REMOVAL OF FLUOBORATE FROM ELECTROPLATING RINSE WATER BY ION FLOTATION

BY

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DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

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CREDITS

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ABSTRACT

A problem exists in the removal of fluoborate from electroplating waste rinse water. The normally used waste treatment methods are not effective and the vacuum evaporation process now being tried is expensive and energy intensive. Experiments were conducted and an alternative treatment process which shows substantial removals of the fluoborate was developed. This can be effectively done using ion flotation techniques. A broad range of surfactants were screened for usefulness in this process and it was found that an aliphatic amine acetate was usable in this process. Operating parameters for the process were investigated, and the removal mechanism was determined to be the replacement of the acetate on the surfactant with the fluoborate, rendering the surfactant adduct available for removal by foam separation or ultrafiltration techniques. These foaming process studies and the studies into the utilization of ultrafiltration techniques provided data for the design of a feasible full size facility utilizing this process.

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I. INTRODUCTION

The Federal Water Pollution Control Act (PL 92-500), also called the Clean Water Act, which was enacted in 1972, and which has been subsequently revised, reflects the recognition of the people that the time has come to minimize the effect that industrial pollution has on our environment. This law advocates the protection of the environment by the attainment by 1983 of "Zero Discharge" to the Nation's waterways of pollutants which are harmful to the environment. Most existing industrial waste water treatment practices are not capable of achieving "Zero Discharge." The metal finishing industry is an example of an industry which will need to develop new technology in order to approach this discharge requirement.

There are approximately twenty thousand facilities classed in the metal finishing industry in the United States. The majority of these facilities are associated with the automotive, electronic, or jewelry industries. There are two general groupings of facilities: job-shops and captive-shops. The treatment of the waste water generated by the processes present somewhat different problems for each of the groups. The job shops electroplate or otherwise provide a finish on a variety of products, for whomever contracts with them. They therefore have a much less uniform waste than does a captive shop, where the product throughput tends to be more steady. This lack of uniformity exacerbates the waste treatment problems; conversely the captive shops and single process job shops can often afford to develop processes where recovery of some value from the waste can be effected.

The major operations performed at metal finishing facilities include the following treatments on the part surface: cleaning and pickling, annealing, case hardening, polishing, buffing, immersion plating, electroplating, phosphating, conversion coating, oxidizing, painting, electropainting, and anodizing.

Metal finishing operations can be divided into three general processes:

1. Cleaning and Conditioning
2. Deposition of Metal
3. Passivation

Cleaning is the final step in preparing a metal surface for finishing. Dirt and oxides must be removed to obtain a satisfactory electroplate, because both the appearance and utility of the finish on the articles depend on a clean surface for the finish.

Inadequate cleaning may result in the following defects:

- Poor Adhesion of the metal applied
- Irregular coverage of the surface
- Pitting of the finish
- Bare Spots where no finish covers the substrate
- Poor Corrosion Resistance, due to a porous covering
- Roughness of the finish
- Hydrogen Embrittlement of the substrate
- Etching of the substrate
- Staining of the finish
- Excessive Graininess of the finish, and
- Powdery Coatings

The deposition of metals onto a substrate is achieved by adding electrons to the dissolved metal ions and reducing the metal ion to the "zero valence," native metal state. The deposition can be achieved either by the electroplating process of by the so called "electroless" process. In electroplating, the surface to be plated is made the electrically negative electrode in a cell consisting of two electrodies in an electrolytic solution. The metal ions in solution, being positive, gravitate to the work piece. At the surface they accept one or more electrons, and are reduced to the native state. The metal then adheres to the properly cleaned and prepared surface, forming a skin of this metal on the surface. The electrons are supplied to the negative electrode (cathode) by a battery, or a rectified power supply. The return path from the cathode to the battery is through the electrolyte, and the return electrode (anode).

In "electroless" plating, no external power source is used. The plating solution is made unstable (super saturated) with respect to metal ions by the use of sequesterents or chelating agents. The metal stays in solution until a nucleation site is offered in the form of a metal surface. The metal from the solution then plates out on the surface wherever the metal is exposed. The electrons are furnished by chemical reducing agents included in the both formulation.

The purpose of the passivation is to reduce the corrosion at the substrate by the environment in which the part will be used. An example is the passivation of steel with a zinc plate - zinc dichromate finish. Steel is quickly corroded in a moist atmosphere, therefore, zinc is used as a sacrificial coating on the steel. Sodium dichromate is then applied to this surface where it reacts with the zinc to form a protective insoluable coating on the zinc surface.

In metal finishing processes, after each stage of treatment of the work piece, water rinses are employed to remove residue of the active solution that the part is being removed from and to reduce the carry-over of this process solutions into the next process. The work piece is transferred from tank to tank, either manually or automatically. Large pieces are carried on racks while smaller parts are placed in baskets or rotating barrels. Each type of transport has associated with it its own inherent rinsing problems. It is much more difficult to rinse a barrel full of small parts than it is to rinse a flat sheet. The soil (or solution) which must be removed clings in the corners and interstices and resists removal. Therefore, more rinse water must be used per square foot of plated surface for barrel plating than for rack plating and for plating intricate parts than for plating parts with large plane surfaces.

The waste water produced in metal finishing operations is generated in two main ways. Concentrated wastes come from the disposing of solution which have become used and expended or which have become fouled. These dumps consist mainly of cleaning, stripping, passivating and anodizing solutions. Dumps are the lesser in total volume, of the two wastes, but the high concentration of chemicals requires special treatment. The dilute wastes, which are the larger volume wastes, come from the rinsing operations. These are the rinse waters used to remove soil and the process solution that has adhered to the surface being plated or which was entrapped in crevices due to the shape of the processed piece. The solution which is carried over from one tank to the other is called drag out. The quantity of drage out of solution into the rinse tank may vary considerably, depending upon the shape of the work piece, wetting properties of the solution, time allowed for drainage, the position of the part on the rack, and the number of pieces being processed. This drag out is the main waste generator. Other generators of waste include accidental spillage, leakage, equipment cleanup and washdown, entrainment of mist in ventilation ducts, regeneration of ion exchange units, and removal of sludge deposits from process tanks.

Depending upon the types of baths which are employed at a specific facility, the waste water stream generated may be either acidic or alkaline. It will also contain toxic contaminants such as cyanide, fluoride or chromate along with metal cations such as copper, zinc, nickle or cadmium and many other pollutants such as surfactans, deoxidants, oil and grease, organic solvents and wetting agents. Acid wastes will predominate at chrome plating, nickle plating, aluminum anodizing, copper stripping, aluminum, copper, and iron packeling, and from several other operations. The waste from most precleaning operations and from zinc and cadmium plating are generally alkaline. The acidity or alkalinity of the waste from each plating shop depends on the product mix being processed, so it varies from time to time at each facility.

There is a great deal of art in the metal finishing industry (as opposed to science). The process operator varies the plating bath constituants, somewhat by "feel," to achieve a specific end result. This somewhat unstructured modification of the bath makes the task of treating wastes more difficult. In general, it may be stated that "the additive which makes for a good plating bath, adversely affects the waste treatment processes."

Many toxic and otherwise hazardous chemicals are used in the metal finishing industry. It is often felt that for operator safety or for ease of waste disposal, certain commonly used chemicals should be eliminated from a process. Substitution of process chemicals is practical only when the substitution does not compromise the required quality of the finished product. One such chemical substitution is the use of fluoborate to replace cyanide as the conducting ion in plating baths. Fluoborate has been found to be an excellent carrier ion which will give a uniform, bright, complete covering. Fluoborate is much less toxic, both to humans and to lesser life forms than is cyanide, and therefore, it provides for a safer plating room working environment. For these reasons, many shops which plate cadmium, zinc, tin, lead solder, copper, nickle or iron are replacing their cyandie baths with fluoborate baths.

Commercial fluoborate electroplating solutions are presently available for the plating of copper, indium, iron, lead, nickle, tin and their alloys. Fluoboric acid also is used in various pretreatment operations, such as stripping and cleaning.

Fluoborate is therefore found in the waste streams from these processes. The concentration of contaminants in these rinse waters is variable, depending upon the rinsing technique which is employed. When a single tank rinsing process is used, the stream will be quite dilute in contaminants, while high concentrations of pollutants would be expected in the rinse water from multiple tank counter-current or series rinsing.

Fluoborate

The fluoborate ion is composed of a centrally located boron ion, surrounded tetrahedrally by four fluorine ions (see Figure 1). The B - F distance is 1.43A° (5,6) with a F-B-F angle of 109°. This gives an ionic diameter of only about 5A°. This small tightly packed ion tends to act more like a single element ion, than like a multi element ion, and forms salts where there is a true cation with no covalent bonding to the anion. The fluoborate ion is reported by Sharp to be diamagnetic, and non polar. Conductivity studies have shown that fluoboric acid is a very strong acid with about the same strength as hydrochloric acid. The acid, and the ionized salts in water solution, are in equilibrium with the hydrolysis product.

$$BF_4 \rightleftharpoons BF_3(OH) \rightleftharpoons BF_2(OH)_2 \rightleftharpoons BF(OH)_3 \rightleftharpoons B(OH)_3 \qquad [1]$$

The alkali metallic salts of fluoboric acid are quite soluble. Ryss (38) shows that at room temperature (17°C:

$NaBF_4$ is very soluble.
KBF_4 is soluble to 3,000 ppm.
$RbBF_4$ is soluble to 2,500 ppm.
$CsBF_4$ is soluble to 9,000 ppm.
NH_4BF_4 is very soluble.

These salts readily form aquo (or amino) complexes. The center group metals, iron, cobalt, nickle, copper, silver, lead and tin all form salts (or hydrated salts) which range from soluble to very soluble.

The bonding in ammonium fluoborate (32) has been investigated using the infrared spectrum. The results are interpreted to show that hydrogen bonding in ammonium fluoborate is very weak as the BF_4 sysmmetry is not upset. The organic amines are of the form $R_nNH_{(4-n)}BF_4$. Fluoboric acid has not been obtained in the free state (40), and it is assumed that the molecular form HBF_4 does not exist in solution. The equilibrium constant of HBF_4 decreases with a decrease in concentration of the solution. The equilibrium is complicated by the electrolytic dissocation of hydrogen fluoride, and in the dilute solutions also by the increased degree of hydrolysis of BF_3OH. BF_3OH is more strongly acid than hydrogen fluoride.

Hydrolysis of Fluoborate

The answers to the problem of the effect of fluoborate on the environment have not been finalized as yet. The United States Environmental Protection (EPA) was asked this question in 1973 (30) and they recognize it but they have not provided an official answer. In exploring for a possible anser it was found that fluoborate hydrolyzes in water to form fluoride and borates (34). This is done in the following manner.

$$HBF_4 + 3H_2O = 4HF + B(OH)_3 \qquad [2]$$

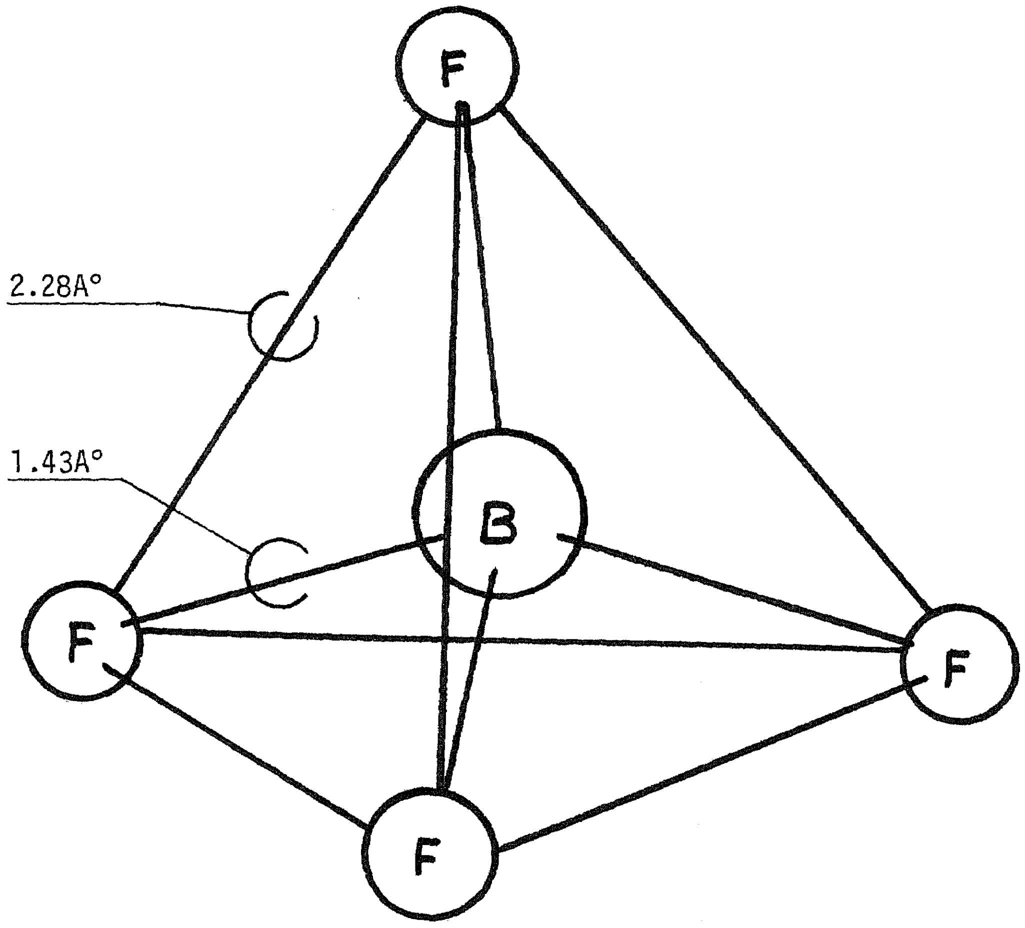
The equilibrium constant which Ryss presents for this reaction is (40):

$$K = \frac{(H_3BO_3)\ (H^+)^3\ (F^-)^4}{(BF^-{}_4)} = 9.772 \times 10^{-21} \qquad [3]$$

The equilibrium constant K for this reaction is sensitive to the concentration of fluoborate in the water and to the pH. This is shown on Figure 2 for concentration and for the range of pH of concern. The values of K also varies with the temperature.

It must be remembered that this Figure shows equilibrium values. The rate of the reactions are very slow at room temperatures. For the overall reaction the K has been shown to vary with temperature as in Table 1 (39).

FLUOBORATE ION TETRAHEDRAL



BF_4^- STRUCTURE

Figure 1

PLOT OF HYDROLYSIS OF BF_4^- WITH pH

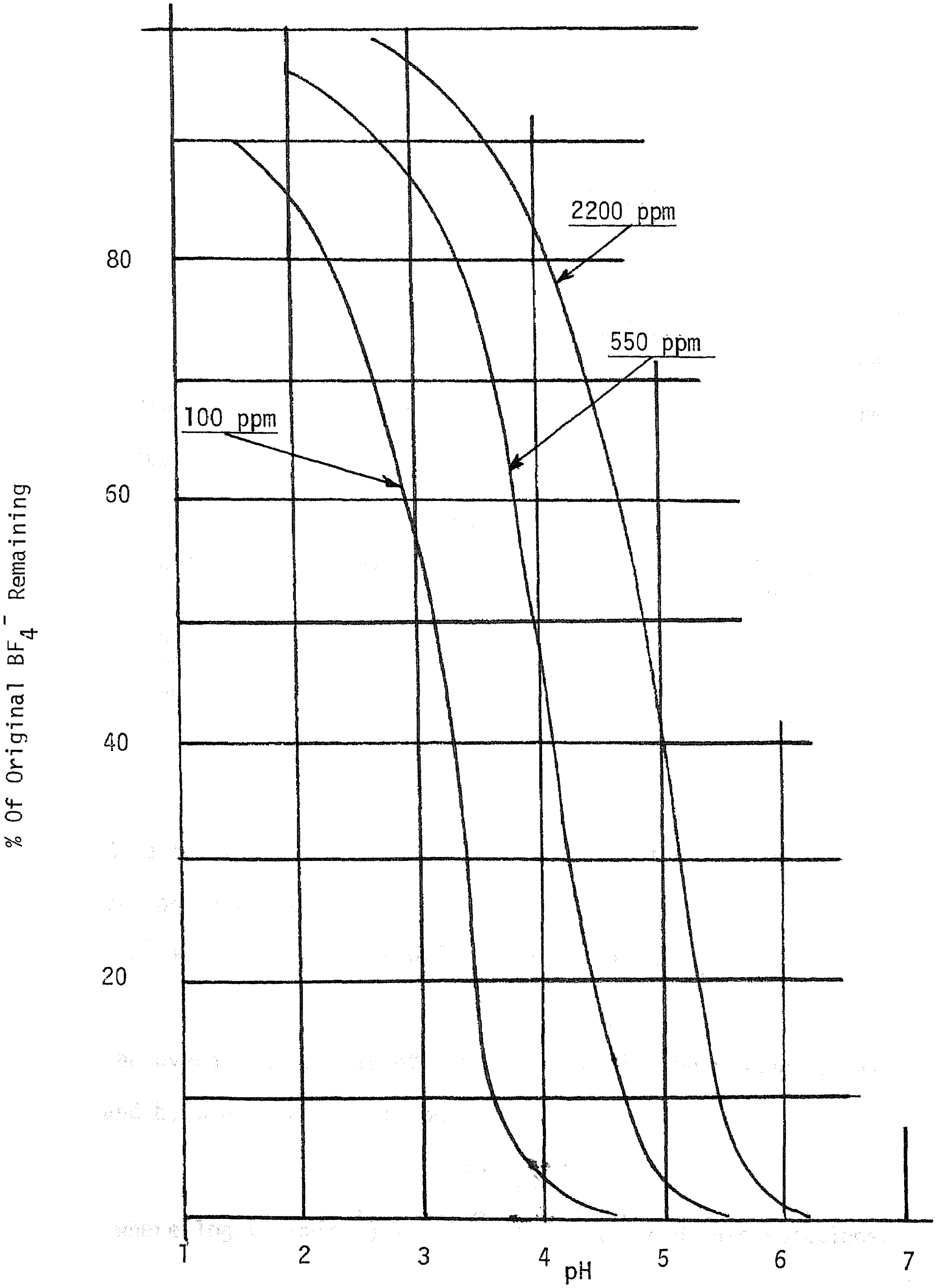


Figure 2

TABLE 1

Temperature °C	$K \times 10^{-21}$
20	8.376
25	9.772
61	16.752
80	19.195
90	22.685
100	25.477

This change in K values, though it appears to be large (a factor of 3 for values shown), does not have a major effect on the hydrolysis - pH equilibrium. Table 2 shows the temperature effect on pH.

TABLE 2 ($K \times 10^{21}$

Temp °C	K=8.376 pH	K=16.752 pH	K=25.477 pH
98	0.6	0.5	0.5
90	1.8	1.7	1.6
80	2.3	2.2	2.1
50	3.0	2.9	2.9
20	3.5	3.5	3.4
5	3.8	3.7	3.6
1	4.1	4.0	4.0

A better representation of the above reactions, showing ionization, might be:

$$H^+ + BF^-_4 + 3H_2O \rightarrow nF^- + (4-n)\ HF + mB(OH)_2 + (OH)^- + (1-M)B(OH)_3$$

The overall time rate of this reaction has been shown by Ryss (38) and by Grassimo (35) to be:

$$\log \frac{C}{Co} = k't$$

where $\log k'\ (\mathrm{min}^{-1}) = \frac{-3730}{T} + 7.11$, for dilute solutions.

The values "3730" and "7.11" vary somewhat, rising with a rise in fluoborate concentration. The constants are 3922 and 7.55 in a one molar concentration. This shows that the reaction is more rapid in the dilute solutions. A plot of values of the percent reduction of fluoborate.

$\frac{\text{Concentration at time of concern}}{\text{Concentrator original}}$ ......$(\frac{C}{Co})$..... against time,
are shown for some representative temperatures on Figure 3. Implicit in this plot is the possibility of a 100% hydrolysis. If the equilibrium is for less than 100% hydrolysis, other considerations must be made and the data would have to be normalized to reflect the hydrolyzed percentage of that portion which would be hydrolyzed at equilibrium conditions. See Figure 2 for plot of $\frac{C}{Co}$ versus pH.

These data show that fluoborate should be completely hydrolyzed at the pH of our natural waters. However, it also shows that a long time is necessary to effect the hydrolysis at ambient temperatures. As an example if 50 ppm of BF_4 were introduced into a natural water, it would take a month to hydrolyze to give 10 ppm of fluoride ion. Fluoborate of itself is apparently not harmful to humans or other life forms (48), but because of the uncertainty of the hydrolysis and the hazard of the product of the hydrolysis, the EPA is concerned with its discharge. They are awaiting further development before putting on discharge limits.

HYDROLYSIS OF BF_4^- IN WATER

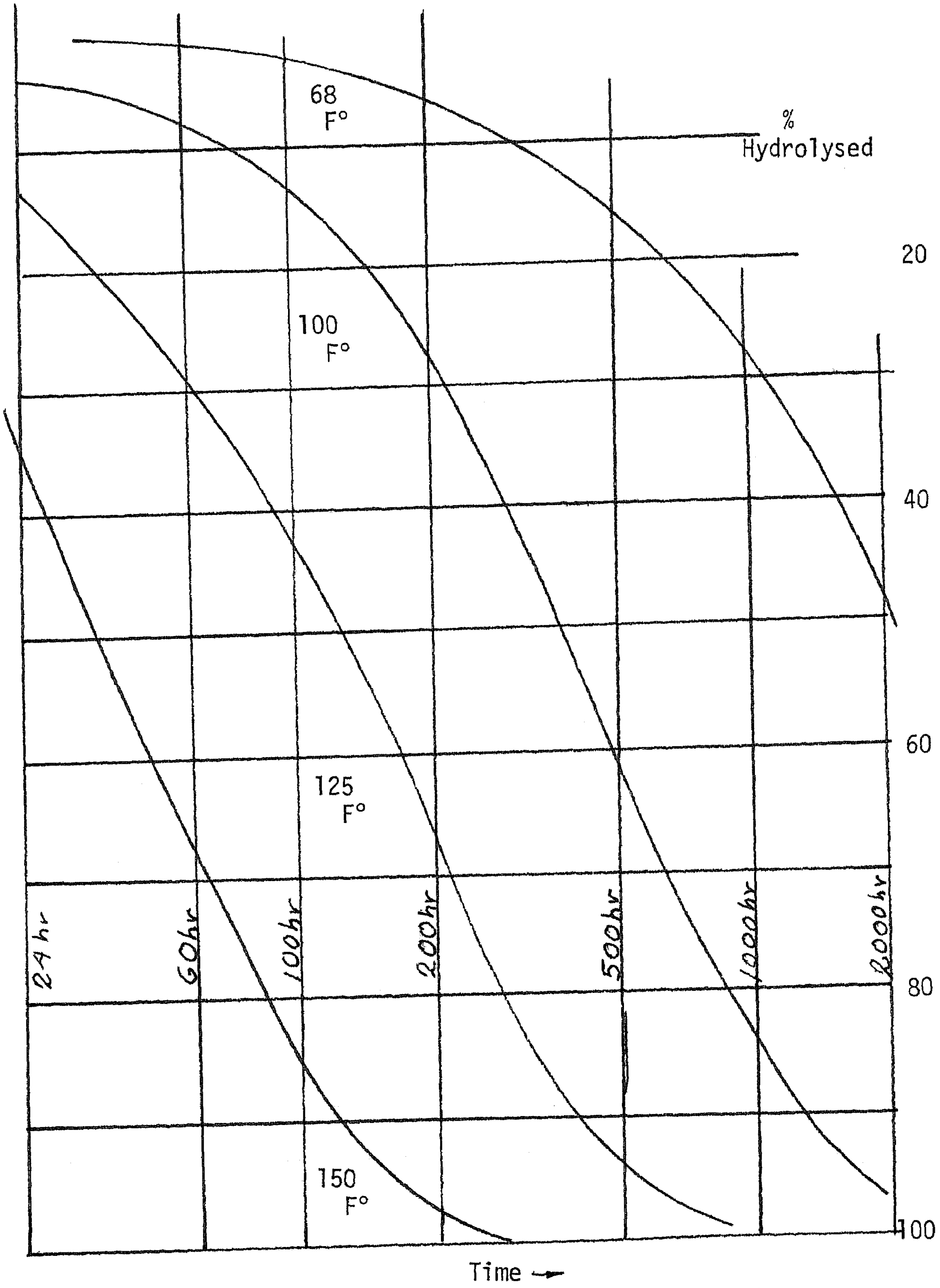


Figure 3

There is no specific discharge limitations on fluoborate at this time. However, when a waste stream is analyzed for fluoride by the approved method (Bellack Distillation) any fluoborate present will be hydrolized and will yield inflated fluoride concentration readings. 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 indicate a National Pollution Discharge Elimination System Permit (NPDES) violation where none exists. If the National goal of protecting our Nation's waters is to be realized, fluoborate must be removed from or kept out of our waste waters.

Industrial Waste Treatment

Waste Water Characteristics

Each electroplating facility has its own specific waste mix (which probably varies from hour to hour). The streams, however, can be segregated to give a generally representative waste composition from a particular process. The waste water with which we are concerned results from the rinsing of metal parts which have been electroplated in a bath containing the fluoborate ion as a constituent.

The discharged rinse water will generally have specific contaminations in the same proportions as the constituents are present in the plating bath. The final concentration of the contaminate will depend on the efficiency of the rinsing, the allowable contaminate on the finished part, and the rate of the makeup water flow to the rinse tanks.

Typical electroplating baths using fluoborate are shown in Appendix 5. From this appendix it can be seen that the fluoborate ion varies from 165 grams per litre (g/l) to 500 g/l with an average of 310 g/l.

The metals vary from 15 g/l to 240 g/l with an average 100 g/l, and the organics average less than 10 g/l. To comply with acceptable rinsing practices (Table 4), the highest of the fluoborate ion or metal ion concentration in the final rinse water after plating should not exceed 37 ppm (8). To have a rinse water of 100 ppm in fluoborate, a two stage rinse would have to be used and the makeup water flow controlled accordingly. The Appendix also shows that for a typical medium sized plating operation, the volume of fluoborate rinse would be about 3,400 gallons per shift.

Existing Treatment Techniques

The current method of control of pollutants from the metal finishing industry includes three general processes. These are the techniques for reducing waste quantity at the source, techniques for removal of the pollutants from the water, and techniques for concentrating the residue for ultimate disposal.

Water conservation is an obvious aid to pollution removal. When the volume of the effluent which must be treated is reduced, the handling and treating pollution costs are reduced for a given process. Most of the water which is discharged comes from rinsing operations. The plated part must be rinsed free of plating chemicals, and this contaminates the rinse water. Over the years by trial and error, the finishing industry has determined the level of contamination which can be tolerated in the final rinse tank and still allow for good plating. Table 3 below is reproduced from the U.S. Environmental Protection Agency's Development Document for Effluent Limitations for the Metal Finishing Industry (2).

TABLE 3

Process	Max Dissolved Solids In Final Rinse, mg/l*
Alkaline Cleaners	750
Acid Cleaners, dips	750
Cyanide Plating	37
Cooper Plating	37
Chromium Plating	15
Nickle Plating	37
Chromium Bright Dip	15
Chromate Passivating	350-750

*mg/l = miligrams of dry solids per litre of solution. This equates to parts per million by weight (ppm). mg/l and ppm will be used interchangeably in this paper.

It is generally desirable to segregate waste flows for specific treatments and for using in waste-to-waste neutralization where practical.

It is generally desirable to segregate waste flows for specific treatments and for using in waste-to-waste neutralization where practical.

Removal techniques considered in the "Best Practicable Control Technology Currently Available"* (48) include both chemical and physical techniques. A typical process schematic is shown in Appendix 6.

The common chemical processes used in waste treatment are:

1. Oxidize cyanide to carbon dioxide and nitrogen.
2. Reduce hexavalent chromium to trivalent chromium.
3. Precipitate fluoride.
4. Neutralize the waste to precipitate heavy metal salts.

The processes 1, 2, and 3 are best done on segregated streams for reasons which will become apparent.

The cyanide oxidation is usually accomplished as follows:

1. Raise the pH to approximately pH 11.
2. Add chlorine or a chlorite to the waste water to oxidize the cyanide to cyanate.
3. Lower the pH to around pH 7.
4. Add chlorine or chlorite to oxidize cyanate to carbon dioxide and nitrogen.

---

*Wording from the Water Pollution Control Act.

5. Flow the waste to the final neutralizing process for completion of precipitation of solids from the waste.

The overall reactions for this process are:

$$CN^- + ClO \xrightarrow{-(OH)} Cl + CNO^- \qquad [4]$$

$$CNO^- + ClO \xrightarrow{-(H)} Cl^- + CO_2 + 1/2(N_2) \qquad [5]$$

The chromium waste from electroplating is mostly in hexavalent state. It is very soluble in this state. Therefore, the chrome must first be reduced to the trivalent state and precipitated as the hydroxide. The reaction of a sulfite with the chrome, affects this reduction, but takes place very slowly at pH's higher than pH 3. Therefore, the waste is first adjusted to about pH 2.5. Then, sulfar dioxide or a sulfite is added, and the reduction proceeds.

The reaction is: (for dichromate)

$$Cr_2O_7^{-2} + 3SO_3^{-2} + 2O^{-2} \longrightarrow 2CR^{+3} + 3SO_4^{-2} + 6O^{-2} \qquad [6]$$

The waste then goes to join the other waste streams. The waste will be neutralized and brought to a slightly alkaline condition so that a pH of about pH 9, the chromouse hydroxide will precipitate. (Minimum solubility of $Cr(OH)_3$ in water occurs at pH 8.6. See Figure 4).

The other specific waste named above is fluoride. Direct addition of lime is the standard technique for reducing high concentrations of fluoride. The lime reacts with the fluoride in the waste water to produce calcium fluoride. Calcium fluoride has a solubility of about 8 ppm at pH 11 (61). An excess of lime is used to drive the reaction as far toward precipitation calcium fluoride as practical. The partially treated waste is then introduced into one of the later neutralization stages so that the precipitate will not re-dissolve.

In most processes the individually treated wastes are brought together at a final pH adjustment process. The pre-treated waste streams and the miscellaneous acid-alkali waste are blended to achieve as much "self neutralization" as practical.

The most general method of treatment of the combined waste is to neutralize it with either lime or sodium hydroxide. This process precipitates the metal hydroxides or hydrated oxides when the pH is in the vicinity of pH 8.5 to 9 (See Figure 4).

$$M^{+a} + a\,(OH)^{-} \longrightarrow M(OH)_a \qquad [7]$$

A flocculating agent, usually a soluble iron salt such as ferric sulfate or aluminum sulfate, can be added to this waste at this point also.

$$Fe_2(SO_4) + H_2O \longrightarrow Fe^{+3} + 3SO_4{}^{-2} + H_2O \qquad [8]$$

$$Fe^{+3} + 3(OH) \longrightarrow Fe(OH)_3 \qquad [9]$$

$$Al_2(SO_4)_3 + H_2O \longrightarrow 2Al^{+3} + 3SO_4{}^{-2} + H_2O \qquad [10]$$

$$Al^{+3} + 3(OH) \longrightarrow Al(OH)_3 \qquad [11]$$

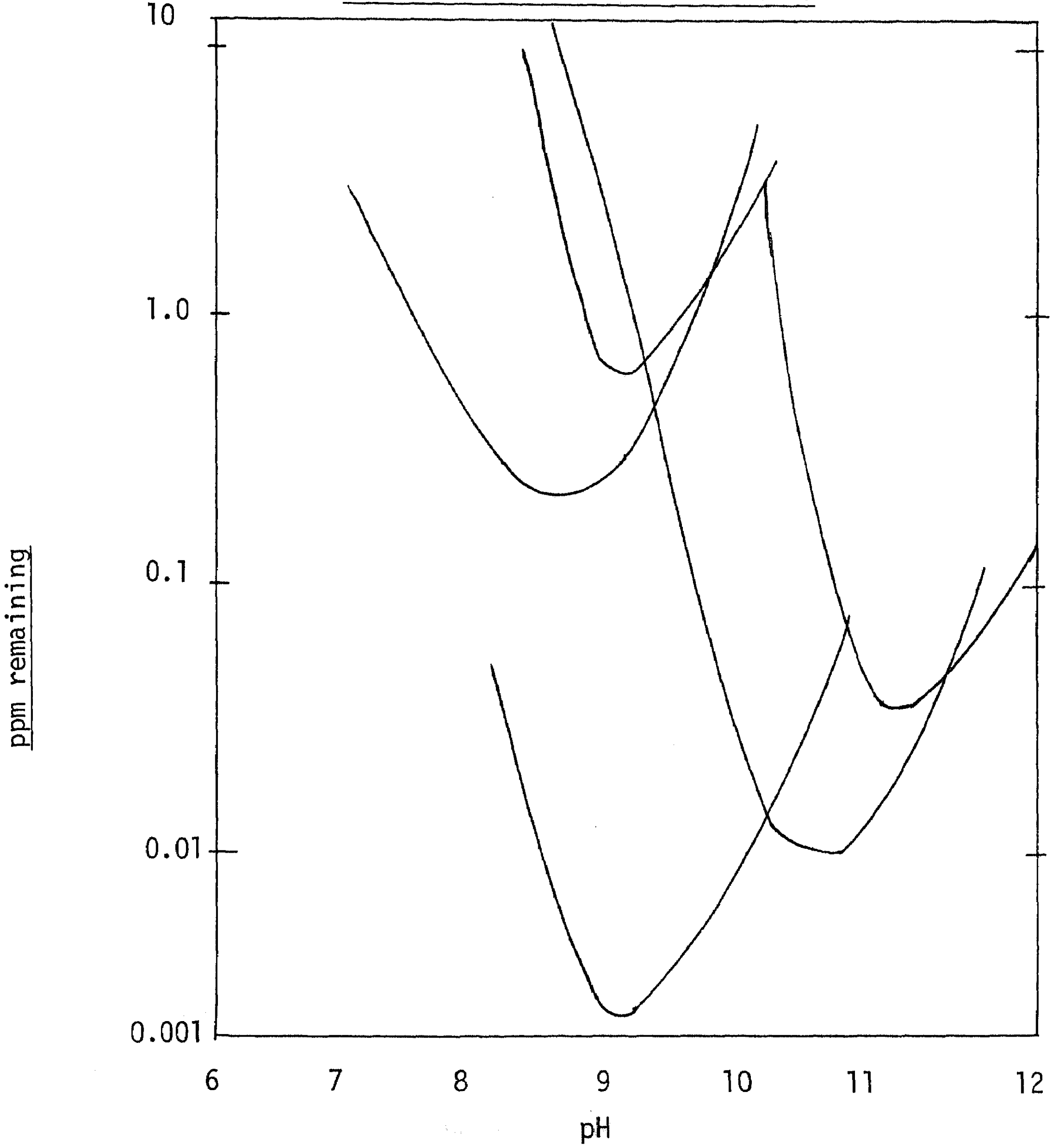
This material assists in the solids removal step by forming a loose iron or aluminum hydroxide precipitate which makes a sludge "blanket." This blanket acts as a filter in collecting smaller particles from a gentle flow and thereby improving the effluent quality.

The waste may then flow to an aeration tank where aire is introduced to oxidize any residual sulfite from the chrome treatment process and to assure that all the iron is in the high valence state.

$$SO_3{}^{=} + 1/2\ O^{\circ} \longrightarrow SO_4{}^{=} \qquad [12]$$

$$2Fe^{+2} + 1/2\ O_2 \longrightarrow 2Fe^{+3} + O^{-2} \qquad [13]$$

Ferric hydroxide is less soluble than ferrous hydroxide, and the ferric also forms a better floc. The de-aeration facility is usually a shallow flume where excess air bubbles are allowed to return to the atmosphere so that they will not float the floc in the removal tank.



SOLUBILITY OF METAL HYDROXIDES

M	Minimum Solubility (ppm)	pH
Iron	1.8×10^{-3}	10.5
Nickel	9.0×10^{-4}	10.5
Zinc	6.0×10^{-2}	9.0
Cadmium	3.6×10^{-3}	11.0
Lead	4.1×10	9.3
Copper	2.5×10^{-4}	9.0
Chromium	2.0×10^{-2}	8.5

FIGURE 4

Just ahead of the solids removal tank, a flocculant aid is usually added. This is a many branched long chain hydrocarbon which spans the flocculant particles helping to hold the blanket together and collecting small particles. Sludge is drawn off the bottom of the solids removal tank and sent to a dewatering process while the treated water over-flows to re-use or to waste. The dewatering may be a single step process, or the sludge may be allowed to settle, with the top water being decanted, prior to mechanical dewatering. There are a number of ways to effect this final dewatering. It may be done using a precoated vacuum filter, a filter press, a centrifuge, or even by precoated pressure filter. The final sludge generally contains 20 to 40 percent solids, and it is usually disposed of into a landfill.

As can be seen from the above, the primary thrust in pollution control is the precipitation and removal of the cations and the fluoride anion and the destruction of the cyanide anion. The other anions commonly used are not particularly hazardous except when they overload the water with their soluble salts. The increased usage of fluoborate however presents a new problem.

Treatment of Fluoborate Waste

There are only a few known processes for the removal of fluoborate from plating rinse waters. The small tight molecule of the fluoborate is not easily rejected by membrane processes such as reverse osmosis or ultra-filtration; and there is at this time no known ion exchange resin which will remove significant amounts of fluoborate from water solution. Battelle Memorial Institute in their January, 1974 draft (2) 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. Tests have proven this suggested method to be unusable because the hydrolysis reaction is too slow for commercial feasibility at any reasonable temperature (Appendix 3). Vacuum evaporation is currently being used as a means of recycling stannous fluoborate rinse waters back into the plating tank as make-up solution. Although this process provides a closed leep, there are many performance problems. A major problem is the precipitation of stannic oxide which pervades the system inhibiting the evaporation and blocking the system. This process is also an extremely energy intensive operation.

Because acceptable technology for the treatment of rinse water from fluoborate plating baths is lacking, this investigation was undertaken to establish the feasibility of using specific ion flotation or ultrafiltration for the removal of fluoborates from dilute concentrations of electroplating waste water.

The optimum process for the removal of the fluoborate ions from the waste waters should provide the following attributes.

It should:

1. Be, as far as practicable, a closed-loop system, with recovery of basic constituants.
2. Require a minimum of energy input.
3. Require a minimum of chemical addition.
4. Minimize the production of sludge or other waste matter.
5. Be practical from a cost of installation and operation standpoint.

The literature search indicated that a process utilizing ion flotation techniques should be explored to determine if a mechanism which could approach these goals could be developed.

Ion Flotation

Flotation processes for use in separation of solid particles from liquids is an old, well-established process in waste removal practices (85) as well as in the process industries (93). For waste removal by flotation, the mechanism is to first add a surface active agent (surfactant) to the waste water and mix it thoroughly. This allows the surfactant to adhere to the particles of soil in the water. Then a foaming process brings the surfactant - solids combination to the surface where it can be skimmed or otherwise removed. Even though these solids are more dense than water, they are buoyed by the air bubble such that their total specific gravity is less than one. The surfactant chain is made such that at one end is hydrophobic, and the other end is hydrophyllic. Because of surface considerations, the hydrophyllic end of the surfactant adheres to the particles of soil while the hydrophobic end tries to remove itself from the water. When an air bubble contacts the hydrophobic end of the surfactant, the surfactant pokes into the air-water interface (to reduce the total energy of the system). The weight of the particles is then balanced by the buoyancy of the affixed air bubbles, and the particle floats to the liquid surface, buoyed by the air bubble.

The flotation of ore in mineral processing is a somewhat more sophisticated mechanism in that the surfactant is engineered to adhere preferentially to only one specific type of solid, thus floating one mineral and allowing other minerals to settle. This ore separation process can be designed specific enough to separate such salts as potassium chloride crystals from sodium chloride crystals (92).

Ion flotation is a relatively recent process. The field has been explored by Seba (93) in South Africa and Grieves (74) in the United States. The concept of ion flotation is different from ore flotation in that a chemical complex is formed between the surfactant and the dissolved ion. In ore flotation or particulate flotation, the surfactant adheres to a solid particle. In waste streams such as from metal finishing operations the item to be removed is not particulate, but is dissolved in solution. The surfactant, therefore, must chemically react with the ion which is to be removed. Most of the work done in the ion flotation field has been concerned with removing metal cations from solution. This is done using anionic surfactants. Grieves (74, 75) has investigated the use of ion flotation for the removal of the anionic chromate ion, but there has been no research into the removal of the anionic chromate ion, but there has been no research into the removal of the fluoborate ion using this process. Therefore, this investigation was made into the use of specific ion flotation for the treatment of fluoborate plating bath rinse waters containing dilute concentration of fluoborate.

The specific areas which were investigated were:

1. The identification of the binding mechanism. Here the type and structure of the surfactant that favors the binding of the fluoborate ion with the surfactant was determined. This allows optimizing of the binding process.
2. The reaction kinetics, this to verify the reaction and to allow for ascertaining the optimum:
    - 2a. Chemical process parameters; where the effects of changing pH, acidity, mole ratio of surfactant to fluoborate, and the interfering ions were studied.
    - 2b. Physical process parameters; where areas of study were, initial contact time (mixing) air feed rates, bubble size, air contact time, and feed direction.

3. The evaluating of this technology for the removal of fluoborate ion from the rinse waters resulting from the operations of nickel stripping, solder plating, tin plating and copper plating.
4. Exploring the means of recovery of the surfactant and the fluoborate ion for reuse in the treatment process and plating baths, respectively, consistent with the closed-loop concept.
5. Ultrafiltration, evaluated as an alternative to flotation for rapid separation of the fluoborate-surfactant complex from the rinse waters.

Data Evaluation

Evaluation of the data obtained from testing the various parameters was done in the following manner. Each experiment was run three times and the evaluated test point is the average of three runs of the experiment using the modification of interest. The Student's "T" test was used to compare these averages with the mean value for the original experiment. The "T" test allows for the comparison of the transformed difference between two averages and a statistical difference which could be expected for experimental error.

The use here of the "T" test for variance of data develops as follows, when comparison is to be made between two means. Let $\bar{x}$, and $\bar{x}$, be the means of two samples from the same population, with sample sizes n_1 and n_2 respectively, and with s_1 and s_2 the corresponding standard deviations of the samples. Then a quantity T_i can be found such that

$$T_{\bar{i}} = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{n_1 s_1^2 + n_2 s_2^2}} \sqrt{\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}} \qquad [14]$$

where Ti is a number indicating how much sample number two varies from sample number one. In this case $\bar{x}$ is the mean of the three results of the experiment as originally run, and $\bar{x}$ is the mean of the results of the experiment as modified and run three times. Therefore, $n_1 = n_2 = 3$ and equation (14) becomes:

$$T2 = \frac{(\bar{x}_1 - \bar{x}_2)}{3\sqrt{S_1^2 + S_2^2}} \sqrt{\frac{9(6-2)}{6}} \qquad [15]$$

$$= \frac{2\ (\bar{x}_1 - \bar{x}_2)}{\sqrt{s_1^2 + s_2^2}} \qquad [16]$$

The sample means ($\bar{x}$) are found as $\bar{x} = \frac{s\text{-}x}{n}$ and the sample standard deviations (5) around found as $s = \sqrt{\frac{(\bar{x} - x_2)^2}{n}}$. Therefore, we can find a numerical "T" value for each of our sets of data.

The "T" s are then compared with tabulated "T" values which show the ranges of values which can be expected as attributable to experimental error and which values of T can be taken as indicating a significant effect on the results of the experiment brought on by the parameter being investigated. For a confidence level of 95% (± 2.5% possible error) and a degree of freedom of 4 (three experiments for each mean) any "T_i" value between - 2.776 and + 2.776 implies that there was no significant difference in the experimental results which was brought on by changing the parameter under study. "T"s with absolute values larger than 2.776 implies that the change in the experiment did affect the results.

II. EXPERIMENTAL

Fluoborate Detection

Until recently there was no good rapid way of determining the quantity of fluoborate in a solution. Wet chemical methods are difficult and time consuming at best. About a decade ago, a specific ion electrode was developed for determining fluoride in solution. The common method for determining fluoborates is thus to first determine the "free" fluoride in a solution, then use an acid digestion process to hydrolyze the fluoborate to give "free" fluoride, which is then determined. The level of boron is also determined as a double check on the method. The fluoborate level is then determined as being one part (mole) per part of boron in solution, or equivalently one part for each four parts of additional fluoride as determined. In recent years a specifc ion electrode has been developed for the fluoborate ion. This is a liquid membrane - ion exchange type probe. An early type was tested by the USEPA's National Environmental Research Center at Cincinnati (98). They found this probe to be usable in dilute solutions with due consideration for interfering substances. Substances which interfere with the liquid membrane, can destroy the probe's usefulness so care must be taken to eliminate these substances from the test solution. This method, while usable, is not yet approved as a "Standard Method" by the

ASTM. It was however found to be reliable and was used in these studies as described below. The equipment used was na Orion Model 404 specific ion meter with an Orion 93-05 fluoborate ion electrode and Orion 90-02 double junction reference electrodie. The outer junction of the reference probe was filled with 0.1 molar ammonium fluoride, and the solution to be tested was made 0.1 molar in a-monium fluoride to buffer the solution and give a constant ion background. The testing procedure was checked as described below, and it was found that the milivolt potential plotted linearly against the log of the fluoborate concentration for the range with which these experiments were concerned. This was the range from one to one hundred fifty parts per million (1.15×10^{-5} molar to 1.73×10^{-3} molar in BF_4) of fluoborate. Higher fluoborate values were also checked and it was found that the plot was linear into the range of 10^4 ppm, within the constraints of these experiments. The slope of the plot is approximately fifty-six milivolts per ten factor concentration of BF_4^-, therefore, linear on a semilog plot. This slope was found to drift with time; therefore a fresh standard plot was made at the time of each reading (or set of readings). An aliquot of each experiment was kept and was used as the "standard solution" at the end of each experimental run as described below under Probe Linearity.

A difficulty alluded to above, which had to be circumvented for these purposes, is that the fluoborate specific ion electrode cannot be used in solutions containing surfactants, because the surfactant destroys the membrane. Therefore, it was impossible to plot any time rates of removal for this reaction. The equipment could find only the starting quantity of fluoborate in solution before the addition of surfactant, and the quantity of fluoborate remaining after all of the surfactant had been removed.

Part of the study was the determination of the time rate of removal of the fluoborate. This required that the equipment be able to determine the fluoborate in the presence of surfactant. The predecessor of the Orion 93-05 probe, the Orion 92-05 Specific Ion electrode, has a replaceable membrane. It, in conjunction with the 90-02 Reference electrode, was found to allow between five and ten good readings before the membrane needed replacement. Thus, the fluorobate, which is in the soluton with surfactant, can be measured. The fluoborate which is bound in the adduct, is sequestered from the solution and therefore it does not register on the measuring equipment. It was effectively removed from action in the solution as soon as it replaced the acetate on the surfactant. A series of tests were made to verify this and to correlate the results of the replaceable membrane electrode tests with the results found after the foaming using this 92-05 electrode and with the 93-05 electrode.

The results of these tests are shown in Table 4, and on Figures 5 and 6. For these tests, the surfactant was added, and a reading of the unbound fluoborate was made. The adduct was then foamed out of the solution, and the amount of fluoborate remaining in solution was determined using the fixed membrane probe. The results of these measurements showed that the difference in readings before an activity and the readings after the activity could be used to give percentage removal (or binding) values.

These are the data which were being sought. Using the methods described, the absolute values of fluoborate in solution can be determined only when compensation for the background of extraneous contaminant is considered (99). However, the absolute values are not necessary for this investigation. The replaceable membrane probe was, therefore, used for the investigation.

Table 4

% Fluoborate Removal from Solution or "Inactivated in Solution"

Molar Ratio Surfactant To Fluoborate	Armac C Flotation	Armac C Mixing	Armac T Flotation	Armac T Mixing
x	y'	y'	y'	y'
2	67.5	70.4	89.1	88.8
2.5		75.2		91.6
3	76.5	77.6	93.1	94.2
3.5	78.7	80.1	93.9	95.6
4	85.2	82.0		95.8
4.25	87.4			
4.5	93.2	85.0		95.2
5.0				95.6
y'=mx+b				
r = Correlation Coefficient	0.983	0.989	0.984	0.847
m - slope	9.65	5.48	3.31	2.09
b - intercept	47.26	60.57	82.64	86.53

Removal of Fluoborate from Solder Bath Rinse

Armac C

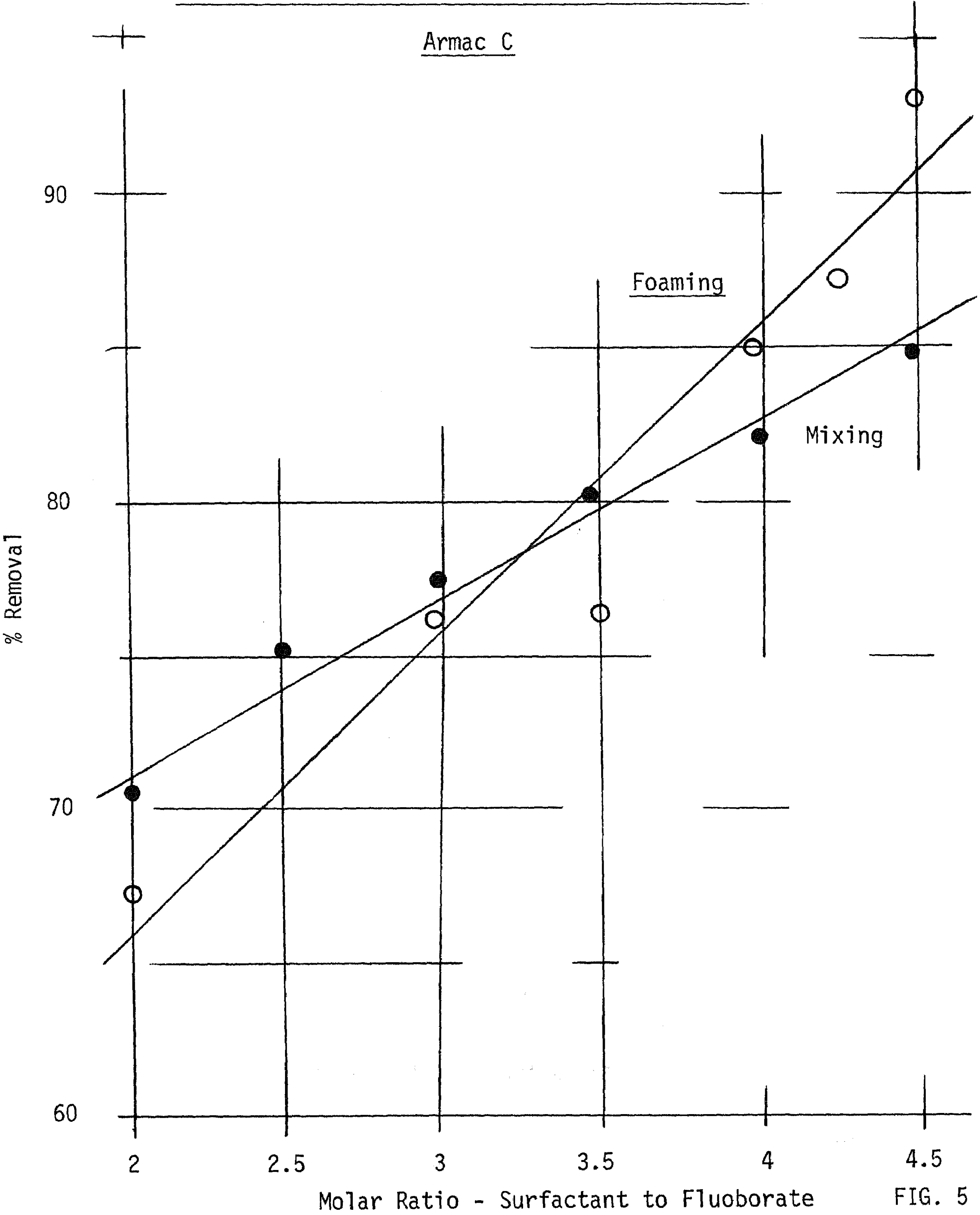


FIG. 5

Removal of Fluoborate from Solder Bath Rinse

Armac T

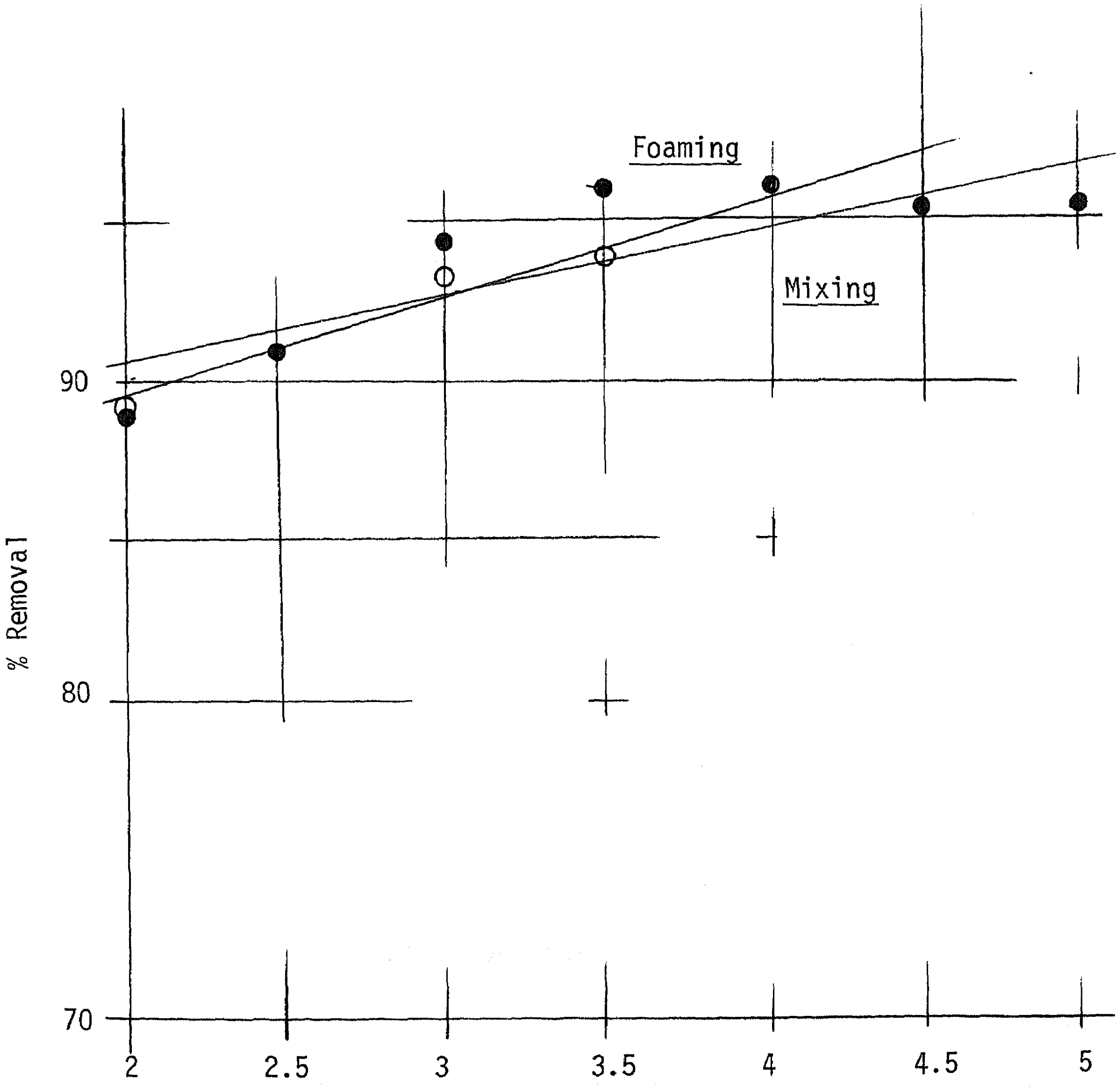


FIG. 6

Probe Linearity

To be useful in this study, the detection probe (Orion 94-05 and 90-02) would have to differentiate in a linear manner, the varying concentrations of fluoborate ion in the actual or simulated plating rinse water. An investigation was therefore made to determine if this could be accomplished.

The solutions for the test were made up using reagent grade sodium fluoborate and deionized water. The most concentrated solution for each test run was precisely mixed, then each subsequent (lower concentration) soluton was made up by suitable dilution of the next stronger solution. Thus ten milileters (ml) of a 5000 ppm solution were diluted with 90 ml of deionized water to give a 500 ppm solution. Then ten ml of the 500 ppm solution were used to make up the 50 ppm solution etc. This method minimizes any weighing error as it is not as critical that the solution be exactly 5000 ppm and the lesser one exactly 500 ppm. The importance is that the lesser solution is accurately one tenth the concentration of the stronger solution. This dilution can be quite precisely made, therefore the percent reductions in fluoborate can be ascertained.

Table 5 shows the results of four test runs with starting concentrations of 5,000 ppm in sodium fluoborate, 10,000 ppm, 20,000 ppm and 50,000 ppm. These were then diluted to one tenth concentrations going to 5 ppm, one ppm, 0.2 ppm and 5 ppm respectively.

The resultant probe reading can then be plotted on a semi-log plot to give a straight line of the type $x = m \log y + b$

where x is millivolt readout on meter

y is soluton molarity in $NaBF_4$

m is lines slope

b is a constant.

To find m, substract xi + 1 from Xi

$$x_i - x_{i+1} = m\,(\log y_i - \log y_i + 1) + b - b \qquad [17]$$

$$= m \log \frac{yi}{yi+1} \qquad [18]$$

If $y_i = 10y_{i+1}$

$$x_i - x_{i+1} = m \log 10 = m \qquad [19]$$

m equals the change in millivolt (MV) reading

m = MV which is the fifth column on the table.

It can be noted from the table that this is an approximately 55 millivolts change for each factor of ten change in the fluoborate concentration. The linearity of the measuring equipment readout versus the transformed fluoborate concentration was therefore confirmed. Figure 7 shows a typical plot of the test results of a set of three removal runs, using 100 ppm of fluoborate. The three lines shown are the straight lines connecting the initial readings of the individual runs with their corresponding diluted solution reading. The starting solution is 100 ppm in sodium fluoborate and the dilute solution is 10 ppm in sodium fluoborate. The final

BF_4- PROBE LINEARITY TEST

$NaBF_4$ in D.I. Water (pp)	Molarity (M)	Millivolt Readout (MV)	Change in MV (σ MV)	Linearity Coefficient r
Run 1				
	4.55 x - Exp			
5,000	10^{-2}	-54	56	
500	10^{-3}	2	56	0.999920
50	10^{-4}	61	59	
5	10^{-5}	120		
Run 2				
	9.11 x - Exp			
10,000	10^{-2}	-72	54	
1,000	10^{-3}	-18	66	0.999558
100	10^{-4}	48	60	
10	10^{-5}	108	56	
1	10^{-6}	164		
Run 3				
	1.82 x - Exp			
20,000	10^{-1}	-72	50	
2,000	10^{-2}	-20	60	0.997343
200	10^{-3}	40	58	
20	10^{-4}	98	54	
2	10^{-5}	142	40	
0.2	10^{-6}	182		
Run 4				
	4.55 x - Exp			
50,000	10^{-1}	-92	44	
5,000	10^{-2}	-48	53	0.999062
500	10^{-3}	5	57	
50	10^{-4}	62	53	
5	10^{-5}	115		

Overall r = 0.996272
With MV (slope) = 55.2

FLUOBORATE REMOVAL TYPICAL PLOT OF TEST RESULTS

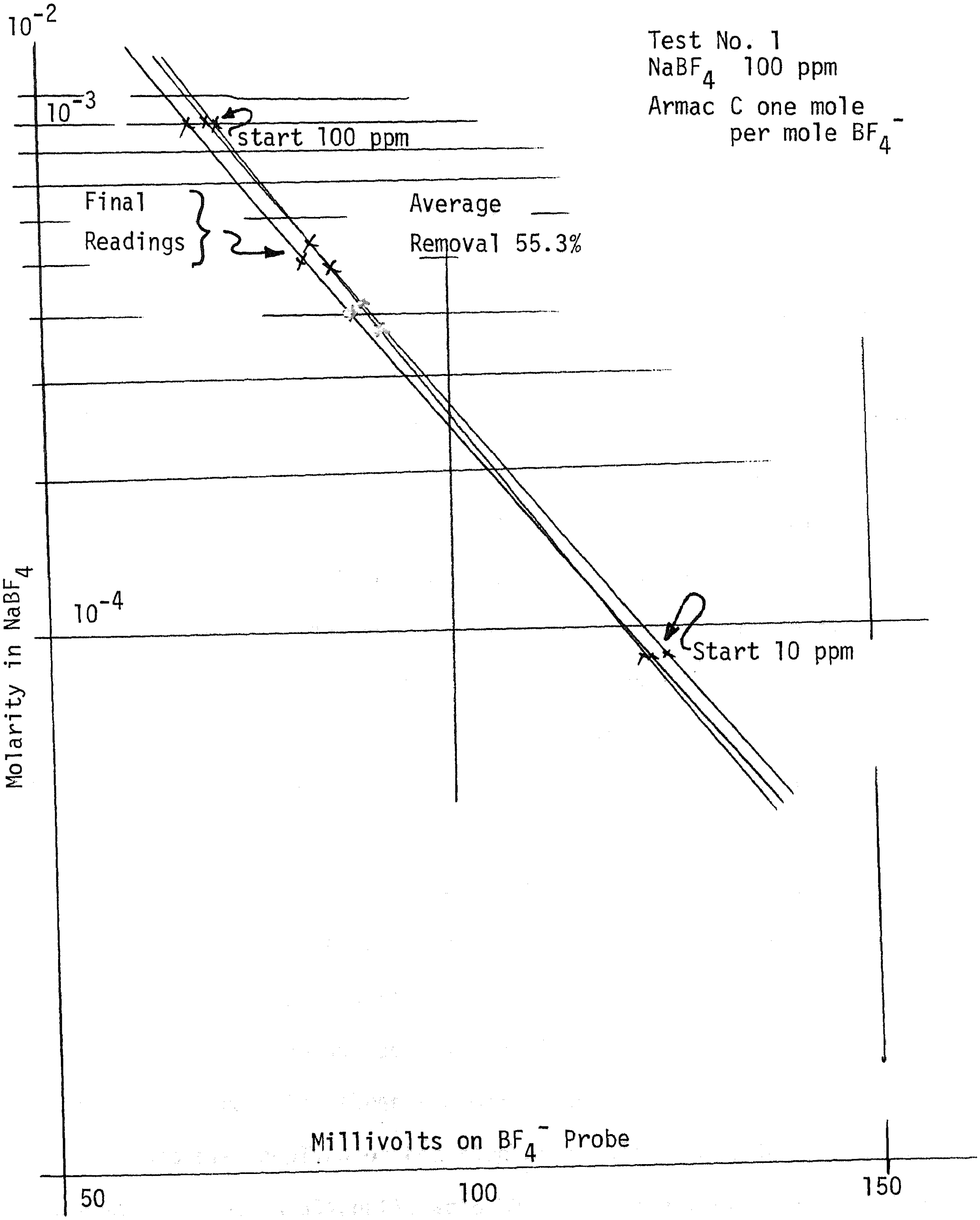


FIG. 7

is 10 ppm in sodium fluoborate. The final readings shown with the three x's are the individual milivolt readings found after the foaming operation on each run. These readings were 84 mv, 85 mv and 87 mv and were plotted each on its "start" line, to show the average removal of 55.3% of the fluoborate.

Surfactants Used In The Study

After the literature search, we concluded that there should be surfactant which could be used efficiently for the removal of fluoborate ion from dilute aquious soluton by ion flotation. The surfactant would be expected to be of the cationic type, further, it would probably be of the aliphatic amine type. The natural attraction of the positive charge on the surfactant for the negative charged fluoborate ion should enhance the coupling of the two and facilitiate the removal of the fluoborate from the solution. The aliphatic amine type cationic surfactant with radicals from 10 to 18 carbon chains form sufficient bubbles which are long lasting to allow total removal by foaming techniques. In order to assure that this is true however, three nonionic and five anionic organic phosphate type surfactants were tested for applicability. We also tested eleven cationic surfactants to cover the range of this type. Appendix 2 lists the surfactans used in this study, and depicts their structure. The three nonionic types were selected to test for a possible coupling of the fluoborate with the oxides of an aromatic amine, an aliphatic acid or a cyclic glycerol ehter. These are expected to represent the non ionic surfactants which could conceivably bind the fluoborate ion or the metal fluoborate salt.

The organic phosphates tested represent the spectrum of the water soluble aliphatic hydrocarbon chain-phosphates. They were screened to assure that they did not couple with fluoborate. The eleven cationic surfactants represent the various types which could be effective in the desired removal. They range from the short chain aliphatic amine, to the aromatics, to the quaternary ammonium derivatives.

The screening of the surfactants was done as follows:

1. A solution of 100 ppm of sodium fluoborate in deionized water was prepared.
2. To 500 ml of the solution, 50 mg of surfactant was added and mixed well.
3. This solution was foamed and the foam was removed, until no more foaming occurred.
4. The remaining solution was tested for fluoborate.

The five organic phosphates showed no removal of fluoborate.

Nine of the three nonionic surfactants showed no significant removals. Two of the cationic surfactants however did not show significant removal. These two were Armac-C, which removed 35% of the fluoborate and Duomac T which showed a 20% removal.

Armac -C and Duomac T differ from the other surfactants in that they contain an acetate group affixed to the amine end of the surfactant. Because of the Armac-C showed better removals of fluoborate than did the Duomac T, this was the surfactant used during most of this investigation.

After the establishment of the mechanical characteristics of the flotation process as investigated here, several additional parameters relating to the structure of the surfactant uses were investigated. For these tests, some additional surfactants were used. These were of the same type as the Armac -C, but with modifications as follows:

1. Armac T is an alkyl amine acetate like Armac C, but with a longer carbon chain. The chain in Armac C average 12.7 carbon atoms long while the Armac T averages 17.1 carbons. This was done in order to see the effect of chain length on the removals.
2. Armac 18D is a distilled product, made to be 90% in stearyl amine acetate (18 carbon chain) 8.5% palmityl and 1.5% margaryl amine acetate. It was used to check the effect that the purity of the surfactant has on fluoborate removal.
3. Armac HT is a hydrogenated talo amine acetate. It also has the 17.1 average carbon chain, but it is a talo amine which has been hydrogenated to transform most the

3. (Cont'd)

oleyl, palmitoleyl, linoleyl and myristoleyl hydrocarbons to their saturated counterpart. This surfactant was used to determine if the degree of saturation of the hydrocarbon has an effect on the fluoborate removal.

The fouteen cationic surfactants used in this study were Amine O, Amine C, Amine S, Amine T, Ammonyx 220, Ammonyx T, Armac C, Armac T, Armac 18D, Armac H, Armac 8D, Duomac T, Atlas G-3634A and Finazoline T. The Ciba-Geigy Amine O, Amine C, Amine S and Amine T surfactants are heterocyclic tertiary amines. The Ammonyx 220 and Ammonyx T obtained from Onyx are a ditallow dimethylbenzyl ammonium chloride and a Cetyl dimethlbenzyl ammonium chloride, respectively. The Armac C, Armac T, Armac 18D, Armac HT, and Duomac T surfactants which were obtained from Armac are a coco amine acetate, as tallowamine acetate, a distilled octadecane amine acetate, a hydrogeneated tallowamine acetate, and a tallowdiamine acetate, respectively. The Atlas G-3634A surfactant obtained from ICI is a quaternary ammonium derivative. The Finetex surfactant, Finazoline T, is an aminoethylimidazoline.

The three nonionic surfactants used in this study, ammonyx CDO, Onyxol 336 and Neutronyx, were obtained from Onyx and are a cocoamidepropyldimethylamine oxide, a lauric acid and an alkylphenol polyglycol ether with ethylene oxide, respectively.

The five organic phosphate surfactants used in this study were Dextrol OC-60, Dextrol OC-80, Dextrol OC-90, Dextrol OC-105 and Dextrol OC-110 and were obtained from Dexter.

Micelle Formation

Surfactants of the type used in this study have been shown to form micelles at relatively low concentrations. A study related to this one (69) found that micelles formed at approximately 12 ppm of Armac C or Armac T in the fluoborate water solution. This critical micelle concentration was determined by measuring the conductivity of the solution as surfactant was added. A sharp decrease in the plot of conductance versus the square root of surfactant concentration at approximately 12 ppm indicated the concentration at which the micelles begin to form.

Equipment and Procedures

The specific ion flotations experiments were carried out in a modified recirculation bath system (see Figure 8) designed to simulate an actual treatment process. The recirculation was required because the length of time required for the foaming was much longer than could be accommodated in a single flow-through tank. The equipment consisted of an eight liter holding tank, a two liter reaction vessel. an eighty liter per hour recirculation pump, and a twelve liter foam collector. The air for foaming was introduced through a porous stone diffuser, the air being controlled by a Brooks R-2-15 rotometer. The surfactant was introduced into the suction line of the pump using a twenty milliliter hypodermic syringe, after the fluoborate plating bath solution was added and thoroughly mixed in the system. The syringe was used because even slow mixing in the sump caused foam to be generated in the holding tank during the makeup.

The experiments were carried out in the followng manner:

The system was cleaned by washing all tanks and tubing, and thoroughly rinsing them with deionized water after each experiment. Then, the system was charged with eight liter of deionized water. The desired quantity of sodium fluoborate or plating bath solutions was added to the deionized water and the solution recirculated for 36 minutes to assure thorough mixing. A series of tests in which the resulting dilute rinse waters solutions were circulated through the system up to 24 hours indicated that the test solutions were completely mixed within 36 minutes. The desired amount of surfactant, which had been dissolved in 200 ml of deionized water, was injected into the system at a rate of 8 ml per minute. The soluton was again recirculated for another 36 minutes to insure complete mixing of surfactant solution with the fluoborate solutions. Air was applied, and the solutions were recirculated continuously until there was no further generation of foam. The foam was removed as it was foamed. The results of these tests are shown on Table 6.

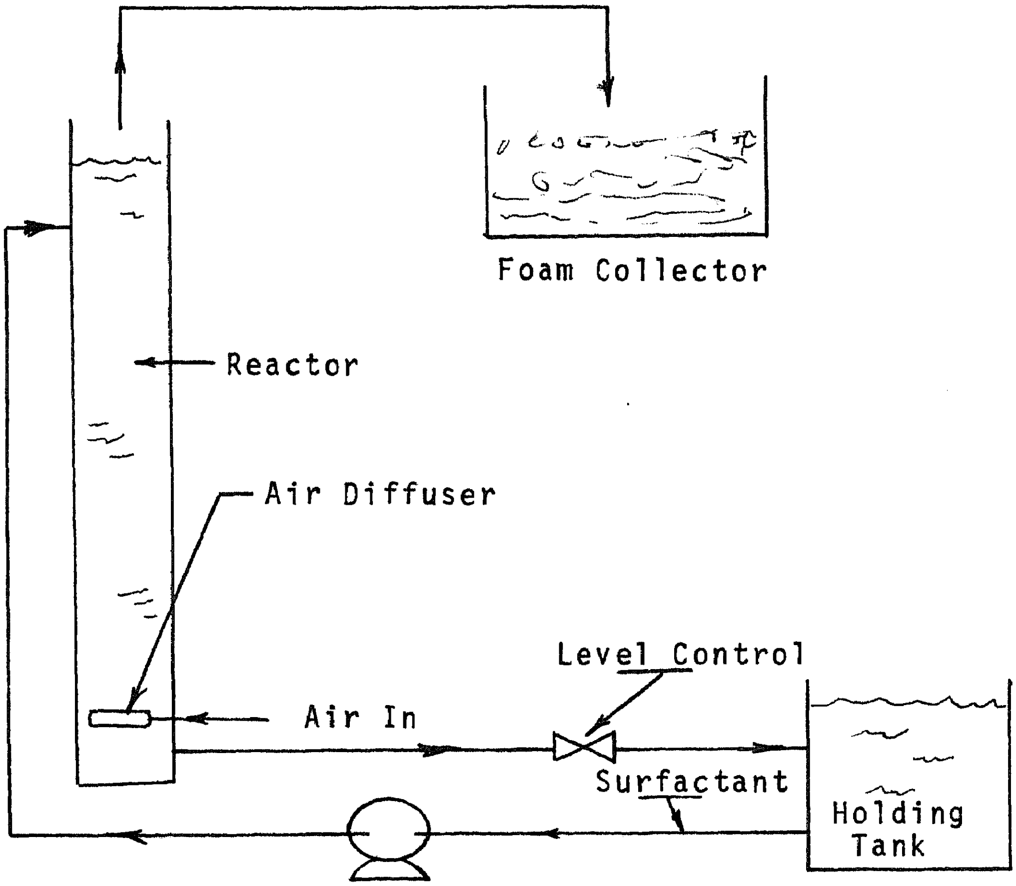


FIGURE 8 FOAMING APPARATUS

Fluoborate Analysis

Analysis of the solutions for the fluoborate ion were carried out using the series 92 and series 93 Orion fluoborate specific ion probes. The 93 series, which was determined to be the more sensitive probe, was used to analyze the solutions that contained no surfactants. The surfactant was observed to have an adverse effect on the probes membrane. Therefore, the series 92 probe was used to measure the fluoborate concentration in the presence of the surfactant because its membrane could be replaced. It was determined the membrane in the 92 series had to be replaced after the measurement of 5 solutions containing fluoborate ion and surfactant. This is discussed in the introduction, page 29.

Ultrafiltration

Simple Cell

The equipment used for initial evaluation of ultrafiltration for removal of the fluoborate surfactant complex from solutions was the Millipore Corporation's 47 mm stirred cell, catalogue number XX 42 047 10. The membranes were Millipore's Pellicon membranes, PSAC type.

The two membranes evaluated were the 1,000 and 10,000 nominal molecular weight (nmwl) membranes. The nmwl is a rough guide to the size above which most molecules are efficiently retained by that membrane.

TABLE 6

TEST TO DETERMINE TIME TO TOTALLY MIX SYSTEM

Test No.	1		2		3	
	Time (Min.)	MV	Time (Min.)	MV	Time (Min.)	MV
	0	200	0	180	0	205
	6	58	6	121	6	115
5 each)	12	56	12	55	12	120
time)	18	54	18	62	18	56
Units)	24	10	24	60	24	57
	30	58	30	62	30	56
all)	36	59	36	62	36	56
readings)	42	58	42	61	55	56
stable)	48	58	48	62		
after)	54	59	60	62		
5 Units)	73	58				

Test performed as follows:

1. Fill thoroughly cleaned equipment with 8 liters of D.I. water and start pumping.
2. When reaction chamber is full to operating level and overflowing to pump sump, add 0.8 grams of $NaBF_4$ into the pump sump. Start timer.
3. At each interval of 6 minutes, remove a 100 ml sample from the overflow tube and check for BF_4^-.
4. Continue sampling until a stable millivolt reading results.

Note: Samples are wasted, so there is an effect due to the removal of 100 ml of solution from the experiment at each sampling. The above results show approximately 1.35% this discrepancy is considered to be minimal.

The simple stirred cell, which is depicted in Figure 9, is a cylindrical plastic unit designed to hold membrane discs for the ultrafiltration of small fluid volumes. The cell barrel is polycarbonate with silicone O-rings for seals at the base and cap. The capacity of the cell is 80 ml, the cell takes a 47 mm membrane disc which has a filtration area of 10.5 cm^2.

In the evaluation of the two different membranes, the set-up that is shown in Figure 9 was used. Seventy-five milliliters of solution was placed in the cell. The pressure applied to the feed solution was maintained at 46 psi. The cell was mounted on a magnetic stirrer and stirred by means of a magnetic stirring bar inside the cell. This minimizes polarization occurring at the membrane. The filtrate was collected in test tubes from the plastic tube which was inserted in the base of the cell.

Initial experiments were run using a solution of 1500 mg/l of tallowamine acetate surfactant and 100 mg/l of fluoborate anion. During the evaluation of the 10,000 and 1000 nmwl membrane a dye test was used to indicate the presence of tallowamine acetate surfactant in the filtrate. The dye test provided qualitative evidence of the presence or absence of tallowamine acetate in the filtrate solution by visual inspection.

Bromophenol blue, which was the dye that was used, gave a rough quantitative indication of the surfactant in solution. When the

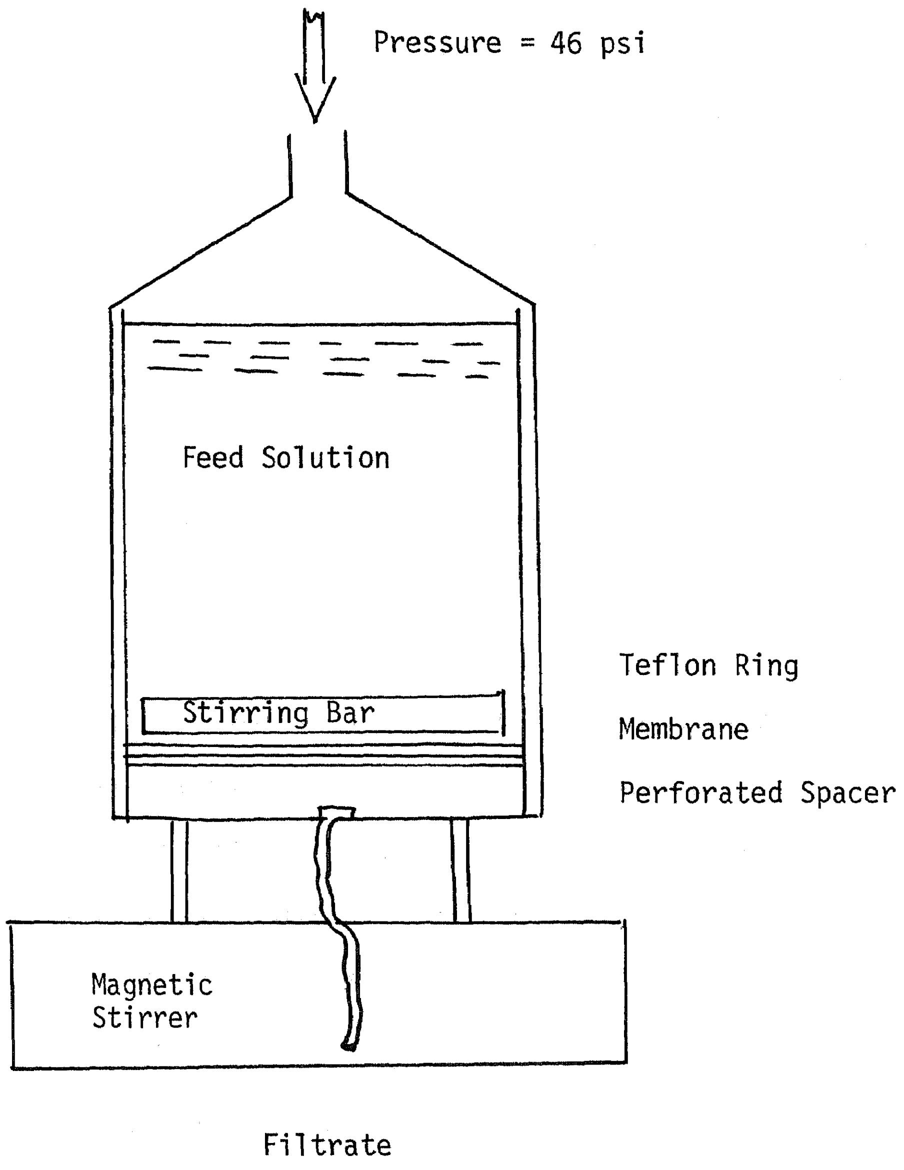


FIGURE 9 SCHEMATIC OF A SIMPLE ULTRAFILTRATION CELL

surfactant was present, a blue color was formed in the solution. When no surfactant was present the solution remained clear and colorless. The deepness of the blue increased as the concentration of surfactant increased. Therefore, the dye test was a good preliminary indication of the passage of the surfactant-fluoborate complex through the ultrafiltration membrane.

The surfactant concentration in the ultrafiltration filtrate solution was analyzed using a Dohrmann Envirotech DC-52D Carbon Analyzer. The presence of fluoborate was observed to have no effect on this analysis.

High Voluem Cassette

Further evaluation of ultrafiltration for the removal of the fluoborate-surfactant complex from solutions was carried out using the 100 nmwl membrane in a Millipore High Volume Cassette System. The Cassette System is 10" wide x 9" deep x 12" high. Membranes for this system have a filtration area of 465 cm^2 (0.5 $ft.^2$).

The system was run utilizing a variable speed tubing pump to transport pressurized solution to the cassette's feed port. Pressure at the feed port was regulated by the pump speed. A needle valve was placed at the retentate port in order to maintain pressure over the entire membrane area. Using this system, two types of experiments were run. They were single pass flow and recirculating flow as depicted in Figures 10 and 11, respectively. During both experiments the same feed solution containing 1500 mg/l of tallowamine acetate surfactant and 100 mg/l of fluoborate was used.

Operating pressures were maintained at 30 psi at the feed port and 21 psi at the retentate port, during the single pass flow experiment. Due to the viscosity of the feed solution, only 5.7 ml of filtrate was collected per liter of feed. In order to remove more fluid from the sample than can be accomplished in one pass, a recirculating flow system was used.

During the recirculating flow experiment the retentate was run back into the sample vessel. The sample vessel was mounted on a magnetic stirrer and the solution was stirred to maintain a homogeneous feed. The pressures were maintained at 30 psi at the feed port and 22 psi at the retentate port.

Breaking the Fluoborate-Surfactant Complex

Addition of Excess Acetic Acid

In an attempt to reverse the equilibrium of the surfactant-fluoborate complex and break the complex, the addition of excess acetic acid was examined. A one liter solution of 100 mg/l of fluoborate and 1500 mg/l of tallowamine acetate surfactant was used. Concentrated acetic acid was pipetted into the solution at an initial volume of 0.5 ml. The solution was stirred utilizing a magnetic stirrer.

The concentrated acetic acid was added in increments of 0.5 ml. After each addition of acid, the concentration of fluoborate was monitored using the Orion 92 series electrode system.

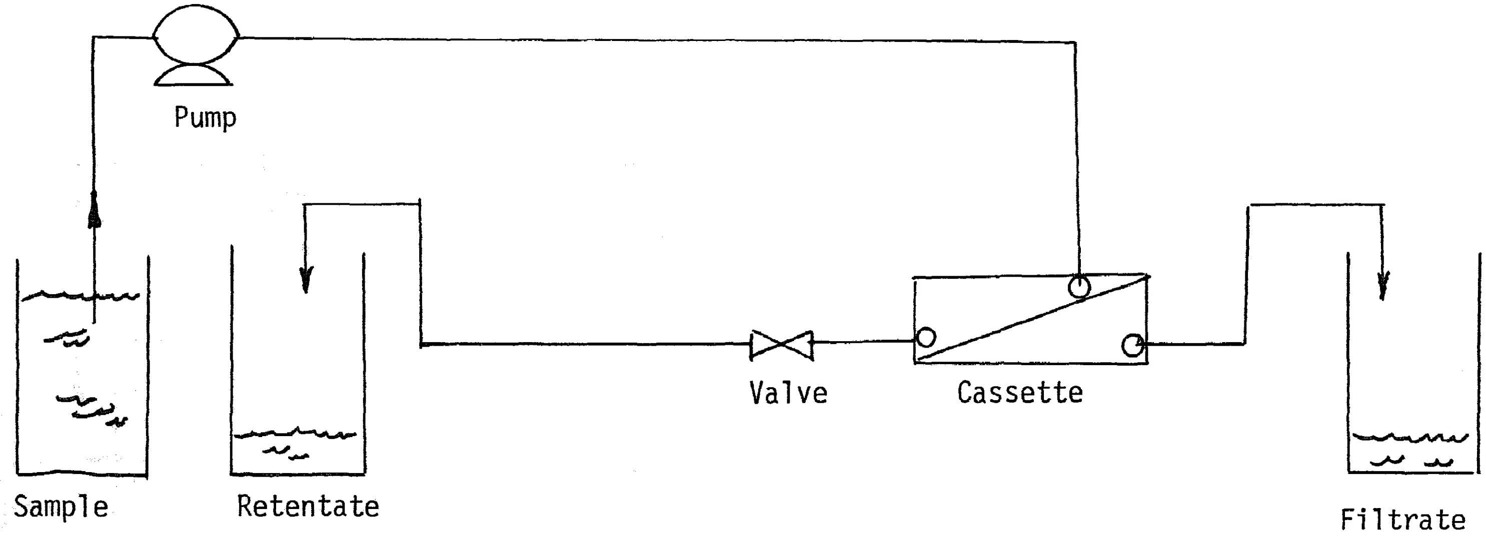


FIGURE 10 - SINGLE PASS FLOW SYSTEM - Ultrafiltration

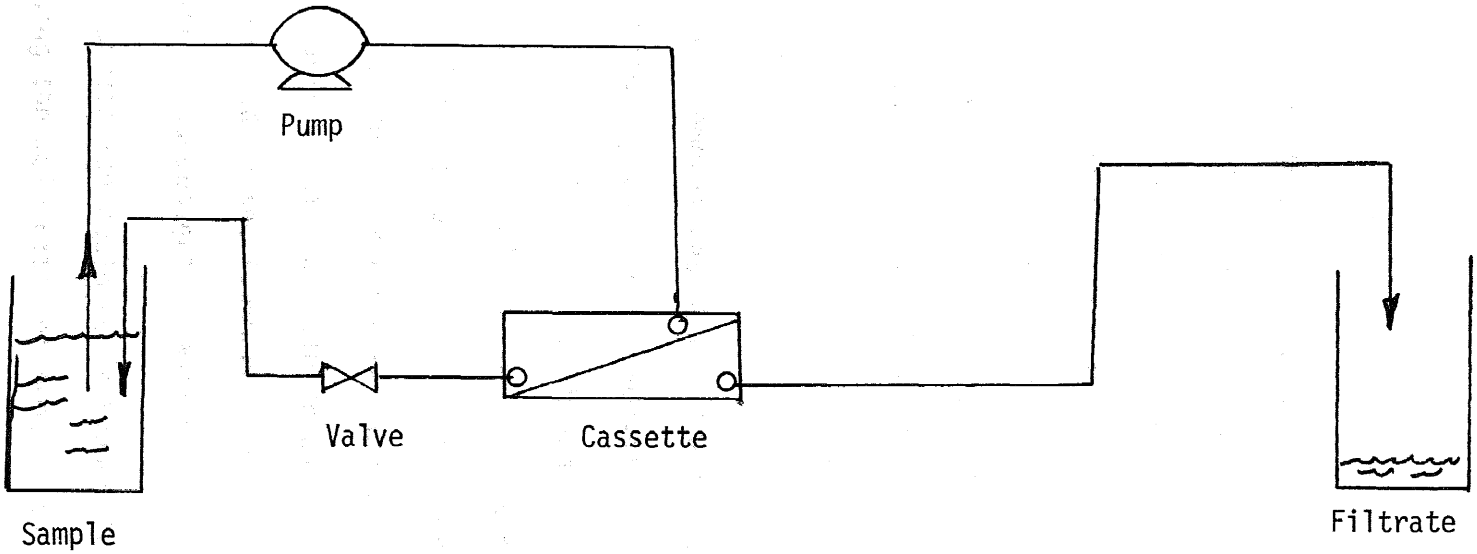


FIGURE 11 - RECIRCULATING FLOW SYSTEM

III. RESULTS AND DISCUSSIONS

The initial phase of this investigation was concerned with identifying the type of surfactant which would remove fluoborate ion. Nineteen surfactants were initially tested using sodium fluoborate solutions. These nineteen surfactants fall into three categories: eleven cationic surfactants; three nonionic surfactants; and five organic phosphate surfactants. The cationic surfactants are primary, secondary and tertiary amines, attached to various radicals. The nonionic surfactants are oxidized alcohols, and organic acids.

Significant fluoborate removal was observed with only two of these surfactants. Approximately 20 percent removal of fluoborate was achieved with Duomac-T and 35 percent with Armac-C during the initial surfactant screening. All of the other surfactants tested showed no significant removal of the fluoborate ion. The Duomac T and Armac C differ from the other surfactants examined in that both surfactants contain acetate groups. The affixed acetate group is replaced by the fluoborate ion and the surfactant and this combination is subsequently removed.

Removal of the fluoborate ion could be increased from 35 to 82 percent by increasing the mole ratio of Armac C to fluoborate from one to one, used in the initial screening, to three to one.

A series of tests were performed on solutions containing different initial concentrations of sodium fluoborate and varying the specific mole ratios of Armac C to fluoborate ion to determine the minimum concentrations to which Armac C could reduce the fluoborate ion. The results indicate that at initial fluoborate concentrations of 100 mg/l and below, the Armac-C can reduce the fluoborate concentration to approximately 18 mg/l, using a surfactant to fluoborate mole ratio of 3:1 (See Figure 12).

Removal of fluoborate concentrations above 100 mg/l using specific ion flotation encountered difficulty. When the initial fluoborate concentration is raised to 150 mg/l, the Armac C reduced the fluoborate concentration to only 48 mg/l using the same mole ratio of 3:1. These results are due to the fact that not all of the surfactant required to provide a mole ratio of 3:1 to treat a fluoborate concentration of 150 mg/l could be dissolved in the solution. An extremely turbid solution resulted. Thus, even though a 3:1 mole fraction of surfactant to fluoborate ion was prepared, not all of the surfactant was available to react with fluoborate ion at concentration of 150 mg/l fluoborate. Coco amine acetate has a molecular weight of about 270 while the fluoborate (BF_4^-) has an ionic weight of 189. Thus 150 mg/l of BF_4^- required 643 mg/l of Armac-C for a three to one ratio.

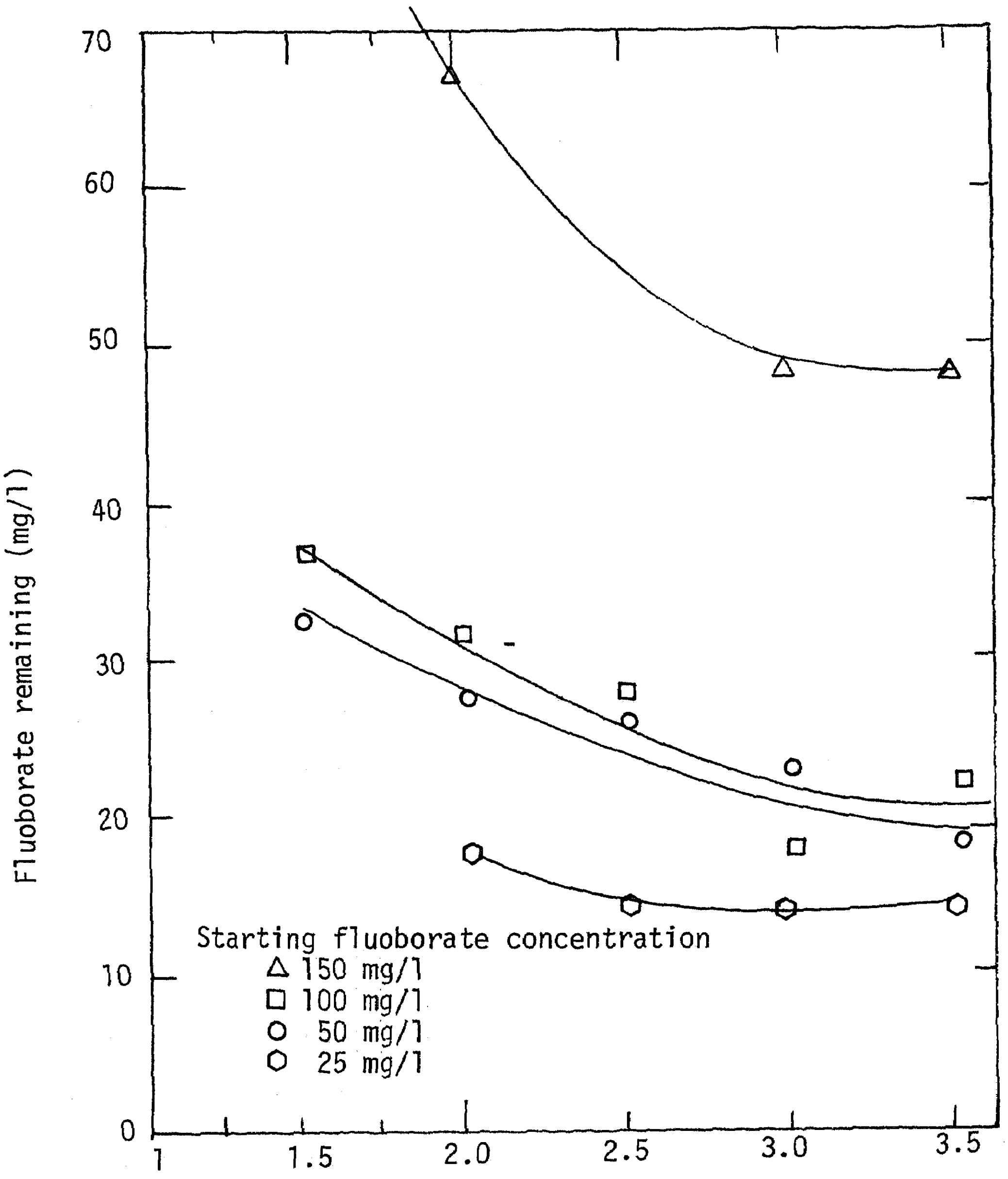


FIGURE 12 Treatment of Dilute Sodium Fluoborate Solution with Armac C

Factors Influencing the Removal of Fluoborate by the Surfactant

The results of the initial screening of the surfactants suggested that the acetate group on the surfactant molecule is involved in the removal of fluoborate ion. In order to test this further, factors which influence the removal of the acetate ion from the surfactant were examined. Sodium acetate was added to the Armac C surfactant so as to reduce the ionization of the acetate group. A 100 mg/l solution of fluoborate was prepared and a quantity of Armac C acetate solution was added to the fluoborate solution to provide a 3:1 mole ratio of surfactant to fluoborate. This resulted in only 61 percent removal of fluoborate ion. When no sodium acetate was added other parameters the same, an 82 percent removal of fluoborate was obtained. These results, shown as "A" on Table 7, indicate that the removal of the acetate ion from the surfactant by ionization is essential for the fluoborate removal.

An increase in acidic conditions should also favor the removal of fluoborate by an acetate surfactant since acidic conditions would favor the formation of unionized acetic acid. A reduction in the final pH of the surfactant-fluoborate solution was found to favor the removal of the fluoborate from solutions by the Armac C. The use of fluoboric acid instead of sodium fluoborate in the mole ratio of 3:1 surfactant to fluoborate decreased the final pH from 6.2 down to 5.0. The removal of fluoborate was increased from about

TABLE 7

Fluoborate Removal using 100 ppm Sodium Fluoborate Solution and Armac-C Surfactant. Three moles of Surfactant were used per mole of $NaBF_4$.

		Fluoborate Remaining In Solution, ppm	Percent Fluoborate Removal
"A" Sodium Acetate added to give 100 ppm in solution		42.1	57.9
		43.7	56.3
		31.2	68.8
	Average		61.0
"B" Acetic Acid added to give 100 ppm in solution		32.8	67.2
		34.9	65.1
		37.4	62.6
	Average		65.0
"C" Hydrochloric Acid added to give 50 ppm in solution		28.7	71.3
		30.0	70.0
		31.1	68.9
	Average		70.1
"D" Hydrochloric Acid added to give 100 ppm in solution		47.8	
		39.4	60.6
		39.1	60.9
	Average		57.9

87 percent up to 92 percent (see Table 8).

The influence of other anions which form stronger acids than fluoboric acid on the removal of the fluoborate by the surfactant was examined. Hydrochloric acid was added to separate solutions containing the 3:1 mole ratio of surfactant to fluoborate ion in amounts sufficient to provide final solutions that contained 50 mg/l and 100 mg/l of hydrochloric acid. Table 7, "C" and "D" show that fluoborate ion removals of only 70 percent and 58 percent were obainted in the solutions containing the 50 mg/l and 100 mg/l of hydrochloric acid, respectively. Thus, the presence of anions which form stronger acids than fluoboric acid inhibit the removal of the fluoborate by the surfactant.

The above results indicate that the fluoborate ion reacts with the surfactant by replacing the acetate group on the surfactant since it forms a stronger acid than acetic acid. However, maximum removal of the fluoborate is achieved with a surfactant to fluoborate mole ratio of 3:1. The use of the 3:1 ratio does not indicate that 3 acetate groups are involved in the removal of one fluoborate ion since each Armac C surfactant molecule contains only one acetate group, but only that not all of the acetate is available for reaction. Effects of micelle formation is discussed below. The three stepwise additions of one mole of surfactant to one mole of fluoborate remaining in the resulting solution after removal of the surfactant fluoborate complex reduced the total number of moles

TABLE 8
Effects of pH on Removal of Fluoborate Ion

BF_4^- Attributed To		Solution Initial pH	Surfactant Solution pH	Final pH	% Removal of Fluoborate
HBF_4	$NaBF_4$				
100%	0%	3.7	6.0	5.0	92
75	25	3.8	6.0	5.6	92
50	50	4.1	6.0	5.8	89
40	60	5.4	6.0	6.2	86
30	70	7.1	6.2	6.2	83
25	75	6.7	6.1	6.1	87
0	100	7.4	6.0	6.3	87

of surfactant required to remove a specific number of moles of fluoborate ion. Only 2.06 millimoles (554 mg) of total surfactant reduces 1.15 millimoles of fluoborate (100 mg) in one liter to 0.21 millimoles (18 mg) by stepwise addition of decreasing amounts of surfactant (see Table 9). The fluoborate which reacted with the surfactant was removed by aeration after each addition of surfactant. In contrast, a single addition of 3.45 millimoles (810 mg) of surfactant was required to reduce the 1.15 millimoles of fluoborate in one liter of solution to the 18 mg. This is approximately the saem removal which required 3 millimoles of surfactant in a "one shot" addition as shown on Fig. 12.

Micelles were observed to form at surfactant concentrations above 12 mg/1. This will limit the number of surfactant acetate groups that are available for replacement by the fluoborate. Since the fraction of the total surfactant molecules in solution that exists as micelles generally decrease as the surfactant solution becomes more dilute, the stepwise addition of decreasing amounts of surfactant to a given amount of fluoborate would increase the fraction of total acetate available for replacement by the fluoborate ion. Thus, it appears that stepwise addition of very dilute solutions of surfactant to minimize the micelle formation will require less surfactant to react with one mole of fluoborate.

TABLE 9. Fluoborate Removal Using Stepwise Addition of Armac C Surfactant to Sodium Fluoborate

Concentration of Armac-C		Concentration of Fluoborate		Fluoborate Concentration remaining after aeration	
mg/l	millimoles	mg/l	millimoles	mg/l	% Removal
310	1.15	100	1.15	52	48
160	0.60	56	0.60	27	52
84	0.31	27	0.31	18	33
				Total Removal	82%

In order to further understand the selective fluoborate ion removals exhibited by the surfactant containing the acetate group, surfactants similar to Armac C but differing in carbon chain length and of different degree of saturation were investigated.

The effect of surfactant molecular size on the removal of the fluoborate ion from a solder plating bath rinse water containing 100 ppm of fluoborate was studied using Armac C and Armac T. The Armac T has the same structure as the Armac C, except that the Armac T has a longer average chain length. Armac T has 16 to 18 carbon atoms in the chain, with an average of 17.1 and Armac C has 12 to 15 carbon chains with an average of 12.7. The test results show that when the carbon chains are longer, a greater removal is effected. Figure 13 is a plot of these results and shows that the removal at a three to one ratio, surfactant to fluoborate, is increased from approximately 80% to 97%.

The treatment of the solder bath rinse water with the surfactant averaging 17.1 carbon atoms results in only 3 mg/l of the fluoborate ion remaining in the rinse water. Reduction of the fluoboric ion concentrations in the solder rinse water to below 3 mg/l using surfactants with chain lengths greater than 18 carbon atoms was not possible because of the marked decrease in solubility exhibited by the surfactants with larger molecular sizes than Armac 18D.

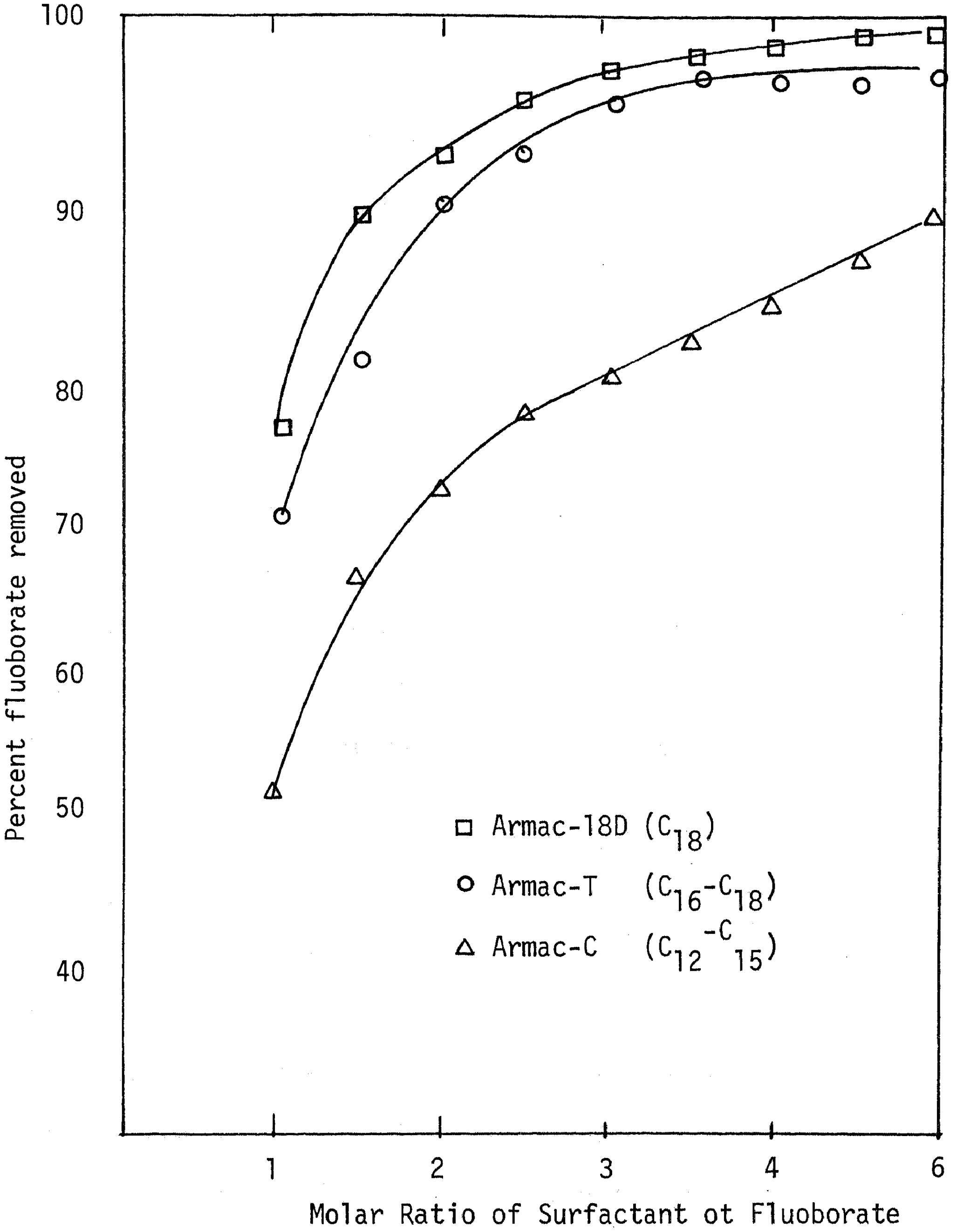


FIGURE 13 Fluoborate removal from Solder Rinse Water Dependence on Surfactant Molecular Size

The removal using Armac T was then compared with removals using Armac 18D. This distilled product is purer in the long chain molecules. There was an increase in the removals using the purer product, as shown on Figure 12. It is therefore confirmed that the longer the carbon chain that the surfactant has the better the removals, consistent with the preceeding paragraph.

The degree of saturation of the carbon chain of the surfactant does not appear to affect the removals of the fluoborate ion. In Figure 13, the removals of fluoborate ion in solder bath rinse water achieved with Armac HT, whose percent fat saturation is 97 percent, is shown to be comparable to that achieved with Armac T, whoe percent saturation is only 58 percent. This is shown for the range of surfactant to fluoborate ion mole ratios studied.

The reaction of the fluoborate ion with the surfactant occurs within a relatively short period of time. The mixing of Armac C with fluoborate in mole ratio of 3:1 resulted in the reduction of fluoborate ion from 87 mg/l to 18 mg/l within 1 minute as shown on Figure 14. These results indicate that contact time of one minute between the surfactant and fluoborate is sufficient for the replacement of the surfactants acetate group by the fluoborate ion prior to removal by aeration.

Process Parameters

Changes in the air feed rate, air bubble size, air diffuser location, inlet feed direction, and mixing time on the removal of the surfactant-fluoborate complex from solution by aeration were investigated because these factors can influence the performance of bubble columns, and will be very important in designing a full scale process.

Varying the air feed rate from 4 cc/sec to 30 cc/sec using a 3:1 mole ratio of Armac C to fluoborate did not improve the rate of removals of fluoborate and surfactant from solution. In both cases, times in excess of 20 hours were required to remove all of the surfactant. However, an increase in the air feed ratios does not increase the amount of solution that is carried over in the foam. This results in a wetter foam and the consequent reduction in the concentration of the surfactant-fluoborate complex in the foam. As an example, two foaming operations were carried out at air feed rates of 15 cc/sec and 30 cc/sec were used. The lower air feed rate provided a resultant foam with a surfactant-fluoborate complex concentration of 4000 mg/l whereas the higher air feed rate produced a foam with a surfactant fluoborate complex concentration of less than 1000 mg/l.

Neither changes in bubble size, air diffuser location nor inlet feed directions with respect to the rising air bubbles were observed to influence the removal of the surfactant-fluoborate molecule in the bubble column. Table 10 shows the results of these tests.

A diffuser change was made to see if different bubble size affected the removal rate. The diffuser used in all but this one set was a 13/16 inch high by 5/8 inch diameter cylinderical porous stone. Its starting bubble size was approximately 0.003 inches (at flow rate of 11 cc per sec.), measured at the surface using a Bosch and Lomb 7X magnifier and micro scale. This would be 85% smaller at the stone, assuming no combining of bubbles in transit. The alternate diffuser was a dished ended cylinder with a diameter of 11/16 inches a cylinder length of 13/16 inches and an overall length of 19/16 inches. Its starting bubble size was approximately 0.007 inches under the same conditions. The results from this variation show that there is no significant difference in the effects of the two diffusers.

To see if bubble travel distance has any effect on removal, the location of the diffuser was changed from twelve inches below the surface to four inches below the surface. This had no effect on the removal rate or the total removal. The bubble travel times were observed to be six to ten seconds to reach the surface, with the diffuser twelve inches below the surface. The time was somewhat dependent on the airflow rate and the direction of inflow of liquid to the column. The time of individual bubbles in the solution was roughly proportional to the distance traveled. It is presumed from this test that the twelve-inch depth is more than is necessary for removal using the other parameters that we have established. It is conceivable, however, that an extended bubble contact time in solution could change the mechanics of the system to give better removal time rates. The effect would be to have more surfactant per air bubble and result in a "heavier" foam with more surfactant-fluoborate combination and less water.

The bubble size was invarient with inflow direction when the rate of liquid inflow was not changed and the counterflow system was maintained, there was no significant difference from the system with the liquid entering normal to the counterflow direction.

Times in excess of 20 hours were required to remove all of the surfactant for each of the above experiments. However, these results indicate that significant variation can occur in the bubble size, and contact time between the air bubble and the soluton influencing the rate of removal of the fluoborate surfactant complex.

Removal of Fluoborate from Electroplating Rinse Waters

A series of tests were performed on rinse water containing 100 mg/l of fluoborate ion by adding different amounts of Armac T to the different rinse waters that are representative of that obtained from solder plating, tin plating, nickel stripping, and copper plating operations. Armac 18D, provided greater removals of

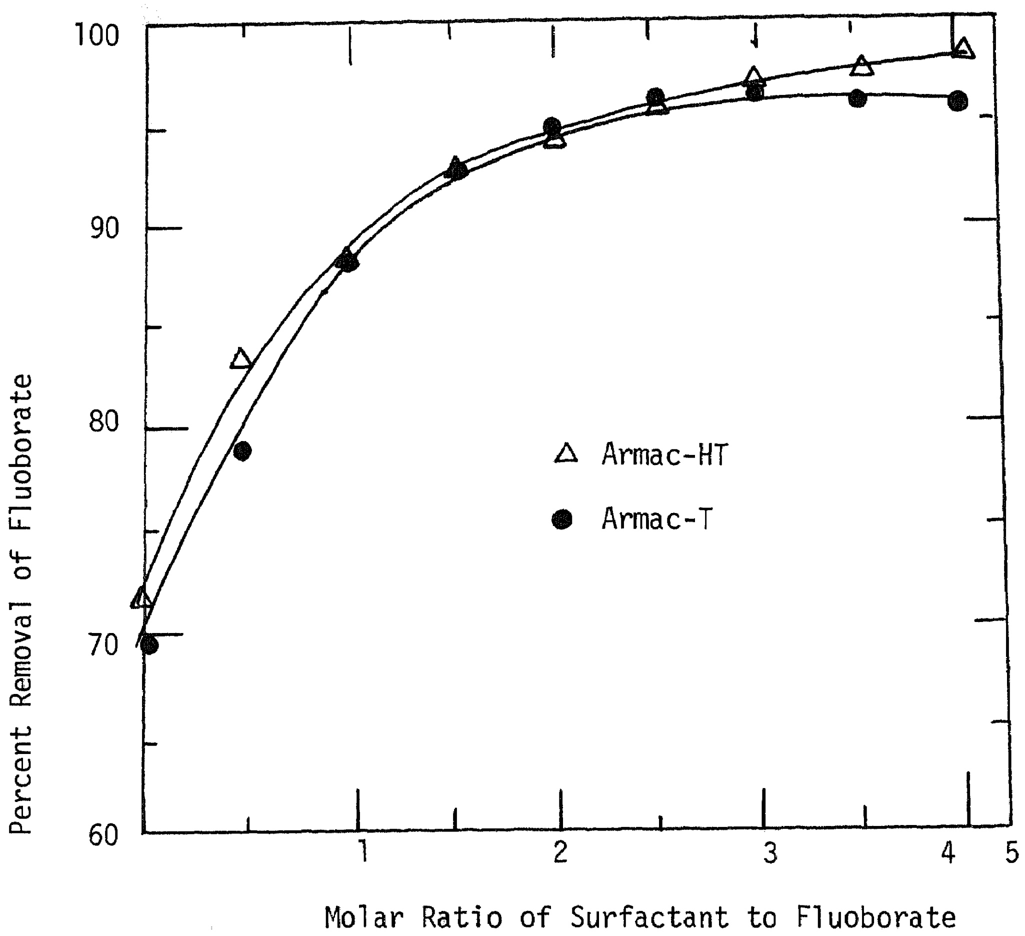


FIGURE 14 Fluoborate Removal from Sodler Rinse Water
Dependence on Surfactant Degree of Saturation

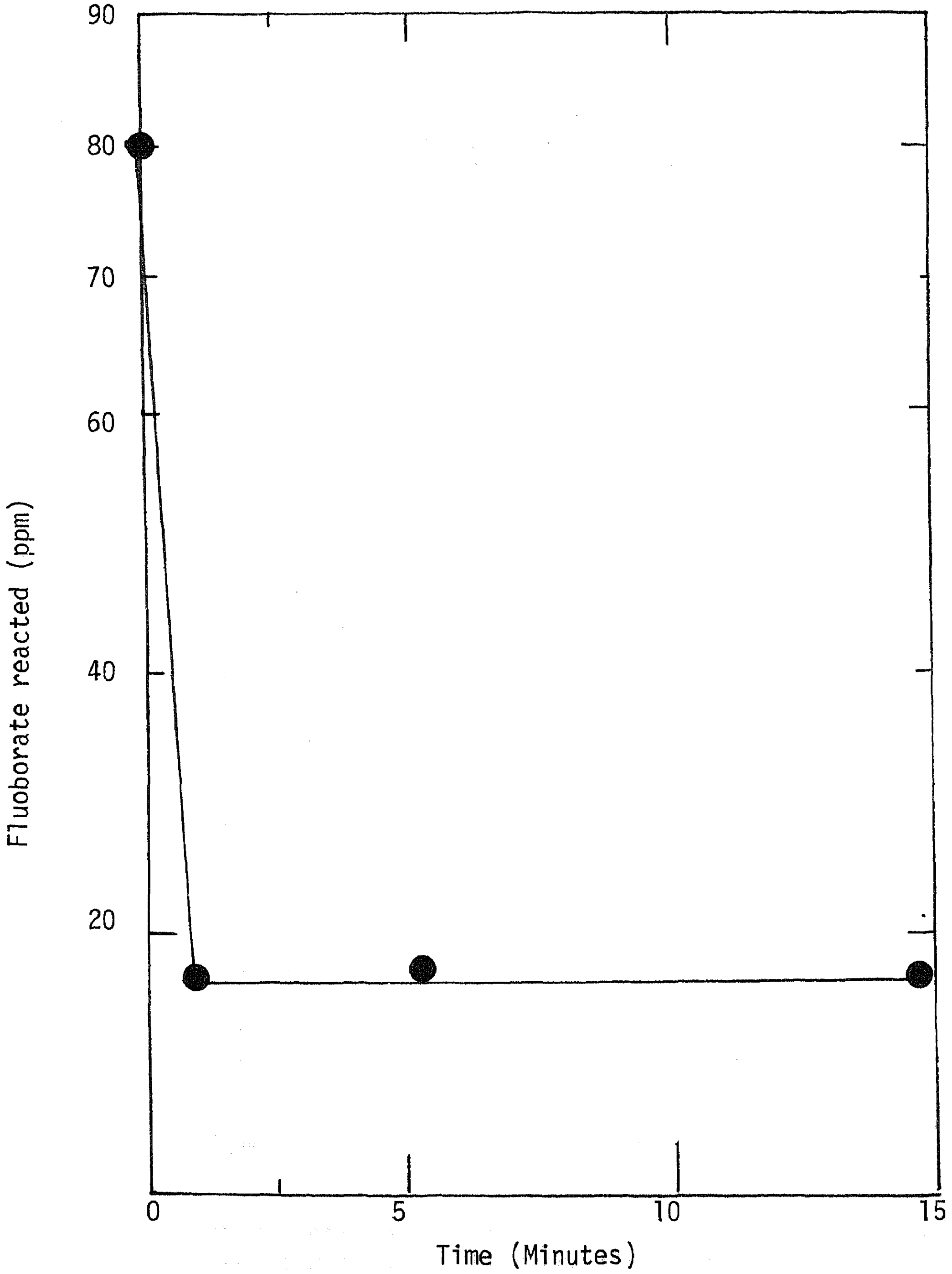


FIGURE 15 Time of Reaction of Fluoborate with Surfactant

Change Process Parameters

Using 100 ppm $NaBF_4$ in solution and a 3 to 1 mole ratio of Armac C to fluoborate, various process parameters were changed. The resultant removals, and the confidence limits are shown below.

Table 10

		x	$\bar{x}$ Average % Removal	T*
	Control	81.9 76.9 82.4	80.4	-
1	Change Diffuser (Bubble Size)	74.7 78.1 79.1	77.3	1.41
	Change Diffuser Location	75.0 80.1 79.8	78.3	0.87
3	Change Inlet	79.1 74.4 84.2	79.2	0.35
4	Extend Time of Mixing	81.3 77.0 83.5	80.6	0.08
5	Step-Wise Surfactant Addition	78.0	79.6	0.32
	Cumulative	-	79.2	

*95% confidence limit is 2.776. :$T < 2.776$ implies no significant difference (See Page 27).

fluoborate ion than Armac T, however the Armac T was used for these studies because it is less expnesive, and would presumably be the choice in a commercial removal process where it is felt that the slightly better removals achieved earlier with Armac 18D would not warrant the additional expense. These synthetic wastes were made up using deionized water and mixing in an appropriate amount of an actual plating bath to provide approximately 100 ppm of fluoborate ion in the solution. This would simulate an actual rinse in a closed loop system where the rinse water is recycled and with losses made up from an evaporator or an ion-exchange type water purification system. The plating baths analysis were:

The solder bath consisted of:

Tin Fluoborate, Sn $(BF_4)2$	18.5 oz./gal.
as Tin	7.5 oz./gal.
Lead Fluoborate, $Pb(BF_4)2$	6.4 oz./gal.
as Lead	3.5 oz./gal.
Free Fluoboric Acid, HBF_4	9.2 oz./gal.
Boric Acid, $B(OH)_3$	.3 oz./gal.
Peptone	0.7 oz./gal.

The tin bath consisted of:

Tin Fluborate, $Sn(BF_4)2$	51.6 oz./gal.
as Tin	20.8 oz./gal.
Free Fluoboric Acid, HBF_4	6.2 oz./gal.
Free Boric Acid, $B(OH)_3$	3.3 oz./gal.

The tin bath consisted of: (Cont'd)

Bone Glue	0.5 oz./gal.
Beta Naphthol, $C_{10}H_7OH$	0.1 oz./gal.

The nickel stripping bath consisted of:

Fluoboric Acid, HBF_4	25.3 oz./gal.
Ortho phosphoric Acid, H_3PO_4	10.6 oz./gal.
Nickel Fluoborate, $Ni(BF_4)_2$	12.2 oz./gal.
as Nickel	3.1 oz./gal.

The copper bath consisted of:

Copper Fluoborate, $Cu(BF_4)_2$	59.7 oz./gal.
as Copper	16.0 oz./gal.
Free Fluoboric Acid, HBF_4	1.6 oz./gal.
Free Boric Acid $B(OH)_3$	2.0 oz./gal.

The results indicate that Armac T can reduce the fluoborate concentration from 100 mg/l to approximately 7 mg/l in the solder and tin plating rinse and nickel stripping rinse waters using a surfactant to fluoborate mole ratio of 3:1. The fluoborate ion in the copper plating rinse water is only reduced to approximately 15 mg/l (see Figure 16). This was probably caused by the copper plating rinse waters being less acidic than the other plating bath rinse water.

The above results are significant in that they indicate that the removal of fluoborate with surfactant is comparable with that which can be achieved with lime precipitation of fluoride in waste streams. The recommended use of lime precipitation of fluoride in waste streams results in a fluoride ion residual of about 8 mg/l in the waste stream.

Reaction Rate

This series of tests is shown on Table 11, Figure 17 and Figure 18. It can be seen that the reaction is instantaneous within the limits of the experiment.

These figures show that while the reaction rate of the replacement of the acetate on the surfactant with the fluoborate is very rapid, it is not stoichiometrically complete. In the test shown on Figure 16, a one to one ratio of surfactant to fluoborate was added. This did not, however, affect a complete removal, but only approximately 32% removal. In the test shown on Figure 18, a 2:1 stoichiometric ratio of surfactant to fluoborate was mixed. Again the reaction rate was in essence instantaneous but the removal was only on the order of 62%. When a third stoichiometric quantity of surfactant was added in test No. 2b, only another 14 ppm of fluoborate was removed. This shows a total removal in the vicinity of 82% for these tests. The balance of the surfactant (73% of the total added) was unreacted.

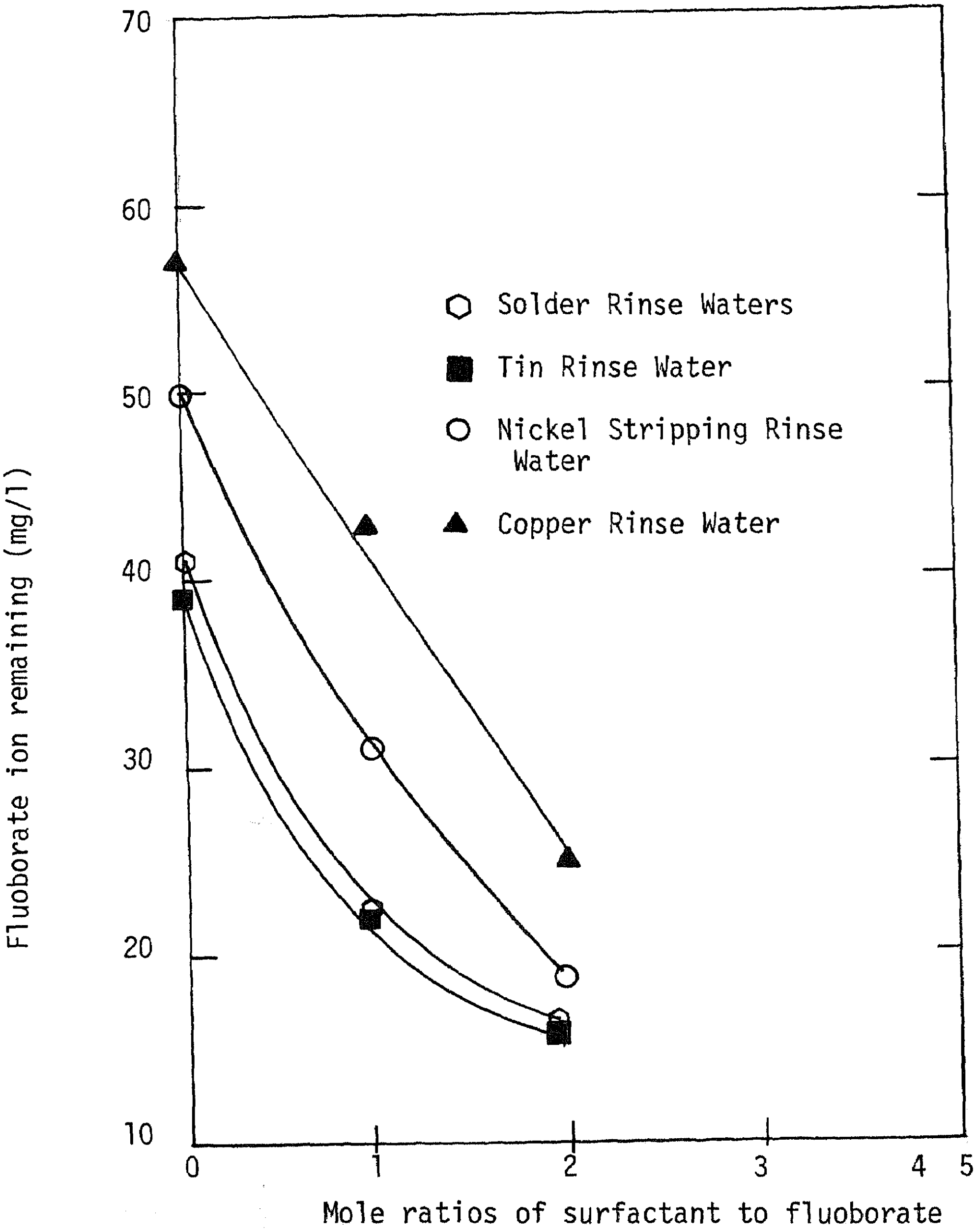


FIGURE 16 Removal of Fluoborate from Plating Bath Rinse Water with Armac T

FLUOBORATE - SURFACTANT REACTION RATE

TEST 1

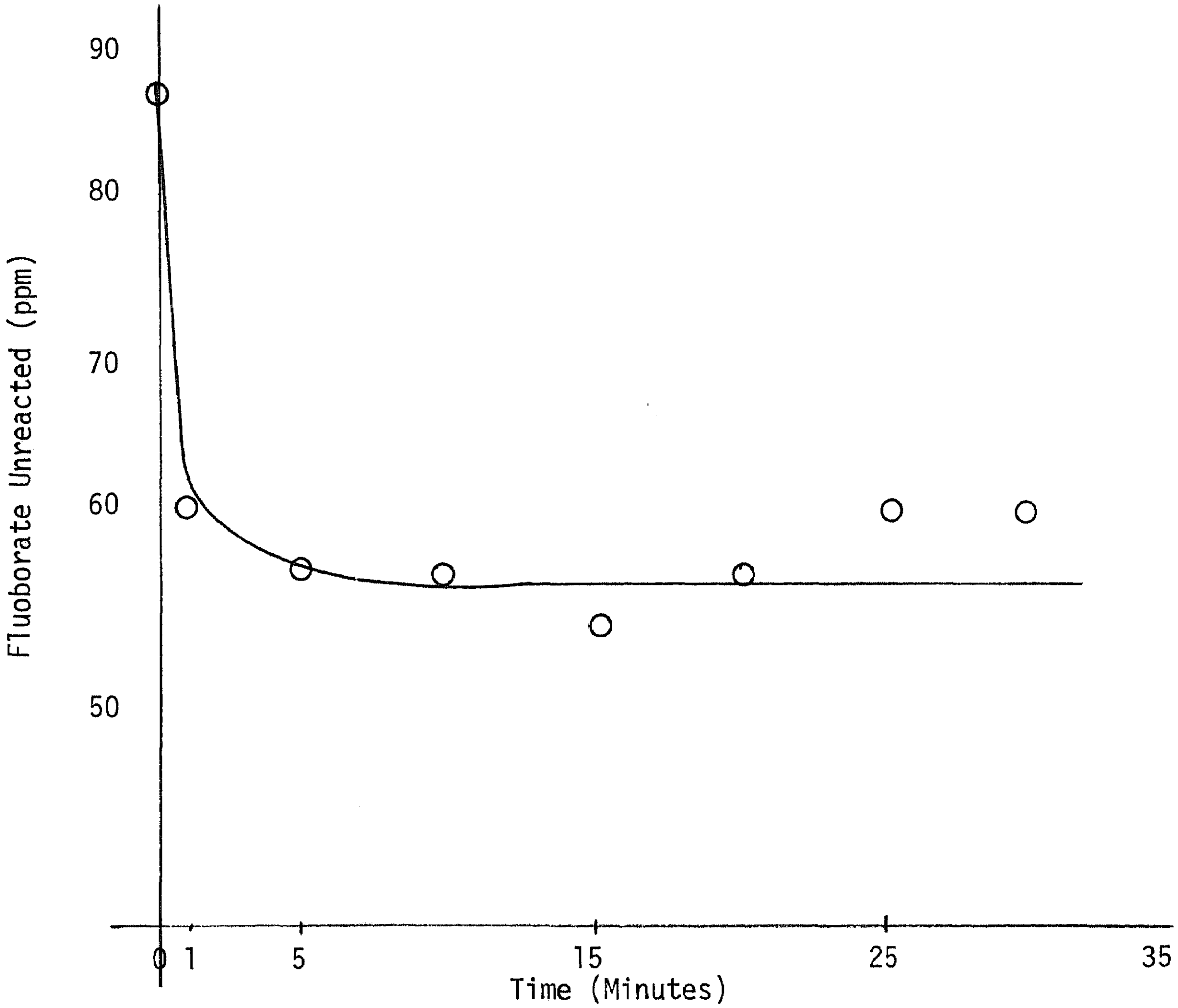
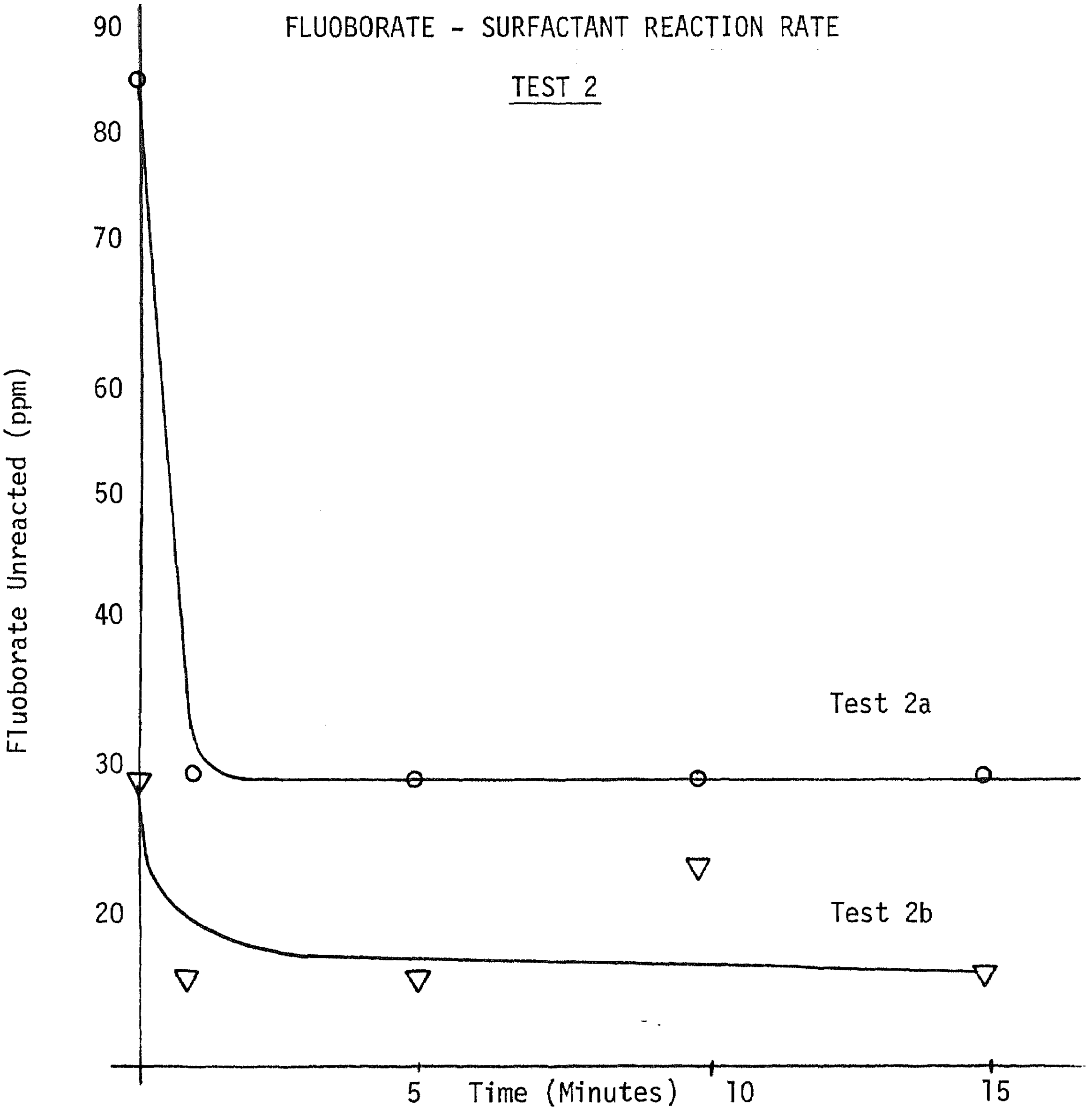


Figure 17



FLUOBORATE - SURFACTANT REACTION RATE

TEST 2

TABLE 11

FLUOBORATE - SURFACTANT REACTION RATE

	Time	MV	ppm BF_4^{--}	% Bound
TEST NO. 1	0	83	86.79	0
	1 min.	93	58.75	32.3
	5	95	54.33	37.4
	10	95	54.33	37.4
	15	97	50.26	42.1
	20	95	54.33	37.4
	25	93	58.75	32.3
	30	93	58.75	32.3
	35	93	58.75	32.3
	45	93	58.75	32.3
TEST NO. 2a	0	85	80.27	
	1	110	30.25	62.3
	5	110	30.25	62.3
	10	110	30.25	62.3
	15	110	30.25	62.3
TEST NO. 2b	0	110	30.25	
	1	126	16.21	53.6
	5	126	16.21	53.6
	10	120	20.48	32.3
	15	126	16.21	53.6

Ultrafiltration

Foaming times in excess of 20 hours were required in the bubble column to remove all the surfactants. Ultrafiltration was examined as an alternate more rapid process for removing the surfactant fluoborate complex. Evaluation of the ultrafiltration membranes utilized a low through-put pressure cell. In the cell, experiments were run with 10,000 and 1,000 molecular weight cut-off membranes. Experiments with the 10,000 molecular weight cut-off membranes were unsuccessful. The solution was not rejected by the membranes.

The 1,000 molecular weight cut-off membranes was effective in filtering a solution of plating rinse water containing fluoborate ions complexed with the Armac T surfactant. A solution of 100 ppm in fluoborate and a three to one stoichometric ratio of Armac T to fluoborate was prepared for the filter test. The filter passed 79.7% of the liquid, containing 21 ppm fluoborate (79% removal of the fluoborate). A second experiment was run, recirculating the concentrate back to the feed side of the filter unit. This experiment yielded 85% fluoborate removal.

Although the molecular weight of Armac T surfactant is approximately 330, (as shown on page A2-4) it was determined from conductivity studies that micelles began forming at 12 ppm. Therefore, at the concentration of surfactant that is required to complex the fluoborate, it will exhibit an apparent molecular weight much greater than 330, and the 1,000 molecular weight cutoff membrane can be used as a separation mechanism.

These ultrafiltration experiments produced the same results as the ion flotation technique, a solution with trace amounts of the surfactant-fluoborate complex and a foam that concentrates the surfactant-fluoborate complex. Foaming times in excess of 20 hours were required to achieve maximum removal of the surfactant-fluoborate complex from solution. The recycled ultrafiltration experiments achieved this separation by industrial scale-up; however, the time required for ultrafiltration can be minimized by increasing the number of membranes used in the ultrafiltration unit.

IV. CONCLUSIONS

This study has shown:

1. The feasibility of treating fluoborate in waste water streams.
2. The removal mechanism in the flotation process.
3. The chemical and physical kinetics of the reaction.
4. The properties of surfactant makeup which enhance removal.

The study has also proven the feasibility of removals of fluoborate from actual plating wastes and has generated the design of a plant scale process which will:

1. Accumulate the waste from a full size plating operation.
2. Batch treat the waste in a timely manner, reacting and subsequently removing the fluoborate ion from the rinse water.
3. Re-using the treated water directly in the rinsing of the plated parts.
4. Recovering the surfactant for reuse in the removal process.
5. Reocvering the fluoborate for reuse in the plating process.
6. And producing a minimum of heavy metal oxide or hydroxide sludge for disposal or subsequent recovery.

Specific Ion Flotation

1. This study has shown that specific ion flotation is feasible for the treatment of waste streams containing approximately 100 mg/l of fluoborate anion, which rinse waste can result from single tank rinsing associated with solder, tin, nickel and copper plating operation. Fluoborate anion concentrations in some of these waste streams were reduced to a concentration of 7 mg/l by the addition of a talloamine acetate surfactant in the ratio of 3 moles of surfactant to 1 mole of fluoborate anion. Fluoborate anion in the waste water from copper plating bath rinsing operation can be reduced to a minimum concentration of 15 mg/l.
2. It has been shown that the removal of fluoborate anion by the surfactant is dependent on replacement of the acetate group on the surfactant by the fluoborate anion. This has been demonstrated to result because the fluoborate ion forms a stronger acid in aqueous soluton than does the acetic acid. The removals of fluoborate have been shown to be inhibited by anions such as chloride which form stronger acids than does the fluoborate acid. Fluoborate anion removals are enhanced by an increase in the molecular weight of the surfactant and by acidic conditions which increase the ionization of acetate groups on the surfactant.

3. The replacement of the acetate group by the fluoborate anion appears to occur on a mole to mole basis. However, a 3:1 ratio of surfactant to fluoborate anion, is required to obtain a sufficient excess of surfactant acetate group to overcome the acetate groups that are lost to the replacement reaction because of micelle formation. Micelle formation was observed to occur at surfactant concentrations above 12 mg/l.
4. The replacement of the acetate group on the surfactant by the fluoborate anion is very rapid. The rate limiting step is the mixing time required to achieve a complete mix upon addition of surfactant to a fluoborate waste stream. The replacement reacton occurs within one minute, whereas 36 minutes is required for mixing the surfactant with the fluoborate solution in the experimental setup used in this study.
5. 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, do not influence the percent removal of the fluoborate-surfactant complex. However, increases in the air feed rate decreases the concentration of the fluoborate-surfactant complex in the foam by removing more liquid with the foam.

6. Ultrafiltration, with recycling of the retentate provide a greater rate of removal of the fluoborate-surfactant complex than aertaion. Five hours were required for removal of the fluoborate-surfactant complex using ultrafiltration, whereas aeration required times in excess of twenty hours.

Potential Application - Plant Design

To further utilize the information developed in this study, a design of a possible system was made to determine the commercial feasibility of the process. The parameters selected for input to the design are those typical to the electroplating industry and the printed circuit board industry. These parameters can be found in several references, especailly in compiled summaries done for USEPA (2,3,48).

The EPA's studies referred to above show that a typical electroplating shop could be expected to plate ten square feet of metal per minute in a bath containing fluoborate. Using an average of forty ounces of fluoborate per gallon of solution (300g/l) calculations (see Appendix 5) show that this area would require nine gallons per minute of rinse water producing a waste containing 100 parts per million of fluoborate. This would give 4313 gallons of waste to be treated per eight hour shift. A batch process as shown on the schematic, Figure 19, could treat the waste. The design considerations are as follows:

1. Two each 6,000 gallon acid resistant tanks would be required, with appropriate valving to allow one tank to collect and blend the waste for an eight hour shift, while the waste from the other tank is being treated. Corrosion resistant materials would be required, so the process could use either would fiberglass-epoxy tanks, or polyvinyl chloride (pvc) lined steel tanks depending on economics, and use fiberglass or PVC pipe.
2. The system would require the operator to add 1140 ppm of Armac "T" to the rinse water, using a mixing loop with the waste water being used as the solvent for the surfactant. Each, approximately 4500 gallon, batch (33,600 pounds) will require 37 pounds of surfactant. This will give a 3:1 ratio of surfactant to fluoborate in solution. This surfactant is to be added into a 250 gallon tank, slow mixed, and allowed to overflow back to the inlet to the blending tank. To minimize micelle formation, the surfactant is to be added in lots of three pound at half hour intervals. The pump is to provide a flow of approximately 100 gpm through this tank.
3. At the end of each shift, the waste flow is to be diverted to the "other" tank and that waste which was accumulated during the previous shift is to be treated. The first step in the treatment is to adjust the pH to approximately 6.3 using sodium hydroxide if necessary. This can be done during the collection

3. (Cont'd)

process if the input waste is found to be uniform. The waste, now thoroughly mixed with the surfactant is pumped through a one micron prefilter and then through the ultrafiltration unit. The pumps should be of the multi-stage centrifugal type, constructed of a material suitable for this service. Each pump is to deliver 15 gpm against a 120 psi head. The pumps, the second of which provide a 100 percent redundancy, should be electrically connected such that each is used on successive batches. Running hour meters should be provided for maintenance purposes.

The one hundred micron prefilter should be sized to provide approximately 25 square feet of filter area (or "flow through" equivalent if string wound cartridges are used). Pressure drop across clean filters should not exceed 5 psi, with the cartridges to be changed when the pressure drop reaches 20 psi. The prefilter is needed to protect the ultrafiltration membranes.

The ultrafiltration system is to use 1000 molecular weight cut-off cellulose acetate membrane and is to be made up of five each, four unit filter banks made of 70 square foot units. Each unit has an approximate capacity of 80 gallons per hour, therefore with one filter bank being back-flushed, the batch of 4500 ballons can be treated in approximately five hours.

4. The permeate (good water) from the ultrafilters is to be delivered to a 9000 gallon storage tank, from where it is to be pumped back for use in rinsing. This water will have approximately 15 ppm of fluoborate and only traces of surfactant. The 15 ppm fluoborate would not adversely affect the rinsing ability of the reused water.

   The concentrate, approximately 6.5% of the flow, would then contain 1365 ppm of fluoborate, and 13,500 ppm surfactant. This would be piped to a holding tank where the fluoborate could be removed by electrolysis and the surfactant reused (this recovery process is not covered in this paper).

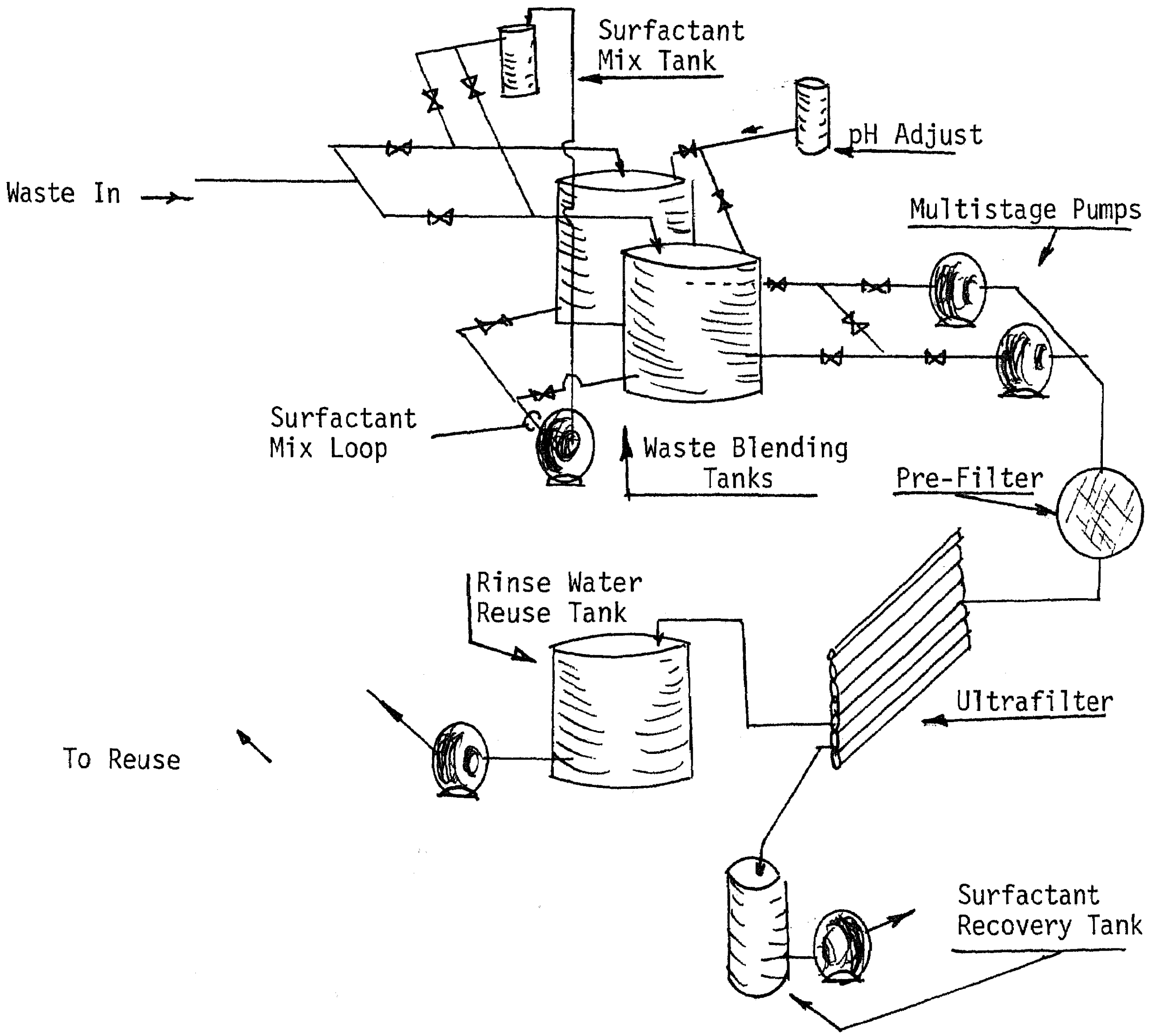


Figure 19 Waste Recovery Schematic

APPENDIX 1

Data Collected

Following are the numerical data from the tests run for the removal experiments.

Fluoborate removal using 100 ppm Sodium Fluoborate Solution and Armac-C surfactant.

Set	Mole Ratio	Milivolt $t=t_o$	 t=end	Plot Slope	BF_4^- Remaining Mole X 1000	 ppm	% Removal
1	1	71	92	56	0.381	41.8	58.2
	1	68	86	56	0.421	46.2	53.8
	1	70	86	55	0.457	50.2	49.8
						Avg.	53.9
2	1.5	67	90	57	0.349	38.3	61.7
	1.5	65	87	55	0.355	39.0	61.0
	1.5	69	90	54	0.366	40.2	59.8
						Avg.	60.8
3	2	70	91	56	0.368	40.4	59.6
	2	70	94	55	0.324	35.6	64.4
	2	68	93	56	0.311	34.2	65.8
						Avg.	63.3
4	2.5	72	97	58	0.324	35.6	64.4
	2.5	70	98	58	0.291	32.0	68.0
	2.5	70	104	56	0.220	24.1	75.9
						Avg.	69.4
5	3	73	111	55	0.183	20.1	79.9
	3	74	116	56	0.158	17.3	82.7
	3	72	109	56	0.194	21.3	78.7
						Avg.	80.4
6	3.5	67	103	57	0.207	22.7	77.3
	3.5	68	101	57	0.238	26.1	73.9
	3.5	68	98	56	0.263	28.9	71.1
						Avg.	74.1
7	4	72	100	56	0.282	31.0	69.0
	4	72	104	56	0.237	26.0	74.0
	4	72	99	54	0.284	31.2	68.8
						Avg.	70.6

This group of experiments shows variation in removals with respect to molar ratio; surfactant to BF_4^- 100 ppm $NaBF_4$.

Fluoborate Removal using 50 ppm Sodium Fluoborate Solution and Armac-C Surfactant.

					BF_4^- Remaining		
Set	Mole Ratio	$t=t_o$	t=end	Plot Slope	Mole X 1000	ppm	% Removal
8	1.5	87	96	56	0.307	33.7	32.6
	1.5	88	95	55	0.335	36.8	26.4
	1.5	88	100	56	0.274	30.1	39.8
							32.9
9	2.5	88	105	56	0.218	24.0	52.0
	2.5	86	99	56	0.260	28.6	42.8
	2.5	88	102	56	0.251	27.6	44.8
							46.5
10	3	88	106	55	0.209	23.0	54.0
	3	87	103	55	0.228	25.0	50.0
	3	87	107	56	0.198	21.7	56.6
							53.5
11	3.5	87	108	55	0.184	20.2	59.6
	3.5	88	113	54	0.150	16.5	67.0
	3.5	87	111	56	0.167	18.3	63.4
							63.3
12	4	86	107	56	0.188	20.7	58.6
	4	86	107	55	0.188	20.6	58.8
	4	88	107	55	0.204	22.4	55.2
							57.5

Variation in removals with variation in ratio of surfactant; 50 ppm $NaBF_4$

Fluoborate Removal using 150 ppm Sodium Fluoborate Solution and Armac-C Surfactant

Set	Mole Ratio	Milivolt		Plot Slope	BF_4^- Remaining		% Removal
		$t=t_0$	t=end		Mole X 1000	ppm	
13	1	62	76	57	0.768	84.3	43.8
	1	62	72	56	0.867	95.2	36.5
	1	61	71	55	0.873	95.8	36.1
							38.8
14	2	61	75	55	0.727	79.8	46.8
	2	61	82	57	0.578	63.5	57.7
	2	62	82	55	0.571	62.7	58.2
							54.2
15	3	62	87	56	0.478	52.5	65.0
	3	61	83	56	0.532	58.4	61.1
	3	62	90	55	0.410	45.0	70.0
							65.4
16	4	62	83	55	0.549	60.3	59.8
	4	61	82	56	0.558	61.3	59.1
	4	61	84	56	0.510	56.0	62.7
							60.5

Variation in removals with variation in surfactant molar ratio 150 ppm $NaBF_4$.

Fluoborate Removal using 25 ppm Sodium Fluoborate Solution and Armac-C Surfactant.

		Milivolt			BF_4^- Remaining		
Set	Mole Ratio	$t=t_o$	t=end	Plot Slope	Mole X1000	ppm	% Removal
17	2	104	114	57	0.147	16.1	35.6
	2	102	109	58	0.166	18.2	27.2
	2	104	116	56	0.136	14.9	40.4
							34.4
18	2.5	104	113	56	0.156	17.1	31.6
	2.5	104	124	57	0.099	10.9	56.4
	2.5	103	122	57	0.102	11.2	55.2
							47.7
19	3	103	117	56	0.123	13.5	46.0
	3	104	121	54	0.108	11.9	52.4
	3	104	117	56	0.128	14.1	43.6
							47.3
20	4	104	121	57	0.114	12.5	50.0
	4	104	119	56	0.119	13.1	47.6
	4	104	125	56	0.095	10.4	58.4
							52.0

Variation in removals with variation in surfactant mole ratio 25 ppm $NaBF_4$.

Fluoborate Removal using 100 ppm Sodium Fluoborate Solution and Armac-C Surfactant.

Set	Mole Ratio	Milivolt $t=t_o$	Milivolt t=end	Plot Slope	BF_4^- Remaining Mole X1000	BF_4^- Remaining ppm	% Removal
21	3	64	106	56	0.155	17.0	83.0
	3	60	98	57	0.188	20.6	79.4
	3	64	103	56	0.177	19.4	80.6
							81.0
22	3	63	104	57	0.167	18.3	81.7
	3	63	106	55	0.148	16.2	83.8
	3	63	105	55	0.150	16.5	83.5
							83.0
23	3	65	101	56	0.203	22.3	77.7
	3	63	96	55	0.219	24.0	76.0
	3	64	103	55	0.174	19.1	80.9
							78.2

Change in air feed rate.
Set 21 - 4 cubic centimeters per second.
Set 22 - 15 cubic centimeters per second.
Set 23 - 30 cubic centimeters per second.

Fluoborate Removal using 100 ppm Sodium Fluoborate Solution and Armac-C Surfactant

Set	Mole Ratio	Milivolt		Plot Slope	BF_4^- Remaining		% Removal
		t=t$_0$	t=end		Mole X 1000	ppm	
24	3	58	98	56	0.170	18.7	81.3
	3	59	94	55	0.209	23.0	77.0
	3	58	101	56	0.150	16.5	83.5
							80.6
25	3	59	93	57	0.228	25.0	75.0
	3	60	99	56	0.181	19.9	80.1
	3	60	98	56	0.184	20.2	79.8
							78.3
26	3	65	98	57	0.230	25.3	74.7
	3	64	102	58	0.199	21.9	78.1
	3	65	102	57	0.190	20.9	79.1
							77.3
27	3	65	102	56	0.190	20.9	79.1
	3	65	98	57	0.233	25.6	74.4
	3	65	109	56	0.144	15.8	84.2
							79.2

Change in mixing time
Set 24 - 24 hour mixing

Change in diffuser location
Set 25 - 4 inches below surface

Change in bubble size
Set 26 - Using different diffuser

Change in inflow direction
Set 27 - Using feed from top of reactor

Fluoborate Removal using 100 ppm Sodium Fluoborate Solution and Armac-C Surfactant.

		Milivolt			BF_4^- Remaining		
Set	Mole Ratio	t=t_0	t=end	Plot Slope	Mole X 1000	ppm	% Removal
28	3	68	89	57	0.383	42.1	57.9
	3	69	89	56	0.398	43.7	56.3
	3	71	99	56	0.284	31.2	68.8
							61.0
29	3	70	96	56	0.299	32.8	67.2
	3	70	95	57	0.318	34.9	65.1
	3	68	91	56	0.341	37.4	62.6
							65.0
30	3	68	86	56	0.435	47.8	52.2
	3	68	90	57	0.359	39.4	60.6
	3	69	91	56	0.356	39.1	60.9
							57.9
31	3	67	98	57	0.261	28.7	71.3
	3	65	94	57	0.273	30.0	70.0
	3	65	92	55	0.283	31.1	68.9
							70.1

Effect of adding:

Set 28 - 100 ppm NaAc
Set 29 - 100 ppm HAc
Set 30 - 100 ppm HCl
Set 31 - 50 ppm HCl

Fluoborate Removal using 100 ppm Sodium Fluoborate Solution and Armac-C Surfactant

Set	Mole Ratio	Milivolt $t=t_0$	t=end	Plot Slope	BF_4^- Remaining Mole X 1000	ppm	% Removal
32	1 on 100	64	70	56	0.701	77.0	23.0
	1 on 77.0	70	94	56	0.264	29.0	62.3
	1 on 29.0	94	101	56	0.200	22.0	24.1
							78.0
33	1 on 100	66	82	56	0.470	51.6	48.4
	1 on 51.6	82	98	56	0.204	26.4	48.8
	1 on 26.4	98	109	56	0.156	17.1	35.2
							82.9
34	1 on 100	74	83	56	0.610	67.0	33.0
	1 on 67.0	83	97	56	0.350	38.4	42.7
	1 on 38.4	97	110	56	0.200	22.0	42.7
							78.0

Effect of adding one stoichiometric quantity of surfactant; foam removal; surfactant foam removal; surfactant and foam removal. (3 step-wise additions)

FLUOBORATE - SURFACTANT REACTION RATE

	Time	MV	ppm BF_4	% Bound
SET 35	0	83	86.79	0
	1 min.	93	58.75	32.3
	5	95	54.33	37.4
	10	95	54.33	37.4
	15	97	50.26	42.1
	20	95	54.33	37.4
	25	93	58.74	32.3
	30	93	58.75	32.3
	35	93	58.75	32.3
	45	93	58.75	32.3
SET 36a	0	85	80.27	
	1	110	30.25	62.3
	5	110	30.25	62.3
	10	110	30.25	62.3
	15	110	30.25	62.3
SET 36b	0	110	30.25	
	1	126	16.21	53.6
	5	126	16.21	53.6
	10	120	20.48	32.3
	15	126	16.21	53.6

These series of tests were made to ascertain reaction rate for the BF_4^- surfactant reaction.

Fluoborate Removal using 100 ppm Solder Fluoborate Solution and Armac-C Surfactant

Set	Mole Ratio	Milivolt		Plot Slope	BF_4^- Remaining		% Removal
		t=t_o	t=end		Mole X 1000	ppm	
37-1	1	86	109	49	5.75	49.9	51.3
37-2	1.5	86	113	49	4.10	35.6	65.1
37-3	2	86	116	52	3.46	30.0	70.5
37-4	2.5	86	120	50	2.88	25.0	75.3
37-5	3	86	120	48	2.62	22.7	77.5
37-6	3.5	86	122	47	2.30	20.0	80.1
37-7	4	86	124	50	2.09	18.1	81.9
37-8	4.5	86	128	51	1.72	14.9	85.0
37-9	5	86	129	49	1.45	12.6	87.3

This series was run for removal of BF_4^- from a simulated solder plating rinse, using Armac-C. This and the next three series show variation in removals using different surfactants. The mole ratios were varied to find optimum removals.

Fluoborate Removal using 100 ppm Solder Fluoborate Solution and Armac-T Surfactant

Set	Mole Ratio	Milivolt $t=t_0$	Milivolt t=end	Plot Slope	BF_4^- Remaining Mole X 1000	BF_4^- Remaining ppm	% Removal
38-1	1	77	107	59	3.75	32.6	69.3
38-2	2	77	131	59	1.47	12.8	87.9
38-3	3	78	148	58	0.66	5.7	94.4
38-4	4	77	159	56	0.52	4.5	95.4
38-5	5	83	162	59	0.41	3.6	95.6
39-1	1	77	104	56	4.04	35.1	67.1
39-2	1.5	78	117	59	2.36	20.5	78.2
39-3	2	76	126	54	1.35	11.7	88.1
39-4	2.5	76	137	57	1.00	8.7	91.6
39-5	3	78	147	57	0.65	5.6	94.0
39-6	3.5	77	145	53	0.51	4.4	95.6
39-7	4	73	148	53	0.52	4.5	95.9
39-8	4.5	78	152	57	0.54	4.7	95.2
39-9	5	77	153	56	0.52	4.5	95.8

These two series were run for removal of BF_4^- from a simulated solder plating rinse, using Armac T, a mixed fat surfactant with an average carbon chain length of 18.

Fluoborate Removal using 100 ppm Solder Fluoborate Solution and Armac-18D Surfactant.

Set	Mole Ratio	Milivolt t=t_o	Milivolt t=end	Plot Slope	BF_4^- Remaining Mole X 1000	BF_4^- Remaining ppm	% Removal
40-1	1	86	110	51	3.86	33.6	68.5
40-2	1.5	86	130	53	1.77	15.4	85.4
40-3	2	86	141	52	1.14	9.9	90.6
40-4	2.5	86	151	52	0.74	6.4	93.8
40-5	3	86	160	50	0.51	4.4	95.7
40-6	3.5	86	163	53	0.50	4.3	95.8
40-7	4	86	173	51	0.30	2.6	97.4
40-8	4.5	86	179	51	0.22	1.9	98.1
40-9	5	86	182	51	0.18	1.6	98.4
41-1	1	90	122	49	2.95	25.6	74.8
41-2	1.5	90	140	46	1.22	10.6	89.5
41-3	2	90	149	52	0.96	8.3	91.7
41-4	2.5	90	160	51	0.61	5.3	94.6
41-5	3	90	169	50	0.38	3.3	96.6
41-6	3.5	90	173	49	0.31	2.7	97.2
41-7	4	90	180	50	0.23	2.0	97.9
41-8	4.5	90	183	50	0.20	1.7	98.2
41-9	5	90	182	48	0.15	1.3	98.6

These two series were run for removal of BF_4^- from a simulated solder plating rinse; using Armac-18D. This is a more pure 18 carbon chain hydrocarbon (90% stearyl).

Fluoborate Removal using 100 ppm Solder Fluoborate Solution and Armac-HT Surfactant.

Set	Mole Ratio	Milivolt		Plot Slope	BF_4^- Remaining		% Removal
		$t=t_0$	t=end		Mole X 1000	ppm	
42-1	1	85	115	50	3.38	29.3	72.8
42-2	1.5	85	126	53	2.10	18.2	83.1
42-3	2	86	132	50	1.38	12.0	88.3
42-4	2.5	87	144	53	0.96	8.3	91.6
42-5	3	86	159	56	0.60	5.2	94.8
42-6	3.5	90	165	56	0.55	4.8	95.3
42-7	4	91	169	55	0.41	3.6	96.5
42-8	4.5	90	173	56	0.35	3.0	97.2
42-9	5	88	170	53	0.29	2.5	97.6
43-1	1	83	105	51	4.64	40.3	65.0
43-2	1.5	83	119	53	2.49	21.6	81.1
43-3	2	83	127	50	1.82	15.8	86.2
43-4	2.5	83	135	51	1.09	9.5	91.7
43-5	3	83	140	51	1.00	8.7	92.4
43-6	3.5	83	149	53	0.73	6.1	94.6
43-7	4	83	157	52	0.52	4.5	96.0
43-8	4.5	83	157	51	0.48	4.2	96.3
43-9	5	83	168	54	0.35	3.0	97.4

This series were run for removal of BF_4^- from a simulated solder plating rinse; using Armac-HT. This is a hydrogenated tallow amine acetate. The hydrogenation increasing the percent saturation from 57.5% to 97%, as compared to Armac T.

Fluoborate Removal using 100 ppm Tin Fluoborate Solution and Armac-T Surfactant.

Set	Mole Ratio	Milivolt $t=t_0$	Milivolt t=end	Plot Slope	BF_4^- Remaining Mole X 1000	BF_4^- Remaining ppm	% Removal
44-1	1	78	104	56	3.79	32.9	65.0
44-2	1.5	82	120	57	2.15	18.7	80.1
44-3	2	79	130	57	1.44	12.5	87.2
44-4	2.5	79	140	56	0.92	8.0	91.8
44-5	3	79	145	53	0.60	5.2	94.7
44-6	3.5	77	146	54	0.56	4.9	95.0
44-7	4	76	139	54	0.77	6.7	93.2
44-8	4.5	77	148	52	0.45	3.9	95.9
44-9	5	75	152	50	0.33	2.9	97.1
45-1	1	75	106	52	2.76	24.0	75.9
45-2	1.5	76	117	51	1.72	14.9	85.0
45-3	2	77	125	51	1.26	10.9	89.0
45-4	2.5	79	134	51	0.88	7.6	91.6
45-5	3	79	142	52	0.65	5.6	93.5
45-6	3.5	79	148	54	0.53	4.6	94.7
45-7	4	79	150	54	0.48	4.2	95.6
45-8	4.5	79	157	56	0.41	3.6	96.2
45-9	5	80	160	57	0.41	3.6	96.2

These sets of tests were run to determine optimum removal of BF_4^- from tin plating rinse, using Armac-T.

Fluoborate Removal using 100 ppm Nickel Fluoborate Solution and Armac-T Surfactant

		Milivolt			BF_4^- Remaining		
Set	Mole Ratio	$t=t_o$	t=end	Plot Slope	Mole X 1000	ppm	Removal
46-1	1	67	89	63	4.64	40.3	58.6
46-2	1.5	67	101	60	3.04	26.4	72.8
46-3	2	68	109	62	2.35	20.4	79.0
46-4	2.5	67	123	62	1.45	12.6	86.9
46-5	3	69	139	65	1.04	9.0	91.6
46-6	3.5	69	140	66	0.88	7.6	91.6
46-7	4	69	145	65	0.78	6.8	93.7
46-8	4.5	69	143	66	0.78	6.8	93.2
46-9	5	71	155	66	0.61	5.3	95.0
47-1	1	62	82	55	6.87	59.6	60.6
47-2	1.5	61	90	54	5.28	45.8	74.8
47-3	2	67	104	53	3.23	28.0	79.6
47-4	2.5	60	109	54	2.37	20.6	89.6
47-5	3	70	126	57	1.50	13.0	90.3
47-6	3.5	62	123	56	1.28	11.1	92.9
47-7	4	69	138	55	0.81	7.0	94.6
47-8	4.5	59	130	58	1.00	8.7	94.4
47-9	5	69	140	54	0.66	5.7	95.5

These sets of tests were run to determine optimum removal if BF_4^- from nickel strip rinse, using Armac-T.

Fluoborate Removal using 100 ppm Copper Fluoborate Solution and Armac-T Surfactant.

Set	Mole Ratio	Milivolt $t=t_0$	Milivolt t=end	Plot Slope	BF_4^- Remaining Mole X 1000	BF_4^- Remaining ppm	% Removal
48-1	1	75	89	50	5.76	50.0	52.2
48-2	1.5	74	93	50	5.18	45.0	58.9
48-3	2	74	107	50	2.58	22.4	79.5
48-4	2.5	73	110	51	2.12	18.4	83.0
48-5	3	79	120	54	1.68	14.6	84.5
48-6	3.5	77	123	53	1.38	12.0	87.3
48-7	4	77	131	53	0.96	8.3	92.6
48-8	4.5	74	133	52	0.83	7.2	93.6
48-9	5	75	136	53	0.73	6.3	94.1
49-1	1	80	93	56	5.22	45.3	52.5
49-2	2	80	108	51	2.81	24.4	74.4
49-3	2.5	77	118	49	1.74	15.1	85.4
49-4	3	81	122	54	1.84	16.0	85.6
49-5	3.5	84	137	53	1.20	10.4	89.4
49-6	4	82	134	54	0.96	8.3	91.6
49-7	4.5	79	141	51	0.66	5.7	94.4
49-8	5	78	140	52	0.67	5.8	94.7

These sets of tests were run to determine optimum removal of BF_4^- from copper plating rinse, using Armac-T.

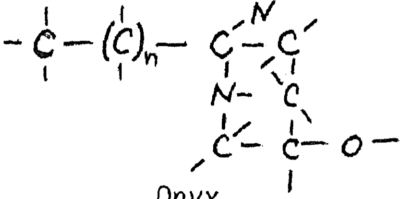
APPENDIX 2

Surfactants Used in the Study

I. Cationic

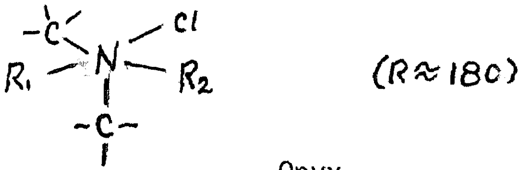
Amine - O, C, S, and T   Ciba-Geigi

These are Heterocyclic Tertiary Amines of the form:
$R - C - N - C_2H_4 - N - C_2H_4 - OH$



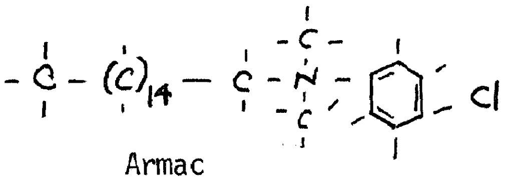
Ammonyx - 220   Onyx

This is ditallo di methyl ammonium chloride



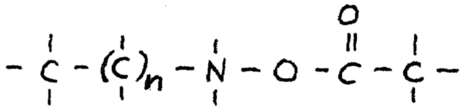
Ammonyx - T   Onyx

This is Cetyl dimethyl benzyl ammonium chloride



Armac C, T, 18D   Armac

These are alkyl amine acetates C for coco T for talo and 18D for distilled octadecane. $R - NH_3 - CH_2 - COOH$

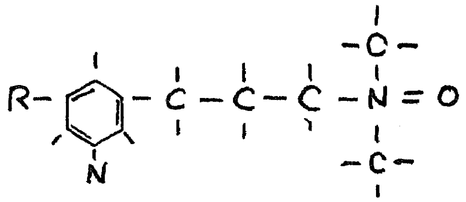


Coco,n ≈ 12
Talo,n ≈ 18
18D,n ≈ 18

Non Ionic

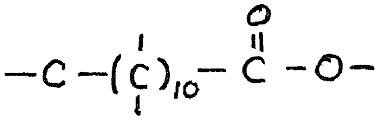
Ammonyx CDO Onyx

This is Coco amido propyl dimethyl amine oxide



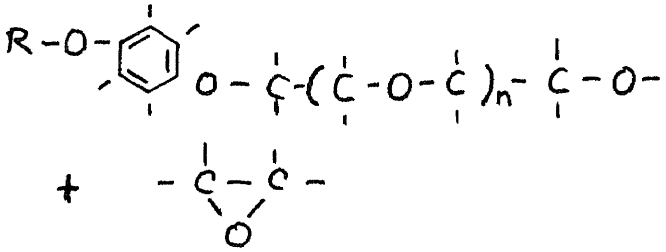
Onyxol 336 Onyx

This is Lauric Acid



Neutronyx 600

This is Alkylphenol polyglycol ether with ethylene oxide



Organic Phosphates

Dextrol OC - 60,80,90,105 & 110 Dexter

AROMATIC AMINE ACETATES USED IN STUDY

Armac-C
(coco-amine)

Chain Length* 12.7 avg.
Molecular Weight 270 avg.

Approximate Composition

Saturated Fats	Chain Length	%
Lauryl	12	50
Myristyl	14	18
Caprylyl	8	8
Palmityl	16	8
Capryl	10	7
Stearyl	18	1.5
Caproyl	8	0.5
Unsaturated Fats		
Oleyl	18	6
Linoleyl	18	1

Armac T
(tallow-amine)

Chain Length 17.1 Avg.
Molecular Weight 330 Avg.

Approximate Composition

Saturated Fats	Chain Length	%
Palmityl	16	29
Stearyl	18	23
Myristyl	14	3
Lauryl	12	1
Margaryl	17	1
Pentadecyl	15	0.5
Unsaturated Fats		
Oleyl	18	37
Palmitoleyl	16	3
Linoleyl	18	1.5
Myristoleyl	14	1

*Chain Length in carbon atoms.

Armac HT (Hydrogenated-tallow-amine)	Chain Length 17.1 Avg. Molecular Weight 332 Avg.

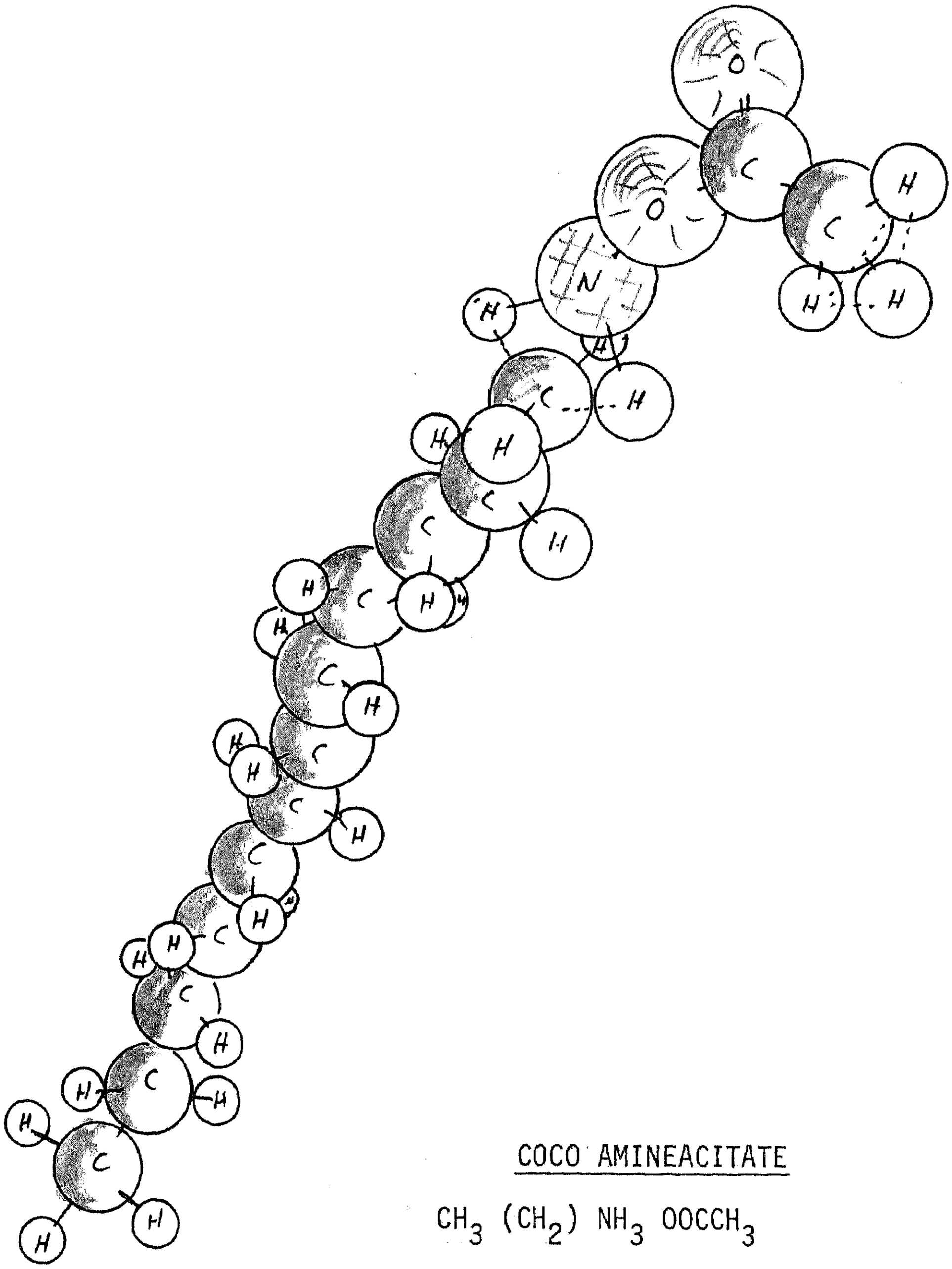
Approximate Composition

Saturated Fats	Chain Length	%
Stearyl	18	60
Palmityl	16	30
Myristyl	14	4
Margaryl	17	1.5
Lauryl	12	1.0
Pentadecyl	15	0.5
Unsaturated Fats		
Oleyl	18	2
Palmitoleyl	16	0.5
Myristoleyl	14	0.5

Armac 18D (H-Octadecyl-amine)	Chain Length 17.8 Avg. Molecular Weight 338 Avg.

Approximate Composition

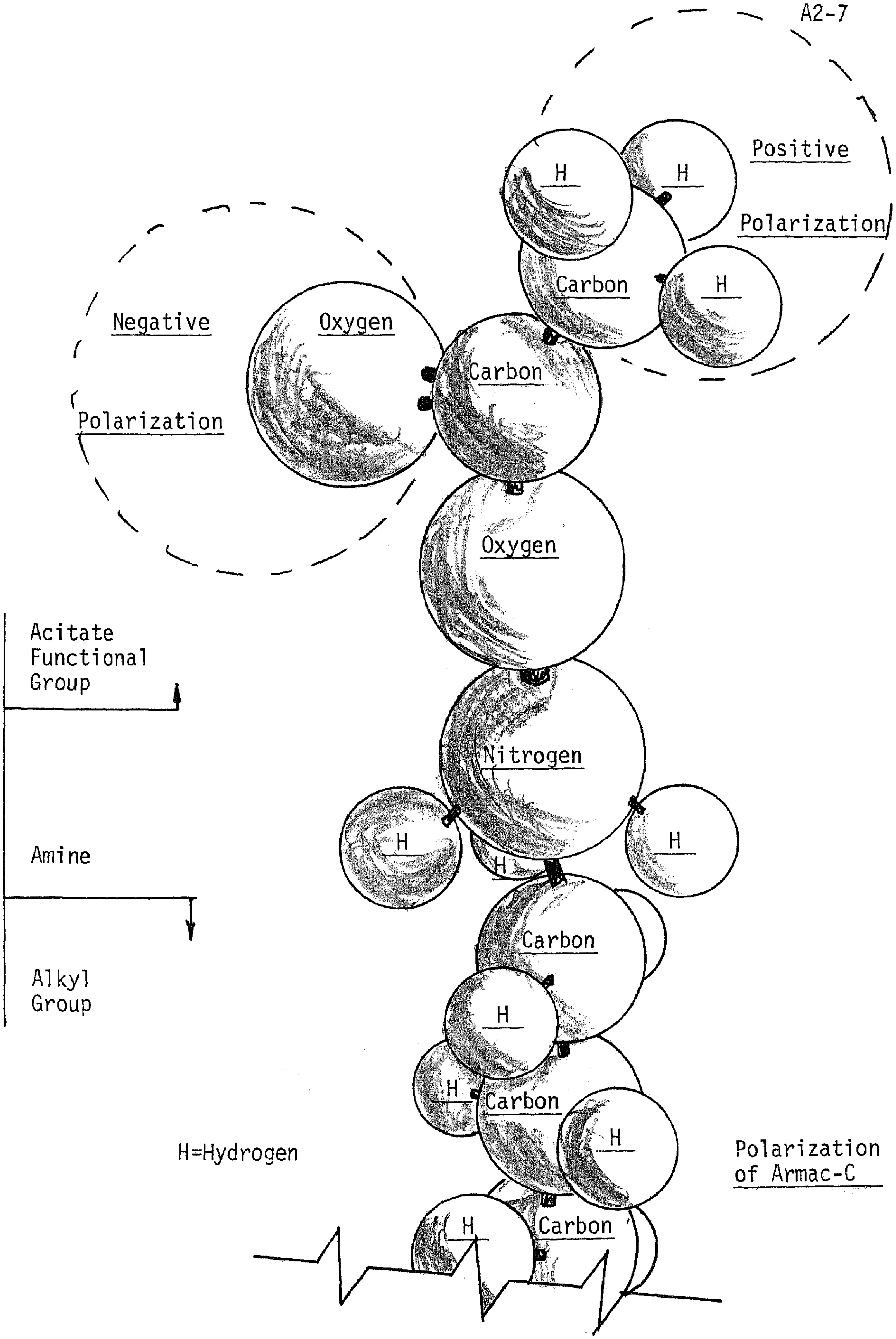
Saturated Fats	Chain Length	%
Stearyl	18	90
Palmityl	16	8.5
Margaryl	17	1.5



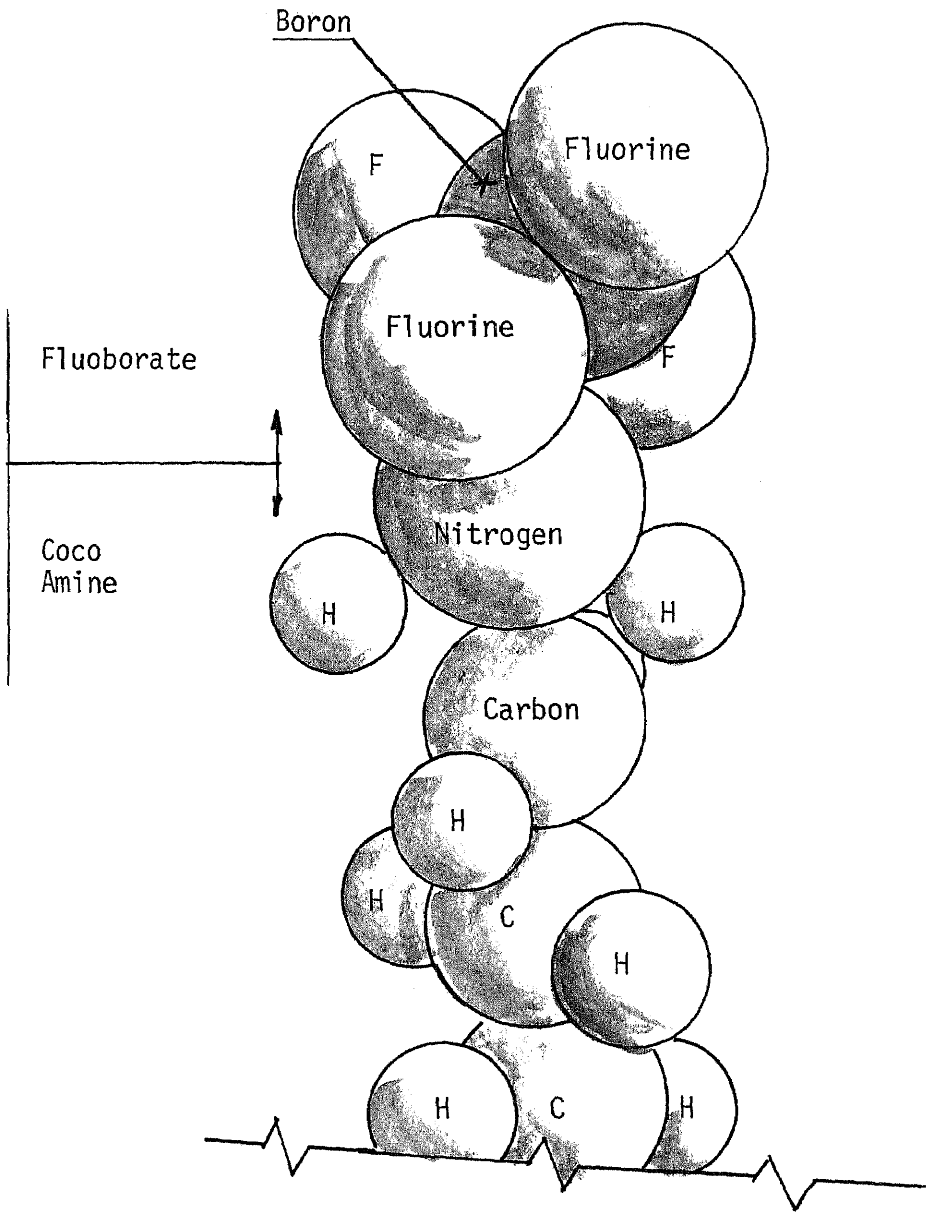
COCO AMINEACITATE

$CH_3\ (CH_2)\ NH_3\ OOCCH_3$

n=11 → 14



Polarization of Armac-C



Fluoborate on
Coco Amine

APPENDIX 3

TEST TO DETERMINE HYDROLYSIS OF BF_4^- WITH LIME ADDITIONS

1. Solutions made up to approximately 400 ppm using the plating solution made up as below:

$Sn(BF_4)_2$	816 g/l	109 oz./gal.
HBF_4	29 g/l	3.9 oz./gal.
$B(OH)_3$	16 g/l	2.1 oz./gal.

2. Solutions adjusted to pH as shown by the addition of hydiated lime.

3. Fluoborate quantity determined after lime addition then after four days at laboratory abient temperature:

	BF_4^- ppm	
pH	Start	Finish
3.3	415	415
6	400	405
9	400	405
10	410	400
11	380	385
12.2	380	380

TEST TO DETERMINE HYDROLYSIS OF BF_4- WITH ADDITION OF LIME AND HYDROGEN PEROXIDE

1. Plating Solution as on previous page, was mixed to give approximately 300 ppm fluoborate. Solution brought to temperature then hydrated lime and 0.1 Molar hydrogen peroxide were added to give a pH of approximately 9 and stoichiometric quantities of peroxide. The reaction are:

$$Sn(BF_4) + H_2O_2 + {}_2H_2O \longrightarrow Sn(OH)_4 + {}_2HBF_4$$

$$HBF_4 + {}_2CaCl_2 + {}_3H_2O \longrightarrow B(OH)_{33} + {}_2CaF_2 + {}_4BCl$$

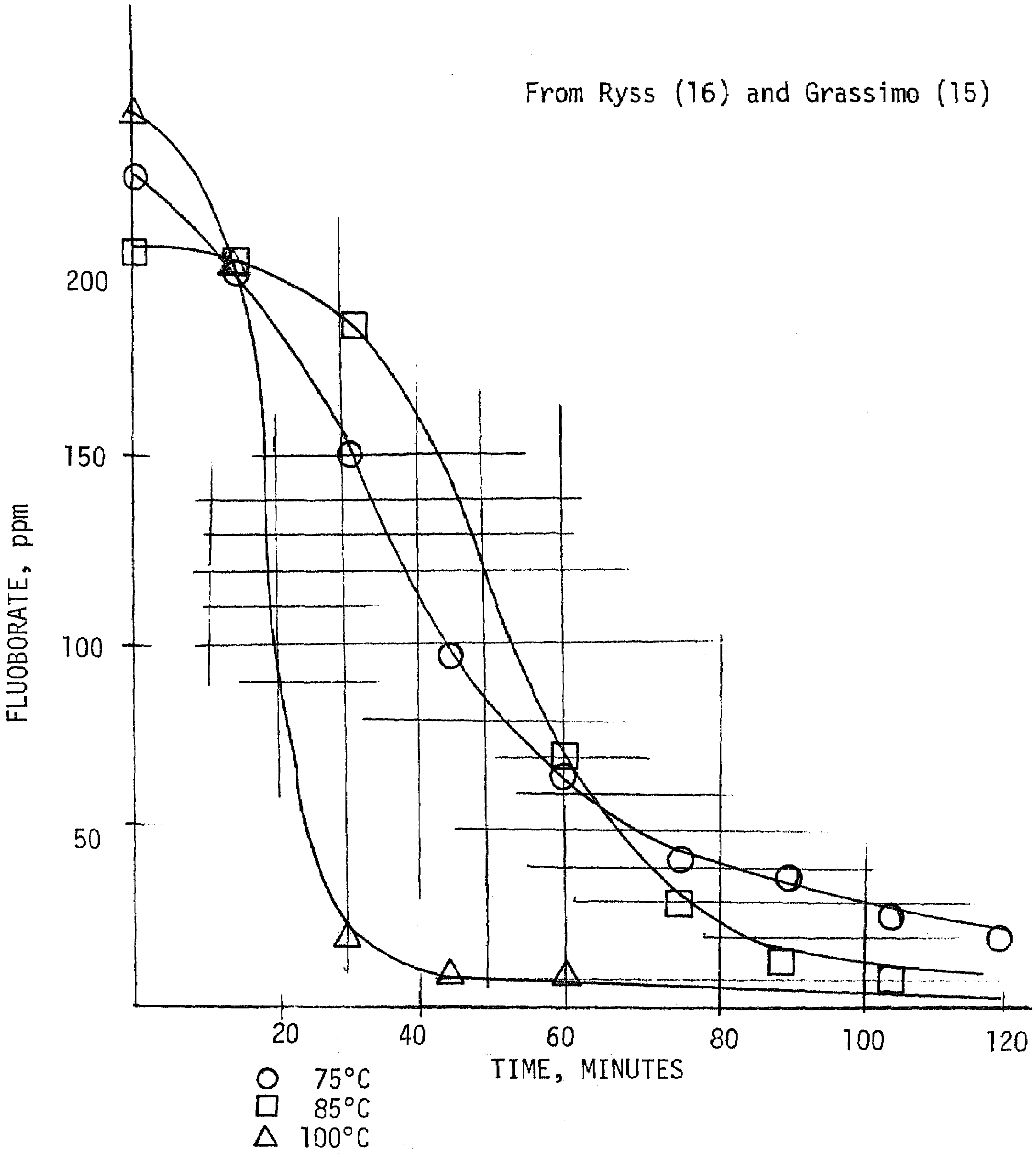
This showed:

Temp = 100°C Temp = 85°C Tempt = 75°C

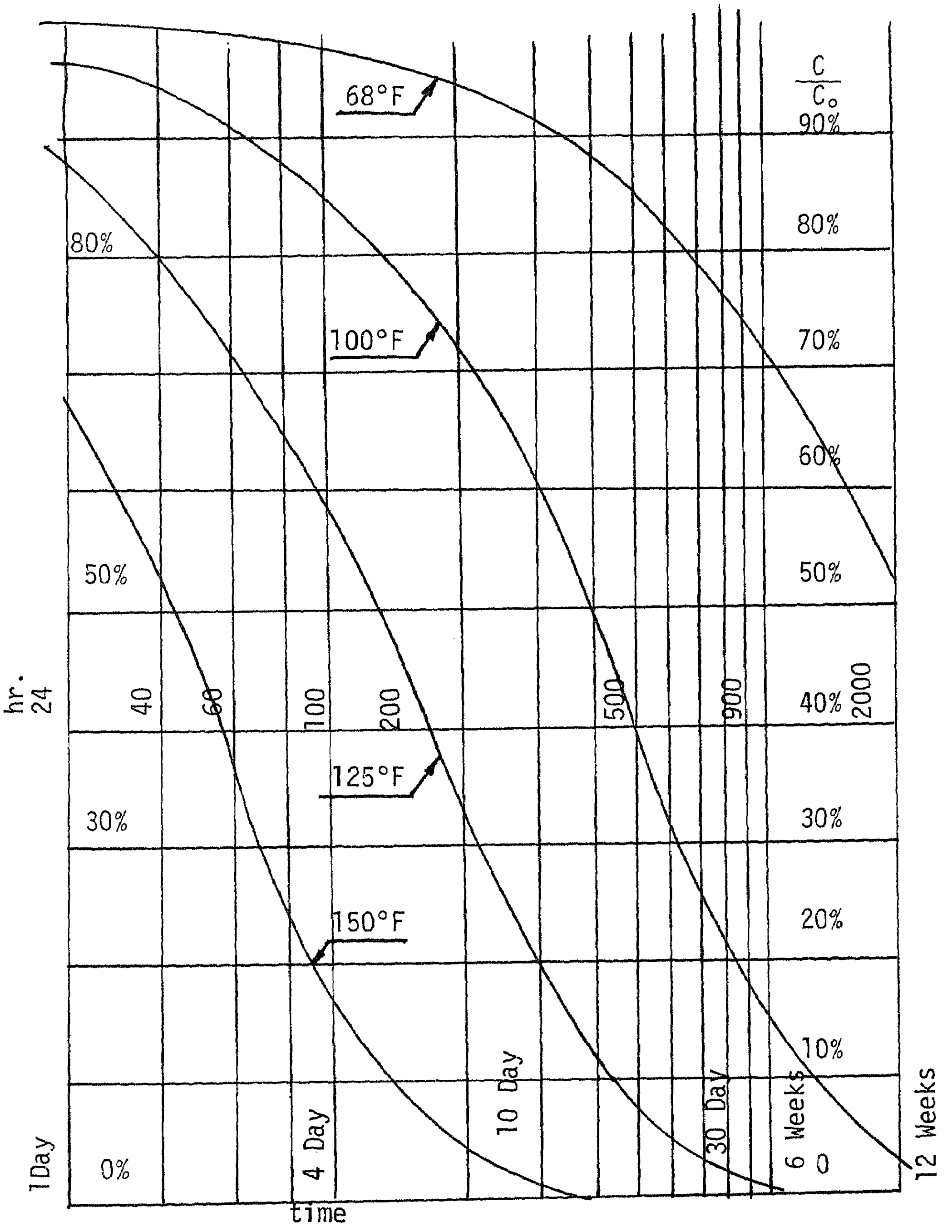
Time (minutes)	BF_4- (ppm)	Time (minutes)	BF_4- (ppm)	Time (minutes)	BF_4- (ppm)
0	246	0	210	0	230
15	205	15	205	15	200
30	18	30	190	30	150
45	8	45	140	45	95
60	8	60	70	60	70
		75	25	75	38
		90	10	90	30
		105	8	105	24
				120	18

FLUOBORATE HYDROLYSIS

In water with 0.1M H_2O_2 = 0.1M $CaCl_2$


From Ryss (16) and Grassimo (15)

HYDROLYSIS OF BF_4^- IN WATER
From Ryss (38) & Grassimo (35)



BF_4- HYDROLYSIS AS A FUNCTION OF pH

pH	.00091M (100 ppm) $\varnothing$	0.005M (550 ppm) $\varnothing$	.02M (2200 ppm) $\varnothing$
2	86.3	96.4	98.8
2.25	81.0	95.0	
2.5	73.5	92.9	
2.75	63.5	90.0	
3	51.0	86.1	95.3
3.25	35.5	80.6	93.1
3.5	19.4	73.1	90.3
3.75	7.0	63.1	87.3
4	1.6	50.1	81.9
4.25		34.7	74.9
4.5		18.6	65.4
4.75		6.5	53.2
5		1.5	38.1
5.25			21.5
5.5			8.5
5.75			2.1
6			1.4

$$\varnothing = \frac{\text{Moles Unhydrolyzed } BF_4^-}{\text{Moles } BF_4^- \text{ Starting}} \times 100 \qquad T = 25°C$$

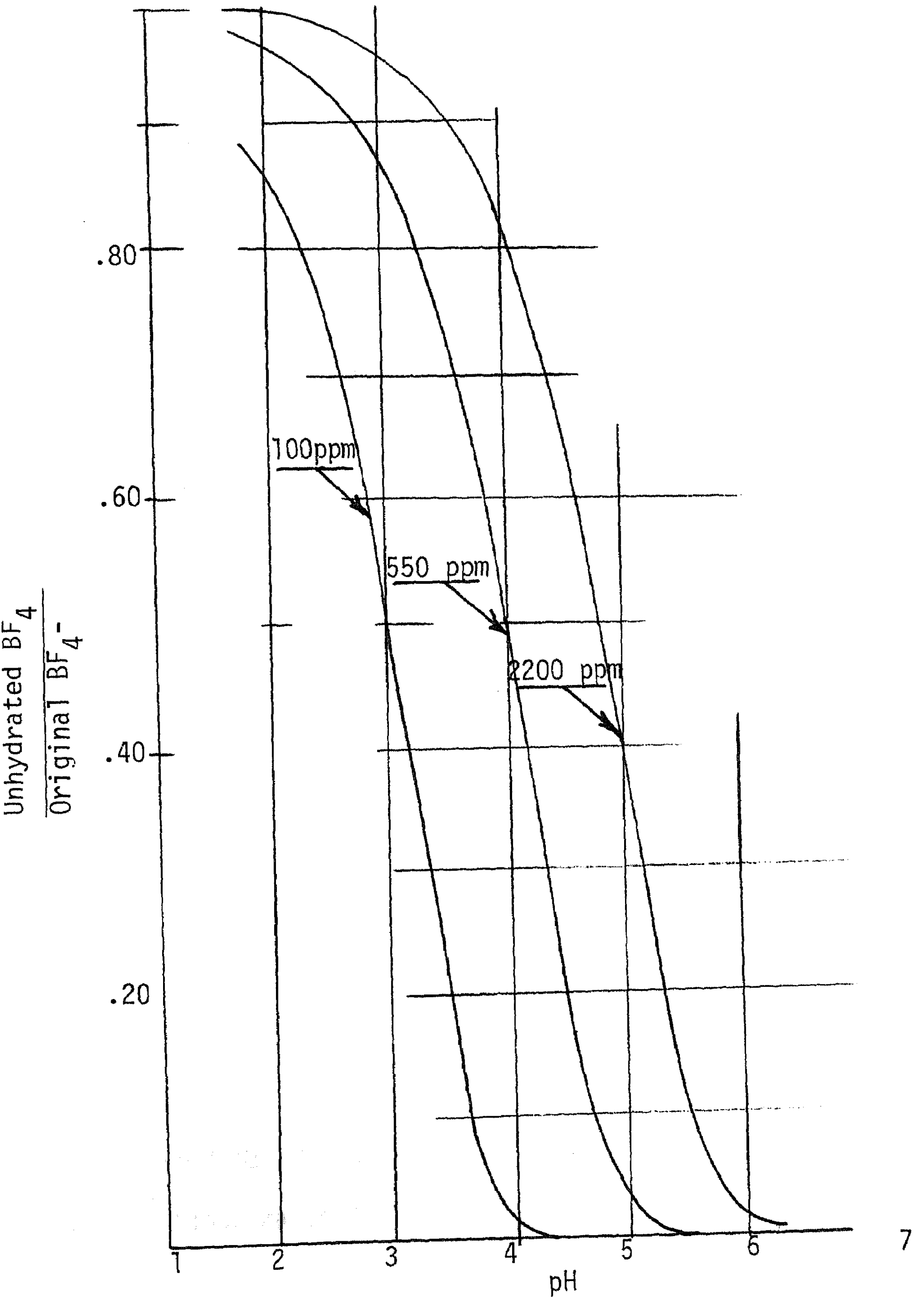
$$\frac{[H_3BO_3]\ [H^+]\ {}^3[F]^4}{[BF_4]} = K = 9.772 \times 10^{-21}$$

$$\frac{[B]\ [H]^3\ [4B]^4}{[M-B]} = K$$

From Ryss (16) & Grassimo (15)

PLOT OF HYDROLYSIS OF BF_4- WITH pH

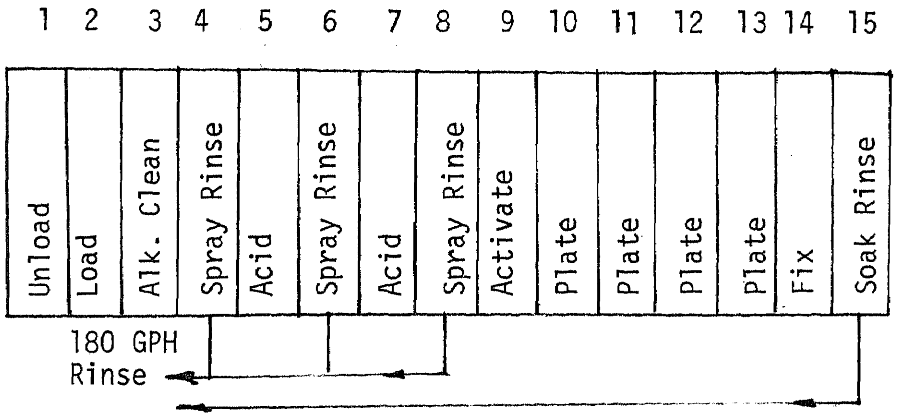
From Ryss (38 & Grossimo (35)



APPENDIX 4

TYPICAL PRINTED WIRING BOARD-SOLDER PLATER

Station



Tank 14		Tank 9		Tank 10 13	
HBF_4	13 oz./gal.	HBF_4	7 oz./gal.	HBF_4	34 oz./gal.
$(BF_4)_2$	5.6 " "	$B(OH)_3$	0.2 " "	$Pb(BF_4)_2$	1.5 " "
$(OH)_3$	1.4 " "			$Sn(BF_4)_2$	3 " "
$(OH_2)_3$	1.3 " "			LPD-Starter	4 " "
				$B(OH)_3$	0.2 " "

Area Plated ≈ 10,000,000 sq. ft. yr.

BF_4^- in Rinse Water ≈ 180 ppm (0.4 lbs./hr.)

APPENDIX 5

ELECTROPLATING BATH COMPOSITION, DRAGOUT AND RINSING

BATH COMPOSITION	OPTIMUM	
Solder Plate (60 Tin-40 Lead)	Gram/Liter	Ounce/Gallon
Stanous Tin	15	2
Lead	10	1.3
Fluoboric Acid	400	53
Boric Acid	25	3.3
Peptone	5	0.7
Copper Plating		
Cupric Copper	15	2
Fluorboric Acid	380	51
Nickle Plate, Standard		
Nickle	55	7.3
Fluoboric Acid	165	22
Nickle Plate, High Speed		
Nickle	110	14.6
Fluoboric Acid	330	44
Tin Plate (Rack)		
Tin	70	9.3
Stanous Fluoborate	194	25.9
Fluoborate Ion	215	28.7
Organic	7.5	1

Tin Plate (Wire)	Gram/Liter	Ounce/Gallon
Tin	120	16
Stanous Fluoborate	295	39.4
Fluoborate	355	37.4
Overall Average		
Fluoborate	307	41

PLATING DRAGOUT CALCULATIONS*

1. BF_4- in Plating Bath 307 g/l (41 oz./gal.) from above.

2. Use 7-1/2 square feet per rack, one rack per minute machine. 0.3 gal. per 1000 square feet dragout.

$$\frac{7.5}{1000}(0.3) = 0.00225 \text{ gal./min.} = \text{Dragout}$$

3. For 100 ppm BF_4 in discharged rinse;

$$(41 \text{ oz./gal.})(0.00225 \text{ gal./min.}) \div (16 \text{ oz./lb.}) = 0.00563 \text{ lb./min.}$$

$$100 \text{ ppm} \Rightarrow (0.00563 \times 10^6) \div (8.345 \text{ lb./gal.})$$

$$\Rightarrow 6.74 \text{ gal./min. rinse rate}$$

$$= 3235 \text{ gal./8 hr. shift}$$

4. An 8 ft. diameter tank contains 376 gal. per ft. so 10 ft. high tank holds 3760 gal.

*Sources - Development document for Effluent Limitation Guidelines, Phase II, Metal Finishing Industry. Prepared for the USEPA by Battelle Memorial Institute, 1974. Electroplating Engineering Handbook, Third Edition, Edited by A. Kenneth Graham - Van Nostrand Reinhold 1971

RINSING CALCULATIONS*

Use Two Stage Rinse $(r=2)$

D = Dragout per rack per operaton $= \frac{7.5}{1000}(0.3)=0.00225$

M = Interval between operations = 1 min.

Q = Rate of fresh water flow = 6.74 gpm

r = Number of rinse operations = 2

Co = Concentration of Dragin to tank #1 = 41.38 oz./gal.

Cei=Concentration of Equilibrium, rinse 1 = 100 ppm=0.013 oz./gal.

Cr = Concentration of Final Rinse

$$Cei = \left(\frac{D}{QM+D}\right)Co + Cr$$

$$Cr = 0.013 - \left(\frac{0.00225}{6.74+0.00225}\right) 41.38$$

$$= 0.000439 \text{ oz./gal.}$$

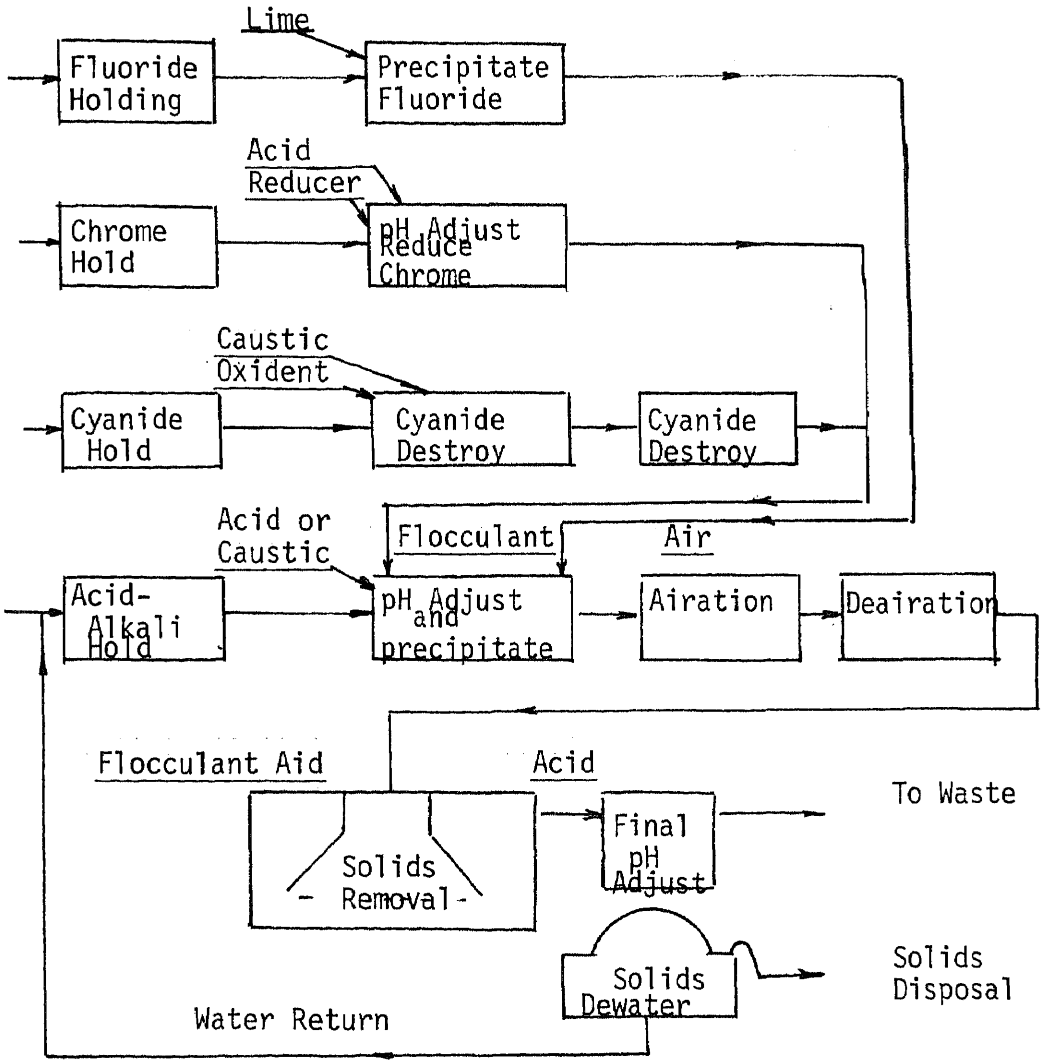
$$= 3.3 \text{ ppm}$$

This 3.3 ppm in the final rinse is well within the purity required (37 ppm).

*Data from previous page.

APPENDIX 6

TYPICAL WASTE TREATMENT PLANT (BPT)



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VITA

Mr. R. H. Haralson is at present a Senior Engineer in Plant and Environmental Engineering, at Western Electric Company, Inc. He and his wife have two young adult daughters and live in Indianapolis, IN. He was born in and raised in the Upper Peninsula of Michigan. He spent time in the service in Europe, Japan and Korea prior to entering college.

Mr. Haralson has a Bachelor of Science - Civil Engineering, from Michigan Technological University and a Master of Science - Metallurgical Engineering, from Lehigh University. He has worked for Western Electric since receiving his Engineering degree. As a Plant Engineer at the Omaha Works, he had responsibility for the start-up and operation of the electroplating waste treatment plant and for the sanitary waste treatment plant. He was active in the WPC Association in assisting in stream standard development, on the education committee and was the chairman of the program committee. He also had many other responsibilities including design and engineering for the bulk and packaged chemical storage handling and distribution.

At the Engineering Research Center in Princeton, he worked with thin films as a Research Engineer, developing a clean room, cleaning locations and clean loading facilities. He also developed a process for determining nuclearaction and growth in tantalum thin films and for increasing the uniformity of coverage in sputtering.

At the Columbus Works, he was involved in Development Engineering in the print and etch and plate printed wiring board manufacture. Here he developed an etchant recycle and copper recovery system and worked closely with the copper clad laminate suppliers to optimize their processes while improving the board output. At Dallas, he again became responsible for an industrial waste treatment plant and was Product Engineer for general electroplating where newer cleaning, rinsing and conservation measures were utilized to minimize waste. He also "had" all environmental, safety and OSHA Engineering. At Western Electric Headquarters he was assigned to work in the water end of the environment where there were four areas of responsibility.

- Prepare conceptual design of waste water treatment facilities
- Interface with regulatory agencies, in this field.
- "Start-up" and "trouble-shoot" waste water treatment facilities.
- Prepare operating instructions and in general act as Engineering Consultants for the various Western Electric locations.

Mr. Haralson's present assignment is at the Indianapolis Works in a Plant and Environmental Engineering Department where he has Engineering and operating responsibilities for the Industrial Waste Treatment Plant (licensed operator of record) and the demineralized water system; along with other "normal" plant engineering functions.

He has published papers on waste treatment and on waste minimization and has been active internally to the company in educating and in proselytizing for the environment.