoms increased the percent of fluoborate ion removed from 80 percent up to 97 percent. The degree of saturation did not have an effect on the amount of the fluoborate ion removed.

A series of experiments were carried out where different concentrations of surfactant solutions were added in a stepwise manner to individual solutions containing the same amount of fluoborate. The results reveal that as the concentration of surfactant in a solution is reduced, the amount of surfactant required to bind with a specific amount of fluoborate becomes less. Stepwise addition of three aliquots of dilute surfactant solution to a solution initially containing 100 mg/l of fluoborate required a ratio of 2.1 molecules of surfactant to 1 molecule of fluoborate ion for maximum removal. The single addition of concentrated surfactant solution to the solution containing the same concentration of fluoborate as above required a ratio of three molecules of surfactant to one molecule of fluoborate ion for the same removals. The stepwise addition of surfactant to the fluoborate solution apparently provides a more dilute surfactant solution with less micelle formation and more free surfactant molecules to bind with the fluoborate. The critical micelle concentration occurred at a surfactant concentration of 12 mg/l.

Operation parameters such as changes in air feed ratio, air bubble size, air dif-

fuser location, and inlet feed direction did not appear to improve the rates of removal of the surfactant-fluoborate complex by flotation. However, increasing the air feed rate produces a wetter foam which results in a reduction in the concentration of the surfactant-fluoborate complex in the foam.

Application of the specific ion flotation to the removal of fluoborate ion in solder plating, tin plating, nickel stripping, and copper plating rinsewaters containing 100 mg/l of fluoborate reduced the fluoborate in the solder plating, tin plating, and nickel stripping rinsewaters to 7 mg/l. The fluoborate in the copper plating rinsewaters was reduced to 15 mg/l. The removal of the fluoborate ion from the copper plating rinsewater by the specific ion flotation is probably less efficient, because this rinsewater was less acidic than the other rinsewaters.

Although flotation was shown to be effective in removing the surfactant-fluoborate complex from the plating rinsewaters, it required foaming times in excess of 20 hours to completely remove the complex from solution using our experimental system. The use of a Millipore High Volume Cassette* ultra-filtration system with 1000 molecular weight cut-off membranes resulted in removal of the complex within 6 hours.

Two approaches were examined for the recovery of the surfactant and the fluoborate for reuse in the treatment process and plating baths, respectively. The first approach which considered displacing the fluoborate from the surfactant by adding excess amounts of concentrated acetic acid was unsuccessful. The second approach used electrolysis to separate the surfactant from the fluoborate ion. The surfactant is plated on the cathode and can be removed from the cathode with concentrated acetic acid to recover the surfactant in the acetate form. Ninety percent of the acetate surfactant was recovered.

Electrodialysis

Application of electrodialysis for treatment of rinsewater containing high concentration of plating reagents required modification of an existing electrodialysis unit. Rapid deterioration of the commonly used platinized titanium anode was encountered when fluoboric acid was used as the electrolyte. Although this anode has been successfully used with nickel

sulfate plating bath rinsewaters and a sulfuric acid electrolyte, it rapidly turns black, cracks, and peels from the titanium metal backing when voltage is applied in the presence of fluoboric acid electrolyte. Apparently, the smaller fluoborate ion can penetrate the porous platinum coating and corrode the metal bond between the platinum and titanium.

The matching of the anion in the electrolyte with that in the rinsewaters is preferred to using another anion such as sulfuric acid electrolyte which is non-corrosive to the platinized titanium anode. The sulfuric acid electrolyte would result in introduction of undesirable sulfate anion into the concentrated streams and ultimately into the plating bath.

Evaluation of Different Types of Anodes

Several different approaches were considered to obtain an anode that would not corrode in presence of fluoboric acid electrolyte. These were (1) increase the thickness of the platinum plated on the platinized titanium anode; (2) plate a less porous metal such as gold on a nickel backing and form a solid solution between the gold and the nickel at the interface by heating; and (3) examine the use of inexpensive conducting materials such as low porosity high density graphite to which voltage could be applied directly.

The use of an inexpensive high density low porosity graphite anode was the only anode that proved successful. It did not corrode in the presence of fluoboric acid electrolyte and it produced a greater current density at lower voltage than the conventional platinized titanium anode.

Treatment of Tin Fluoborate Rinsewaters

A 114-liter reservoir of tin fluoborate rinsewater containing 2400 mg/l of stannous ion, 525 mg/l stannic ion and 6500 mg/l of fluoborate ion were treated by electrodialysis. After 12 hours of operation using 13 ion pair membranes at .012 amperes/cm² current density, the stannic ion was reduced to 75 mg/l and the fluoborate ion was reduced to concentrations below 150 mg/l. The stannous ion which is the desirable ion in plating baths is preferentially removed from the feed. The stannous ion is reduced to concentration levels approaching zero within 8 hours. The stannic ion is removed at a much slower rate than the stannous ion from the feed. The rate of removal of stannic ion increases after removal of the stannous ion.

The volume ratio of product to feed for the treatment of tin fluoborate rinsewaters was approximately 1:27.

The percent stannous ion in the product is observed to remain essentially well above 80 percent even though the stannous ion in the feed has been reduced from 83 percent down to 23 percent (see Table 1).

Table 1. Changes in Percent Stannous Cation in Feed and Product with Time During the Electrodialysis Treatment of Tin Fluoborate Rinsewater

Time (hours)	%SN^{+2} Feed	%SN^{+2} Product
0	83	
0.5	83	85
1.5	70	86
2.75	67	87
3.75	45	89
4.75	39	89
6.00	23	72

The concentration of stannous ion, stannic ion, and fluoborate ion in the product was 45 gm/l, 6.7 gm/l and 140 gm/l, respectively. These concentrations represent a 95 percent recovery of stannous ion, 48 percent recovery of stannic ion, and 70 percent recovery of fluoborate ion originally present in the feed.

Treatment of Solder Fluoborate Rinsewaters

The treatment of solder fluoborate plating bath which contains stannous, stannic, lead, and fluoborate ions in its rinsewaters was carried out under the same conditions employed for the treatment of the tin fluoborate plating bath rinsewaters.

The stannous ion is again observed to be preferentially removed from the feed. After eight hours of operation, the stannous ion is reduced from about 275 mg/l to below 5 mg/l, whereas, the stannic ion concentration in the feed was reduced from about 185 mg/l to only 165 mg/l. Reductions in the lead ion are comparable to the stannous ion. The lead concentration in the feed was reduced from about 190 mg/l to below 5 mg/l. The fluoborate ion was reduced from 1920 mg/l to about 220 mg/l.

The volume ratio of product to feed for the treatment of solder fluoborate rinsewaters was approximately 1:36. The stannous ion was again preferentially concentrated in the product and averaged above 80 percent even though the per-

cent stannous ion in the initial feed is only 62 percent. The concentrations of stannous ion, stannic ion, lead ion, and fluoborate in the product were 6.5 gm/l, 5.9 gm/l, and 11 gm/l, respectively. This represents a 92 percent recovery of the stannous and lead ions, 88 percent recovery of the fluoborate ion, and 11 percent recovery of the stannic ion.

Treatment of Copper Fluoborate Rinsewaters

The electrodialysis treatment of the copper fluoborate rinsewaters was carried out under the same experimental condition as the tin and solder rinsewaters. The copper ion in the feed was reduced from initially 2500 mg/l to less than 40 mg/l in approximately four hours. In this period of time, the concentration of the fluoborate ion in the feed was reduced from 7500 mg/l to 65 mg/l.

The volume ratio of product to feed for the treatment of copper fluoborate rinsewaters was approximately 1:17. The concentration of copper and fluoborate ions in the product was 40 gm/l and 120 gm/l, respectively. These product concentrations represent a 97 percent and a 90 percent recovery of the copper and fluoborate, respectively, originally present in the feed.

Rates of Mass Transfer

The rate of mass transfer of the ions across a square centimeter of membrane surface from the feed to the concentrate is dependent upon the cations in the rinsewaters and the plating bath rinsewater that is being treated. Comparable rates of mass transport across one square centimeter of membrane surface were obtained for the stannous ions from both the tin and solder rinsewater feed, respectively (see Table 2). The solder rinsewater feed is also removed at approximately the

Table 2. Rate of Mass Transport of Cations and Fluoborate from the Tin, Solder, Copper, Fluoborate Rinsewaters

	Plating Bath Rinsewaters Rate of Mass Transport (mg/hr. cm²)		
Ions	Tin Fluoborate	Solder Fluoborate	Copper Fluoborate
Sn^{+2}	1.7	1.9	
Sn^{+4}	1.9	1.4	
Pb^{+2}		1.4	
Cu^{+2}			41
BF_4^-	28	12	94

same rate. The stannic ion on the other hand shows a mass transport rate that is some 10 times slower than the rates obtained with the stannous and lead ions. The copper ion on the other hand exhibits a 20 times faster mass rate of transport than either the stannous or lead ions.

The rate of mass transfer of the fluoborate anion also appears to be dependent upon the plating rinsewater. The rate of mass transport exhibited by the fluoborate anion in the copper bath rinsewater is the highest followed by the fluoborate ion in tin and solder bath rinsewater in decreasing order, respectively (see Table 2).

Analysis of Electrolyte

The electrolysis or hydrolysis of the electrolyte was not observed as evidenced by monitoring the pH and fluoborate concentration. Both the pH and fluoborate concentration in the electrolyte showed no change during the electrodialysis treatment of the tin, solder, and copper fluoborate rinsewaters.

Conclusions

The specific ion flotation applied either separately or in the combination with electrodialysis appears to be feasible for the closed-loop treatment of waste rinsewaters resulting from solder, tin, nickel, and copper plating operations. The combined use of both processes provide for recovery of plating bath chemicals at concentrations that approach plating bath strength with a treated effluent suitable for reuse as rinsewater.

Specific Ion Flotation

1. Specific ion flotation using a commercially available alkylamine acetate surfactant is feasible for the treatment of dilute rinse wastestreams from solder, tin, nickel, and copper plating operations to provide a product that can be reused as rinsewater.

2. Fluoborate anion concentration in the solder, tin, and nickel fluoborate rinse wastestreams can be reduced to a concentration of 7 mg/l. Fluoborate anion in the copper plating bath rinsewaters can be reduced to a concentration of 15 mg/l.

3. The removal of fluoborate anion by the surfactant is dependent on replacement of the acetate group on the surfactant by the fluoborate anion. Removals are inhibited by

anions such as chloride which form stronger acids than fluoborate acid.

4. Fluoborate anion removals are enhanced by an increase in the molecular weight of the surfactant and by acidic conditions that increase the ionization of acetate groups on the surfactant.

5. Excess surfactant is required to make up for the acetate groups that are lost to the replacement reaction because of micelle formation which occurs at surfactant concentrations of 12 mg/l.

6. The replacement of the acetate on the surfactant by the fluoborate anion occurs within one minute. The rate limiting step in this process is the mixing time required to achieve a complete mix upon addition of surfactant to a fluoborate wastestream in the laboratory system used in this study.

7. The fluoborate-surfactant complex can be removed from solution by aeration. Air bubble size, air diffuser location, and inlet feed direction with respect to bubble rise, does not influence the rate of removal of the fluoborate-surfactant complex.

8. Increases in the air feed rate decreases the concentration of the fluoborate-surfactant complex in the foam by removing more liquid with the foam.

9. Ultrafiltration with recycling of the retentate provides a four times greater rate of removal of the fluoborate-surfactant complex from the rinsewater than aeration.

10. Electrolysis is suitable for splitting the fluoborate-surfactant complex to recover the surfactant. The surfactant is concentrated at the cathode and can be dissolved from the cathode in the acetate form with concentrated acetic acid.

Electrodialysis

1. Electrodialysis appears feasible for the treatment of concentrated fluoborate-containing rinse wastewaters. It provides a product that approaches plating bath concentrations and an effluent that can be further treated by the specific ion flotation process.

2. The use of a high density, low porosity graphite anode in an electrodialysis unit provides greater re-

sistance to chemical corrosion and greater current density for a given applied voltage than the more commonly used platinized titanium anode.

3. The graphite anode's resistance to chemical corrosion permitted the highly corrosive fluoboric acid to be used as an electrolyte to match the anion in the feed.

4. The rate of transfer of stannous ion and lead ion from the feed to the concentrate is significantly greater than the rate of transfer of stannic ion from the feed to the concentrate. This difference in the rate of transfer of the cations minimizes the build-up of undesirable stannic ion in the plating baths from reuse of the electrodialysis product.

Recommendations

The recovery of plating bath chemicals and the closed-loop treatment using electrodialysis with newly developed graphite anode and specific ion flotation of rinsewater containing fluoborate anions from solder, tin, copper, and nickel plating operations has been shown to be feasible. There are a number of advantages in using electrodialysis and specific ion flotation for the treatment of rinsewater containing fluoborate. Electrolysis treatment preferentially concentrates the desirable stannous ions in the product stream from a mixture of stannous and stannic cations commonly present in the rinsewaters. The product contains cation and anion concentrations that approach plating bath strength. The development of the graphite anode which is resistant to the corrosive nature of fluoboric acid provides an anode which is approximately one-fortieth the cost of the commonly used platinized titanium anode and allows the fluoborate electrolyte to be used to match the fluoborate anions present in the rinsewaters. The use of an electrolyte in the electrodialysis unit containing anions that match the anions in the feed is desirable to avoid contamination of the product produced from electrodialysis treatment. In addition, the surfactant used in the specific ion flotation treatment of rinsewaters containing low concentrations of fluoborate can be recovered along with the fluoborate anion by electrolysis.

In view of the above, the commercial feasibility of using electrodialysis in combination with specific ion flotation to provide a closed-loop treatment system should be established on a pilot scale. The engineering parameters and costs asso-ciated with the design, assembly, and operation of both systems must be determined. Also, this pilot-scale effort should identify the methodology that will allow rapid mixing of the fluoborate rinsewaters with the alkylamine acetate surfactant solutions at concentrations that do not favor micelle formation. In addition, the long-term stability of electrodialysis membranes (longer than 60 hours) toward the fluoboric acid electrolyte should be evaluated since frequent replacement of these membranes can lead to unacceptable operating costs. The replacement of the graphite anode after a period of time should not significantly contribute to the operating costs of the electrodialysis unit since its replacement cost is approximately one-fortieth of that required to replace the commonly used platinized titanium anode.

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The complete report, entitled "Removal and Recovery of Fluoborates and Metal Ions from Electroplating Wastewater," (Order No. PB 85-200 038/AS; Cost: $11.50, subject to change) will be available only from:
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