

[54] **DEFLUORINATION OF WET PROCESS
PHOSPHORIC ACID**

[75] Inventors: **Ashok Babubhai Amin**, Trenton,
N.J.; **Robert Lee Bristow**, Lakeland,
Fla.

[73] Assignee: **American Cyanamid Company**,
Stamford, Conn.

[22] Filed: **March 15, 1971**

[21] Appl. No.: **124,099**

[52] U.S. Cl. **423/321**

[51] Int. Cl. **C01b 25/16**

[58] Field of Search **23/165, 165 B**

[56]

References Cited

UNITED STATES PATENTS

2,987,376	6/1961	Gloss	23/165
2,933,372	4/1960	Manning	23/165
3,151,941	10/1964	Hollingsworth et al.	23/165
3,193,351	7/1965	Miller et al.	23/165

FOREIGN PATENTS OR APPLICATIONS

1,456,263 9/1966 France

Primary Examiner—Oscar R. Vertiz

Assistant Examiner—Gregory A. Heller

Attorney—Robert P. Raymond

[57]

ABSTRACT

A process for the defluorination of phosphoric acid containing dissolved aluminum is described.

11 Claims, 12 Drawing Figures

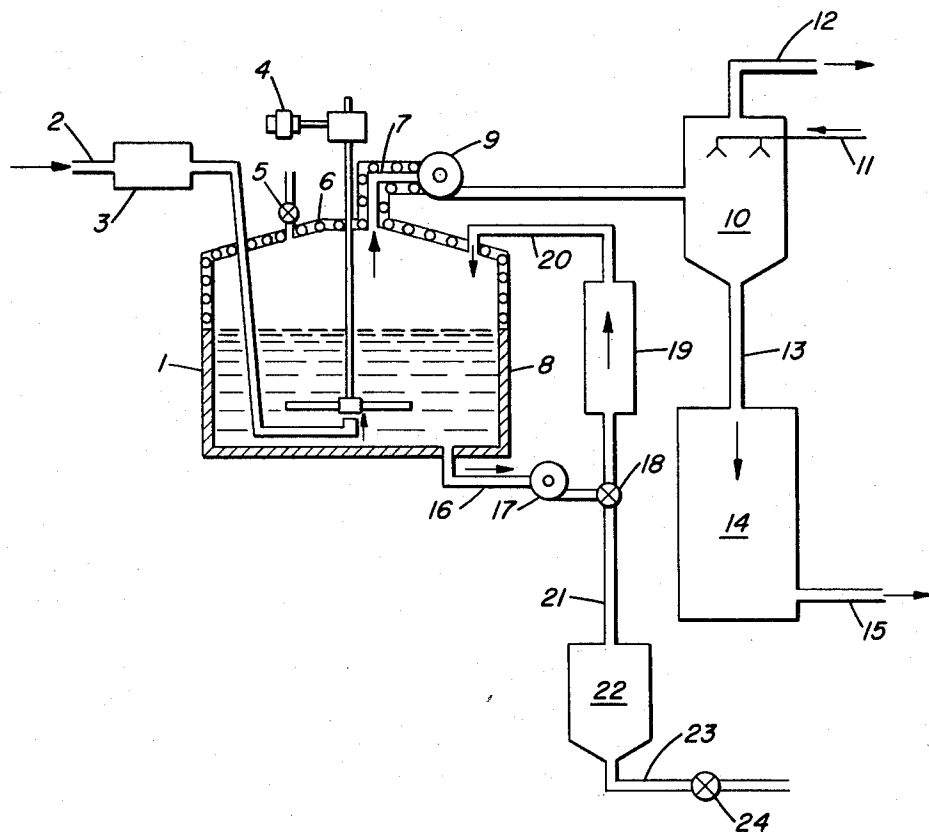


FIG. 1

INVENTORS
 ASHOK BABUBHAI AMIN
 ROBERT LEE BRISTOW
 BY
Robert P. Raymond
 ATTORNEY

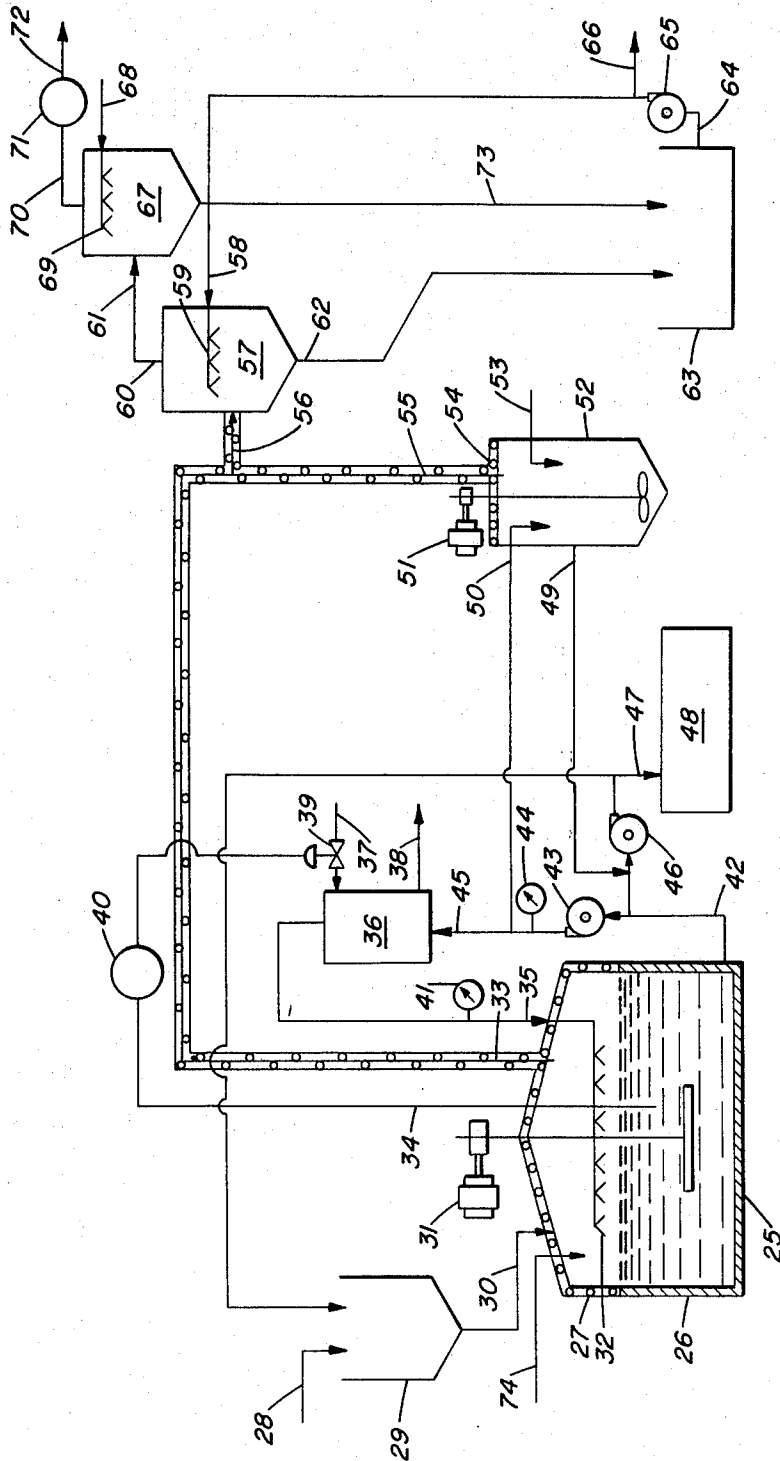


FIG. 2

INVENTORS
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY *Robert P. Raymond*
ATTORNEY

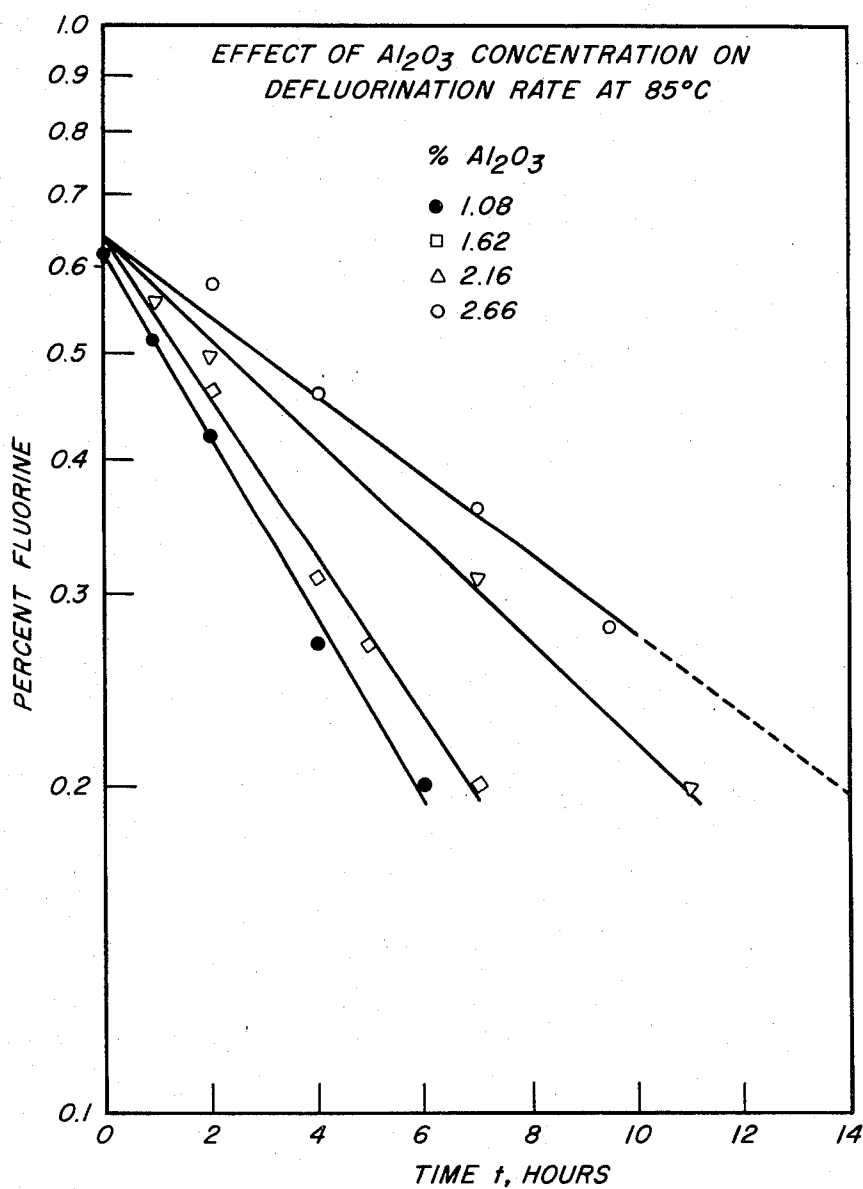
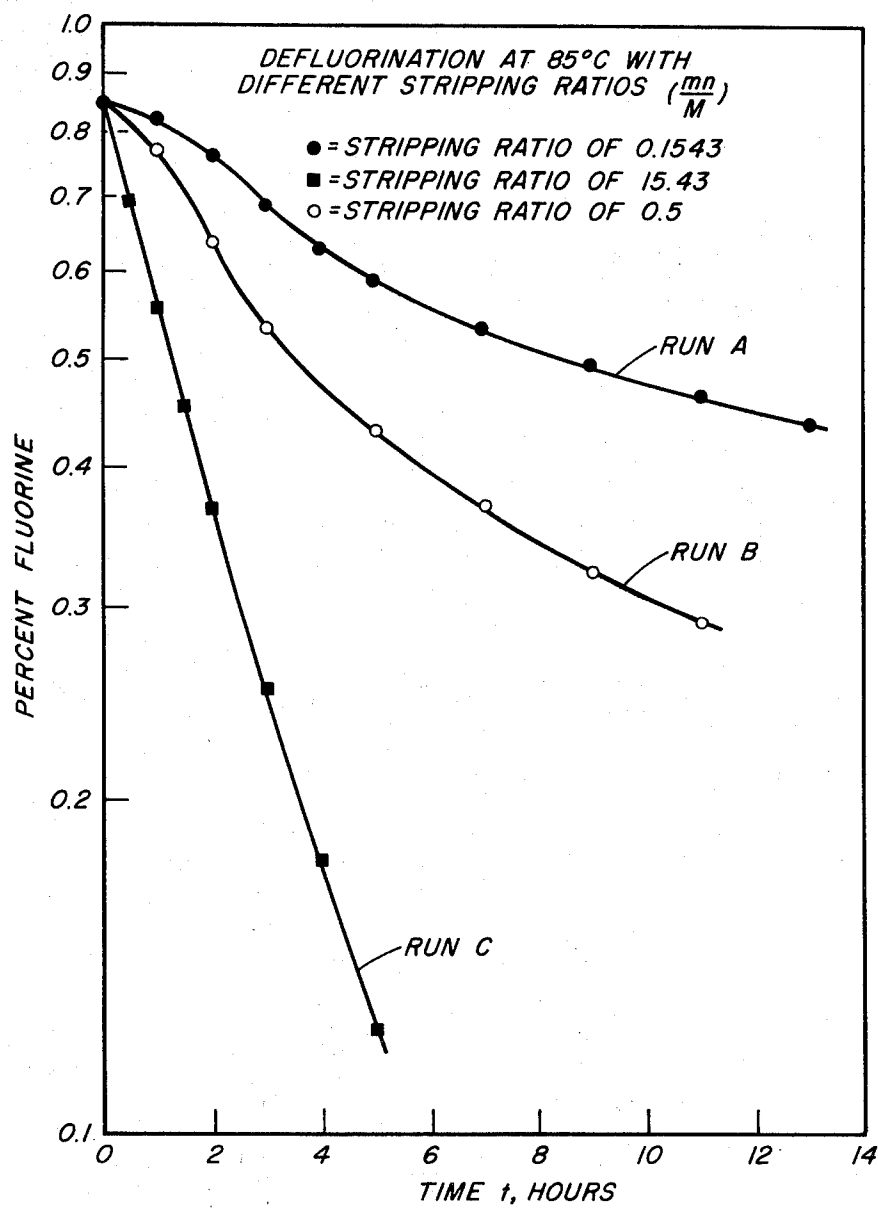


FIG. 3

INVENTORS
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY *Robert P. Raymond*
ATTORNEY

**FIG. 4**

INVENTORS
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY

Robert P. Raymond

ATTORNEY

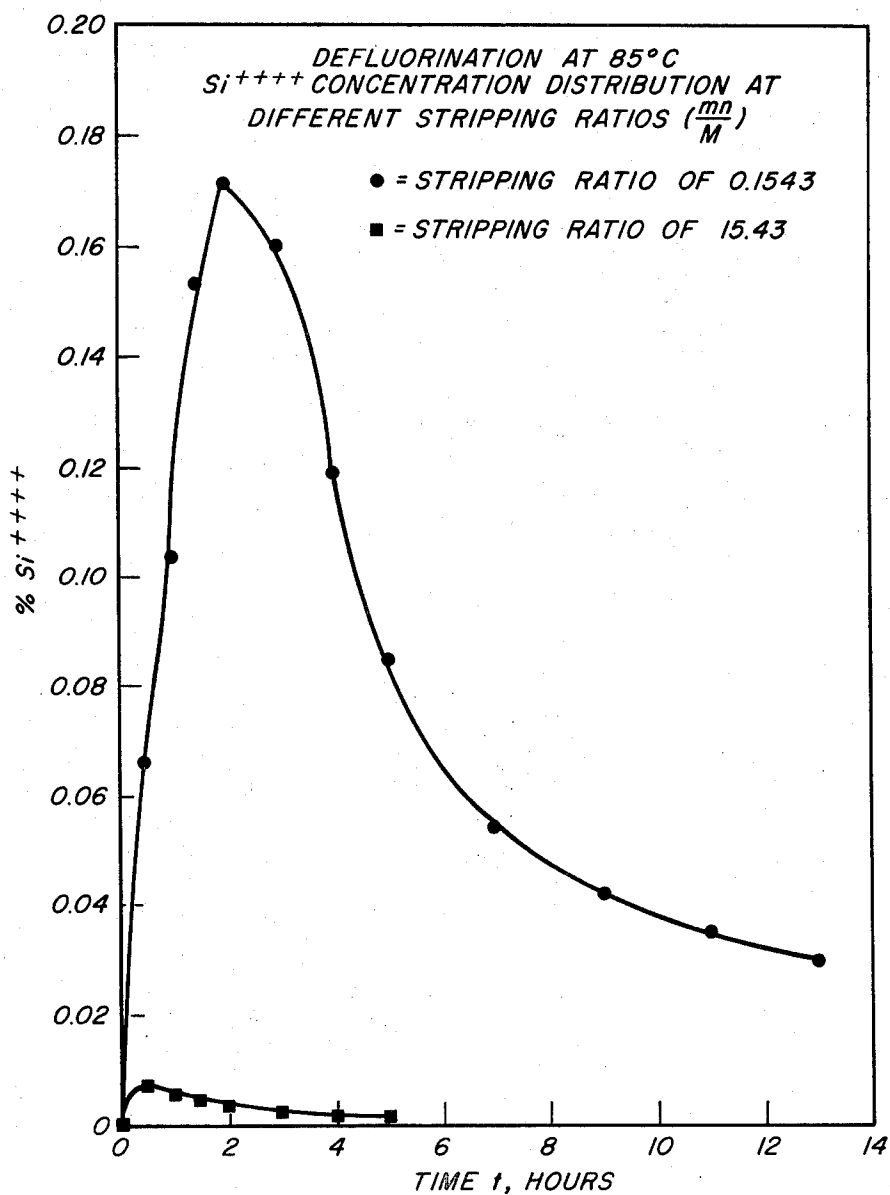


FIG. 5

INVENTORS
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY
Robert P. Raymond
ATTORNEY

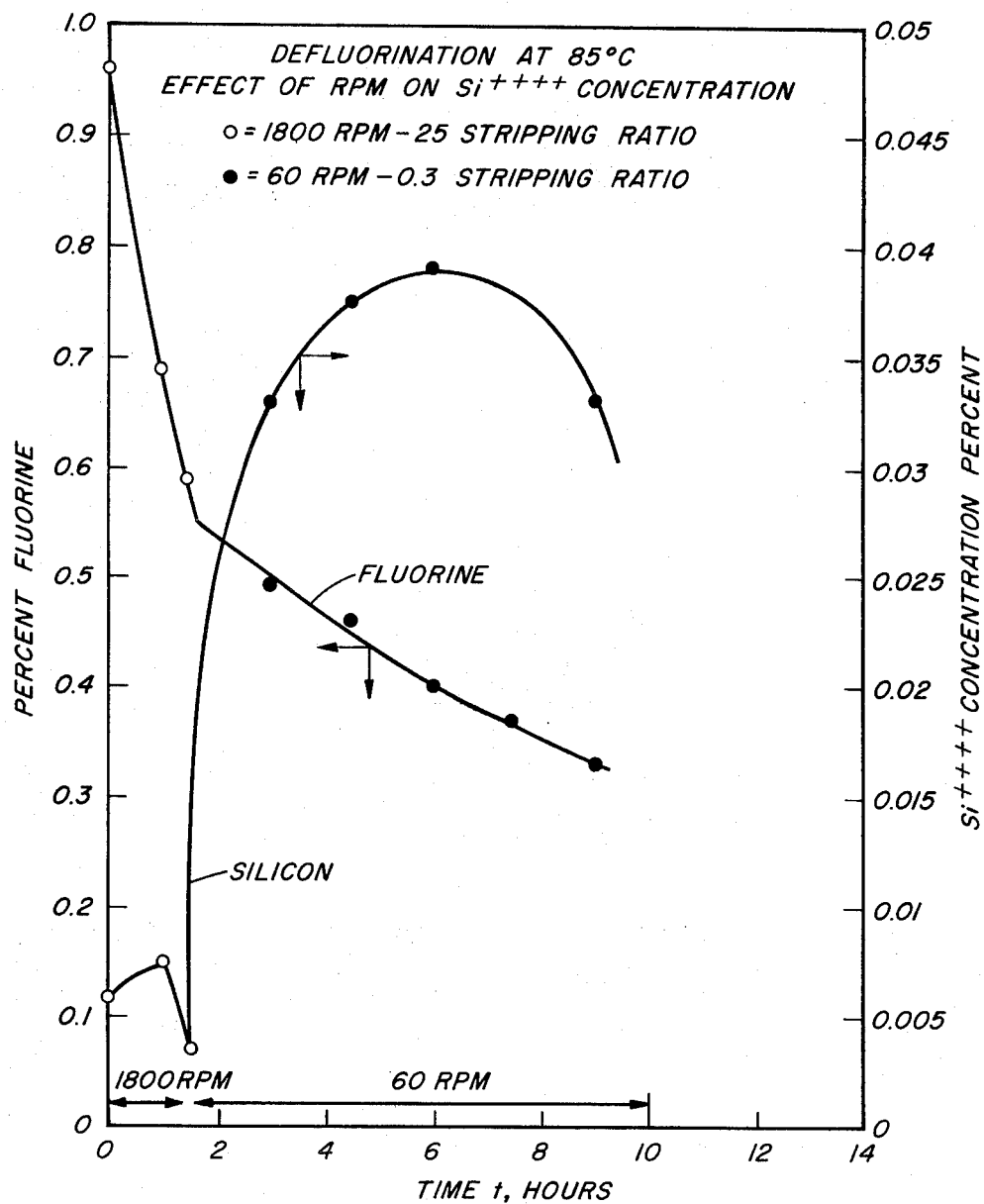
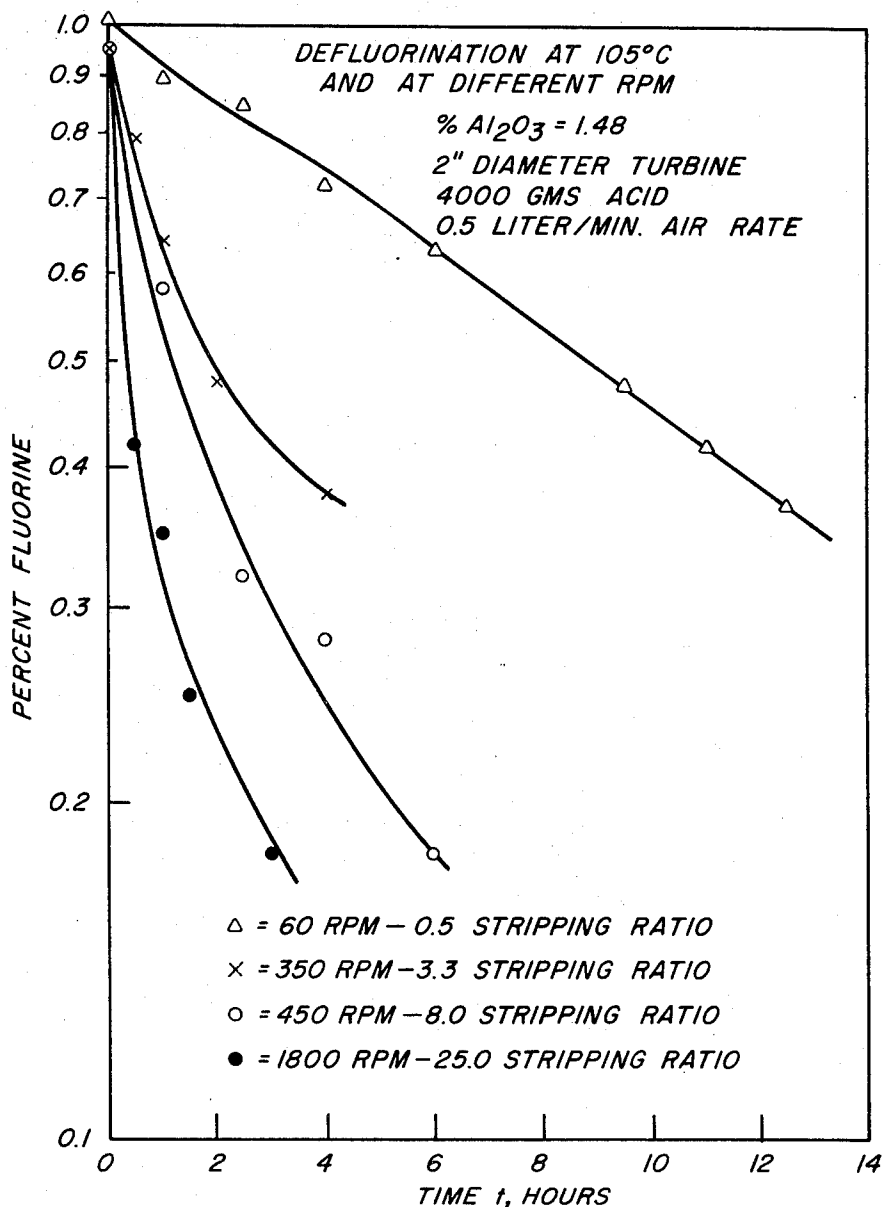


FIG. 6

INVENTORS
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY
Robert O. Raymond
ATTORNEY

**FIG. 7**

INVENTORS
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW

BY

Robert O. Raymond

ATTORNEY

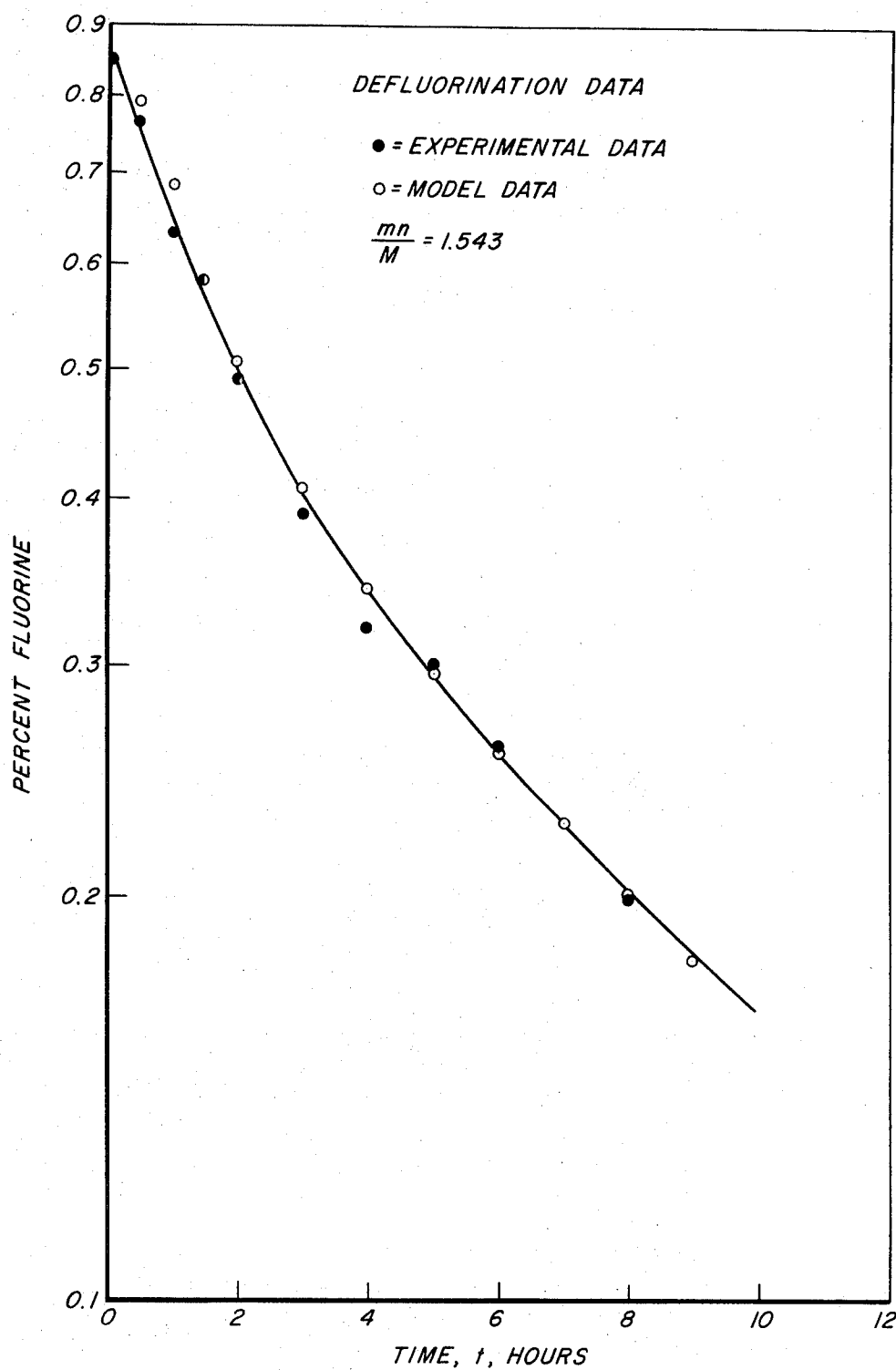


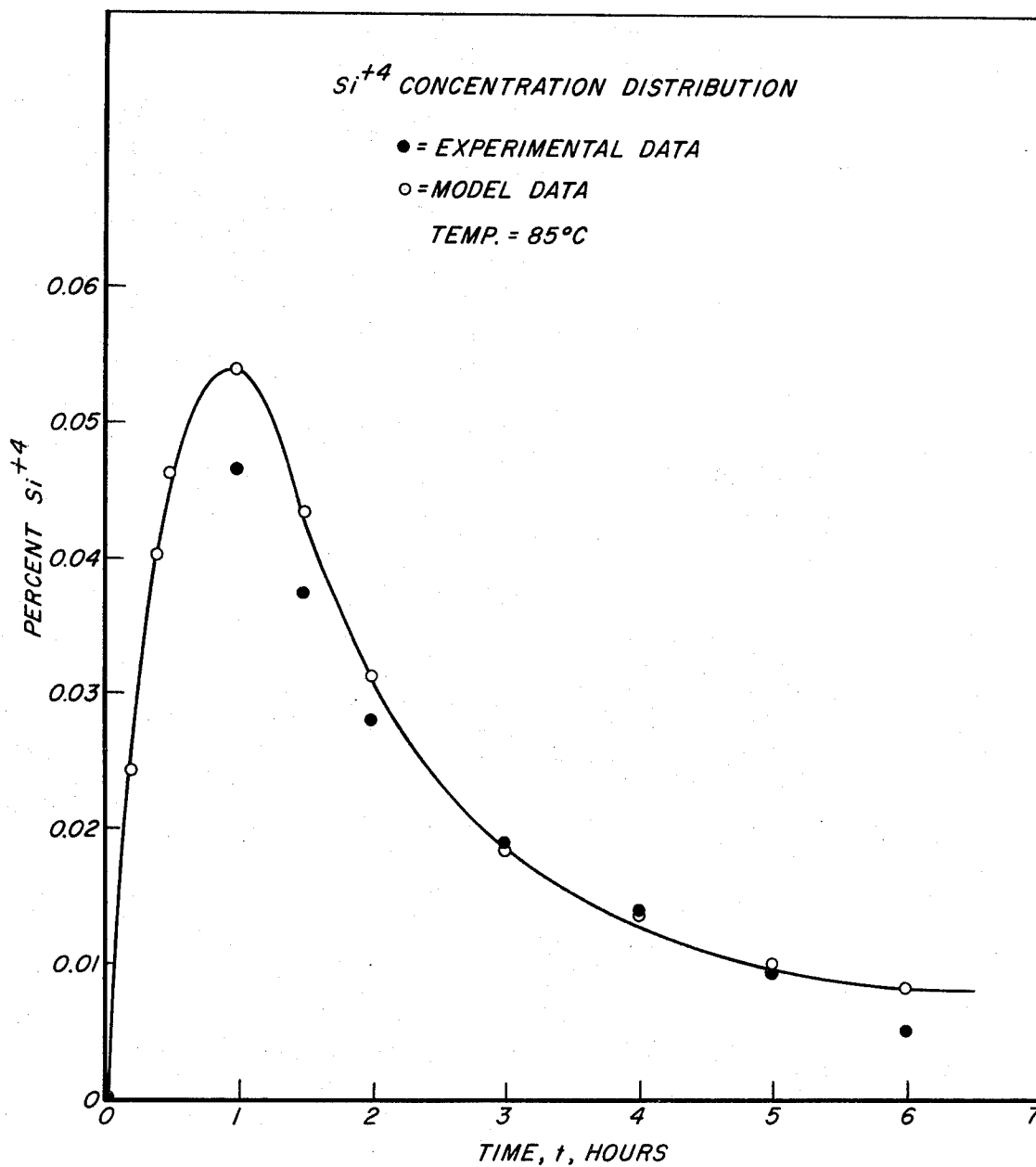
FIG. 8

INVENTORS.
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW

BY

Robert O. Raymond

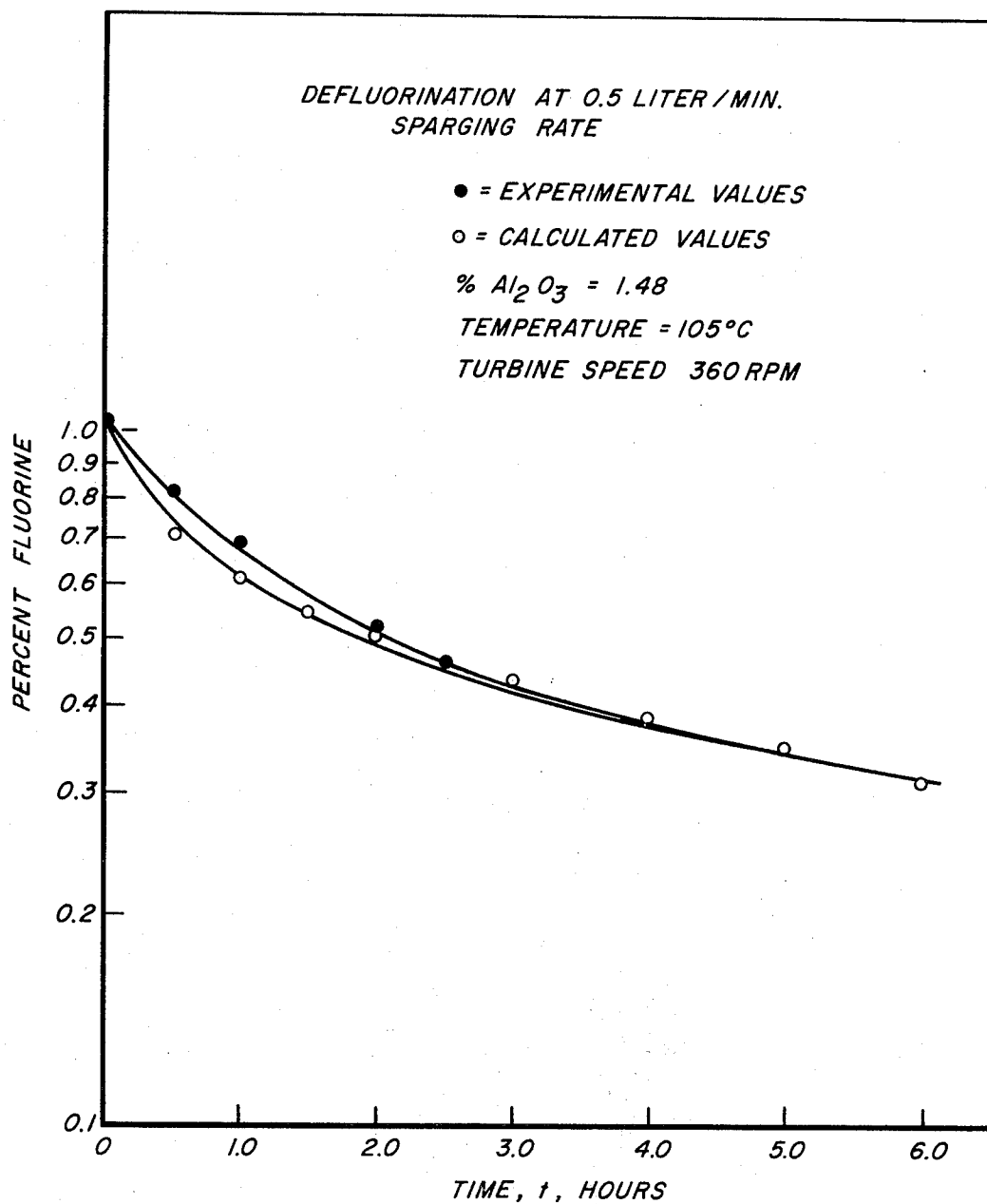
ATTORNEY

**FIG. 9**

INVENTORS.
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY

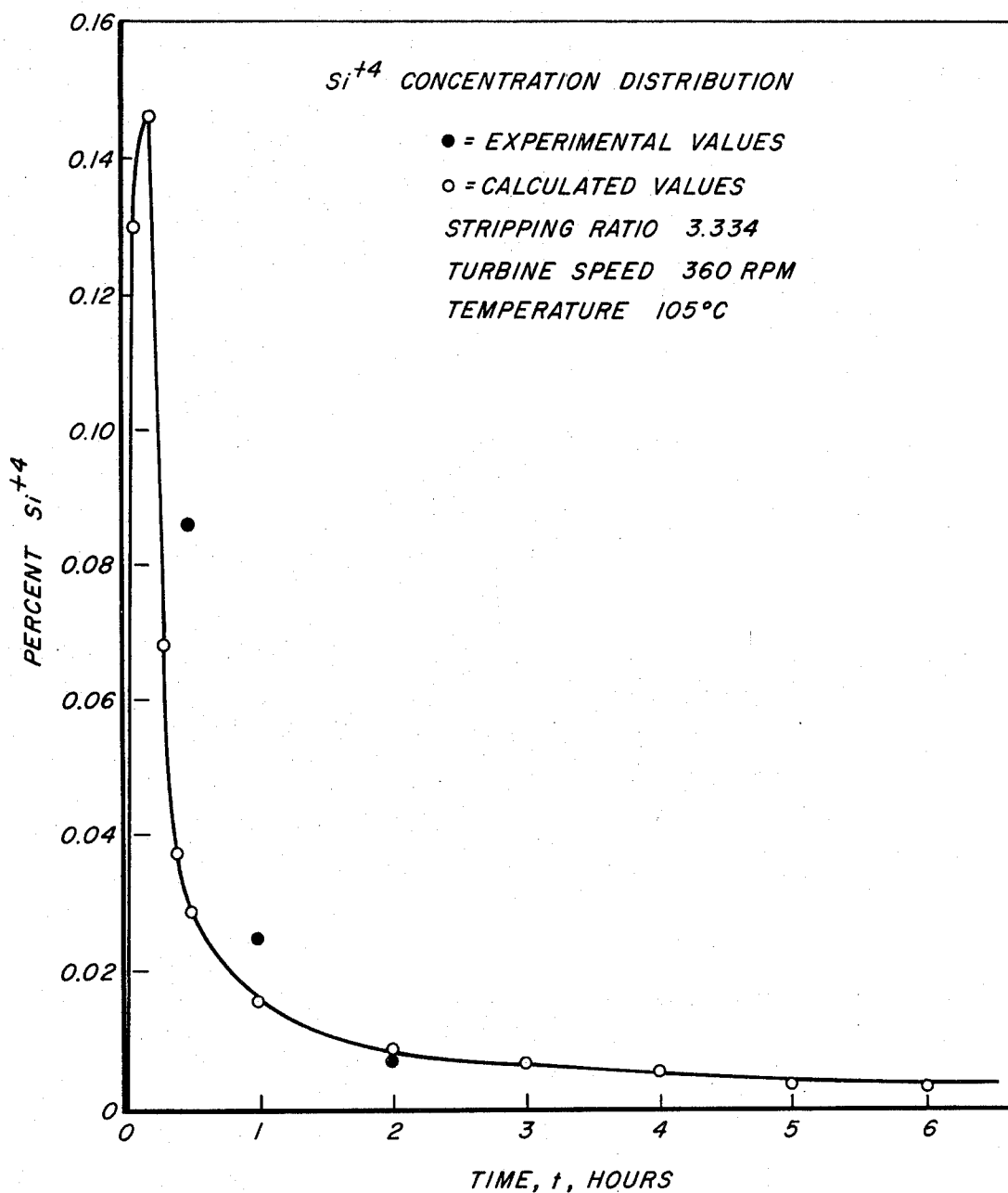
Robert B. Raymond

ATTORNEY

**FIG. 10**

INVENTORS:
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY

Robert B. Raymond
ATTORNEY

**FIG. 11**

INVENTORS.
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW
BY

Robert B. Reynolds

ATTORNEY

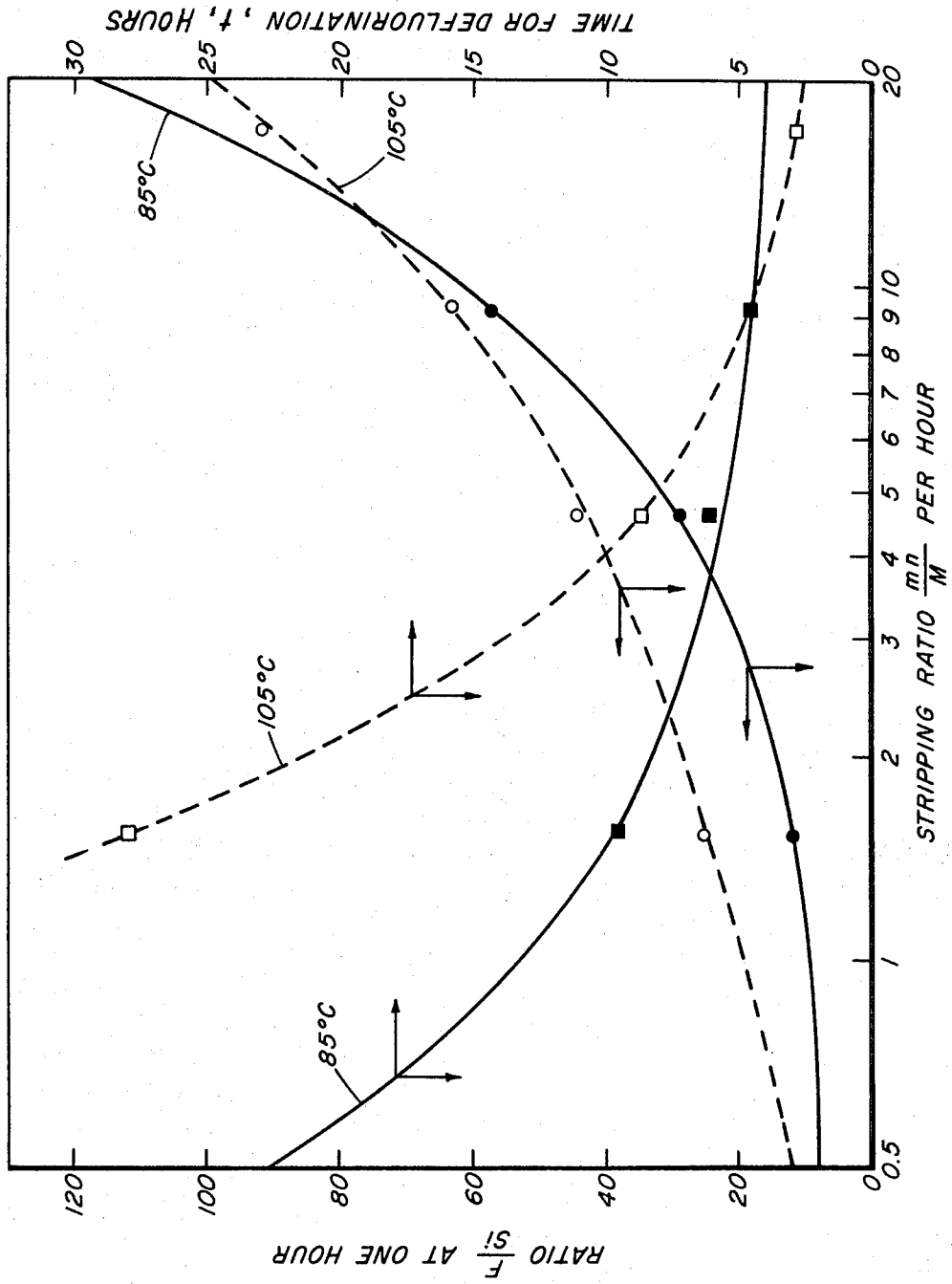


FIG. 12

INVENTORS.
ASHOK BABUBHAI AMIN
ROBERT LEE BRISTOW

BY *Robert S. Raymond*

ATTORNEY

DEFLUORINATION OF WET PROCESS PHOSPHORIC ACID

The present invention concerns a process for defluorinating wet process phosphoric acid which contains dissolved aluminum.

BACKGROUND OF THE INVENTION

There has developed in recent years a substantial need for phosphates which are suitable for use in preparing materials such as calcium phosphates to be used as animal feed supplements. Unfortunately, the phosphate rock from which such phosphoric acid is prepared contains significant amounts of fluorine. For the manufacture of high quality plant fertilizers and animal food supplements, the fluorine level must be reduced to contain less than 1 part by weight of fluorine per 100 parts by weight of phosphorus. Accordingly, numerous processes have been developed in an effort to produce defluorinated wet process phosphoric acid in a convenient and economic manner.

One method which has been devised to effect defluorination of wet process phosphoric acid concerns the addition of silica to boiling phosphoric acid whereby the fluorides are removed as SiF_4 vapor. Several problems have been encountered by such a process. The use of high temperatures such as are encountered in boiling the wet process phosphoric acid necessitates the use of expensive corrosive resistant equipment as well as substantial energy. Furthermore, it has been found that when one attempts to reduce the fluorine concentration in the wet process acid prepared from materials such as the Florida phosphate rock, defluorination subsists at a fluorine concentration of about 0.4 percent.

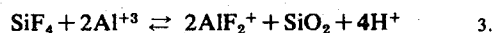
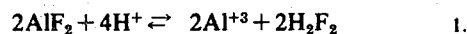
Accordingly, it is an object of the present invention to overcome one or more of the above problems. These and other objects will become apparent from the description and examples which follow.

THE PRESENT INVENTION

It has been found that defluorination of wet process phosphoric acid containing undesirable amounts of fluorine can be achieved by admixing the acid with an amount of silica at least about stoichiometrically equivalent to the fluorine to be removed therefrom and heating the silica acid mixture in the range of from about 75° C. to about 105° C. but below the boiling point of the mixture. Removal of fluorine as SiF_4 is then achieved by establishing a gas-liquid interface with the heated mixture wherein said interface is sufficient to establish a stripping ratio of from about 0.5 to about 20. The vaporized SiF_4 is thereafter removed from the presence of the acid mixture while maintaining its temperature above the condensation temperature of SiF_4 .

It has been found that where wet process phosphoric acid as prepared from phosphate rock which contains substantial amounts of aluminum, the fluorine contained in the phosphoric acid is present as aluminum fluoride complexes such as AlF_2^{+1} and AlF^{+2} ions. It is believed to be the existence of such complexes which causes the removal of silicon tetrafluoride from acid generated from Florida phosphate rock so difficult in comparison with that prepared from substantially aluminum free European rock.

The reaction scheme which prevails where silica is added to wet process phosphoric acid containing from about 0.8 percent to about 2.2 percent or higher by weight of dissolved aluminum can be expressed by the following reaction scheme:



The overall forward reaction is expressed by the reaction of (1) and (2) above. The overall reverse reaction is expressed by reaction (3) above. It can be seen from the equations above that where the concentration of dissolved SiF_4 (probably existing as SiF_6^{-2}) increases, the equilibrium expressed in reaction (3) is shifted to the right favoring the formation of aluminum complexes which precludes the removal of fluorine by volatilization. This is expressed by the following generic equation:

$$dX/dt = k_1[F] - k_3[\text{Al}^{+3}]^2X \quad \text{Equation I}$$

wherein X is the percent of Si^{+4} in the acid, dX/dt is the rate of change in X due to the reactions above, k_1 and k_3 are the overall rate constants for the forward and reverse reactions, respectively, F is the concentration of total fluorine in the acid at Time t and Al^{+3} is the concentration of free aluminum ions (other than AlF_2^{+1}).

It is apparent from equation I above that where the concentration of dissolved silicon, denoted by X , is permitted to increase during the course of the defluorination, the rate of defluorination will decrease proportionally. This is experimentally manifested by conducting defluorinations with various concentrations of dissolved silicon. Such experiments show that satisfactory defluorination is a function of dissolved silicon concentration. Equation I also shows the detrimental affect of high concentrations of aluminum in the acid. The adverse effect of such concentrations is minimized in the practice of the present invention by maintaining the dissolved silicon concentration, X , at a very low level, whereby the total value of the term $k_3[\text{Al}^{+3}]^2X$ is minimized.

Since dissolved silica concentration is proportional to the total fluorine concentration in the acid at any fixed rate of stripping, the preferred level of silicon concentration is expressed by the ratio: (wt. %F/wt. %Si) Since dissolved Si^{+4} concentration is inversely proportional to the degree of stripping, there is a preferred or critical degree of stripping which corresponds to the preferred or critical range of silicon concentration. The degree of stripping is indicated by the ratio; mn/M (called the stripping ratio herein). In this expression, M is the total amount of a batch acid to be defluorinated; m is the amount of acid which is being contacted with the inert gas for stripping per hour; and, n is the fraction of dissolved silicon which is removed as SiF_4 by stripping.

In the practice of the present invention, the SiF_4 stripping can be conveniently achieved by one of three methods.

The first method of the present invention involves the mass transfer of acid by spraying into a current of inert gas. This can be achieved, for example, by

equipping a vessel containing M gallons of acid to be defluorinated with a means for recycling m gallons of acid per hour through a stream of inert gas, wherein the recycled acid is in the form of a plurality of sprays of sufficient number and size to establish the previously indicated stripping ratio. This can be achieved by an apparatus such as that described in FIG. 2 of the attached drawings.

The second process involves the use of sparging with a current of inert gas whereby the gas bubbles are sufficiently small size to establish the previously indicated stripping ratio. This can be achieved by introducing a stream of gas at the base of a high speed turbine blade stirrer such as that described in FIG. 1 of the attached drawings. In this case, M is the total volume of acid to be defluorinated; m is the volume being contacted with air per hour; and n is the fraction of dissolved silicon removed from the acid m by stripping. It is obvious that the values of n can range from 0 to 1 depending on the acid/gas interface area which has been created.

The third process which can be employed in the practice of the present invention employs a combination of sparging with an inert gas and an acid spray recycle as described in methods one and two above.

The instantaneous defluorination rate is related to the dissolved silicon concentration and the stripping ratio. In any given short interval of time, the amount of fluorine which is transferred to the inert gas in a recycle spraying process such as that described above, must be equal to the amount of fluorine lost by the acid. This can be expressed by the following equations:

$$M \cdot dF/dt = mn (2.71 X) \quad \text{Equation 2}$$

or

$$(dF/dt)/2.71 X = mn/M \quad \text{Equation 3}$$

wherein dF/dt = the rate of defluorination; X = the dissolved silicon concentration; 2.71 = the weight ratio of fluorine to silicon in SiF_4 ; and, mn/M = the stripping ratio.

Equation 3 is a general expression which can be used in the analysis of both the spraying, sparging and spraying-sparging methods described above. In the sparging type procedures, where it is not physically possible to measure the stripping ratio, it can be determined by the use of these equations, by measuring the rate of defluorination and dissolved silicon concentration at any given time.

The defluorination of wet process phosphoric acid containing high concentrations of aluminum can further be described by Equation 4 below. This equation is derived by means of the kinetic Equation 1 above and the material balances of the process. The equation is as follows:

$$d^2F/dt^2 = (2.71 mn)/M k_1 F - (k_3 [Al^{+3}] + (mn/M) (dF/dt) \quad \text{Equation 4}$$

The concentration of dissolved silicon can be expressed using a derivation of Equation 2 above:

$$X = -(M/2.71 mn) \cdot dF/dt \quad \text{Equation 5}$$

The values of the forward reaction rate constants for different Al_2O_3 concentrations and temperatures can be found experimentally by observing defluorination kinetics of small batches of acid in the laboratory under conditions of extremely high stripping ratios, in which

case the dissolved silicon concentration in the acid approaches 0 and the kinetic expression becomes:

$$-(dF/dt) = k_1 F \quad \text{Equation 6}$$

The value of the reverse reaction rate constant k_3 is found by measuring dF/dt , d^2F/dt^2 and X at any given time from the start of the defluorination and then employing this data in Equations 3 and 4 above. The data obtained by experimental defluorination and computer simulated runs is in very close agreement.

The preferred quantity of silica employed in the practice of the present invention is from about 0.8 to about 2.0 pounds of silica per pound of fluorine contained in the acid to be defluorinated. It is also preferred to employ silica having a surface area from about 10 to about 500 square meters per gram. It is generally preferred to employ diatomaceous silica or spraydried silica gel as the silica source.

The preferred inert gas is air; however, other inert gases such as carbon dioxide, nitrogen, argon and the like may be employed in lieu thereof or in combination therewith.

The processes of the present invention are further described by reference to the figures herewith.

FIG. 1 is a diagrammatic representation of a sparging apparatus suitable for use in the defluorination of the present invention.

FIG. 2 is a diagrammatic representation of a spraying apparatus which is suitable for use in the practice of the present invention. A suitable apparatus suitable for conducting the spray-sparge process of the present invention may be envisioned as an embodiment of both the spraying elements of FIG. 2 and the sparging elements of FIG. 1.

Now referring to FIG. 1, it can be seen that the defluorination is effected in an insulated reactor 1 adapted to receive a stream of stripping air through conduit 2 which is optionally heated by means of the heat exchanger 3. The conduit is adapted to discharge the air stream beneath the motor driven turbine blade agitator 4 whereby said air stream is dispersed throughout the wet process phosphoric acid contained in the reactor in the form of minute air bubbles. The reactor is further equipped with a valved air port 5 to allow air to be drawn through the reactor above the acid surface to strip the dispersed acid droplets and an exit port 7 to permit withdrawal from the reactor of the fluorine containing gases which have been stripped from said acid droplets. Withdrawal is achieved by actuation of the blower 9. The reactor is further equipped with insulation 8 to aid in the maintaining of the phosphoric acid temperature and heating means, such as, tracing 6, in the reactor dome and exhaust conduit to permit heating of the vessel walls in contact with the fluorine containing gases to a temperature above the condensation temperature or dew point of said gases. The reactor is also equipped with a means for circulating the acid mixture to facilitate the mixing of the acid, silica and air and to permit the maintenance of proper temperature for the acid defluorination process. To effect this circulation of acid, a conduit 16 having its inlet orifice disposed in the bottom of the reactor is equipped with a circulation pump 17 of such capacity to provide a recirculation rate of at least about 3 percent per minute, and preferably, between about 3 per-

cent and 20 percent per minute of the total acid mixture under treatment. As indicated, conduit 16 is equipped with a valve adapted to permit the flow of the acid through heat exchanger 19 whereby the temperature of the recirculating acid may be adjusted as desired prior to the reintroduction of the acid to the reactor via conduit 20. The valve 18 is further adapted to permit withdrawal of the defluorinated acid through conduit 21 into storage tank 22 from which it may be withdrawn through conduit 23 by opening valve 24. As previously indicated, removal of the fluorine-containing gases is effected by actuation of blower 9. Also, said blower may be vented into the atmosphere without disruption of the process of the present invention. It is preferred to exhaust the fluorine-containing gases into a scrubbing tower 10 to prevent atmosphere contamination and to recover the fluorine-containing compounds. This is achieved by introducing said gases into the water shower produced by spraying means 11 whereby the fluorine-containing gases are extracted from the exit gases to form an aqueous solution of fluorosilicic acid which is discharged through the bottom of the scrubbing tower through conduit 13 into a acid-storage vessel 14 from which it may be extracted as desired through conduit 15. The scrubbed exit gases are removed through conduit 12.

In operation of the apparatus of FIG. 1, it is generally preferred to charge about 1.1 pound or a slight stoichiometric excess of silica per pound of fluorine contained in the acid to be defluorinated. Diatomaceous silica or spray-dried silica gel having a surface area between about 10 and about 500 square meters per gram and preferably between 10 and 40 square meters per gram is employed as preferred silica sources. The silica may be charged through port 5 or other suitable conduit (not shown). The wet process phosphoric acid, which is also charged into the vessel through port 5 or other suitable conduit (not shown) has a P_2O_5 content between about 45 percent and 62 percent with a preferred range of from about 50 percent to about 54 percent with a fluorine content of from about 0.3 percent to about 3.0 percent. The percent of dissolved aluminum, generally expressed as aluminum oxide, will typically be in the range of from about 0.8 percent to about 2.2 percent. In each case, the percents indicated are by weight. The acid feed is generally maintained at a temperature of from about 75° C. to about 105° C. but below the boiling point of said acid. It is generally preferred to employ a sparging air stream having a temperature of between about 24° C. and about 105° C. It is generally preferred to employ the sparging gas at a rate of from about 1 to about 5 cubic feet of air per minute per ton of acid to be defluorinated; however, depending on such factors as the acid impurities, the P_2O_5 , aluminum and fluorine content, the temperature, degree of agitation, silica concentration and its solubility in the acid, as little as about 0.5 or as much as about 10.0 cubic feet of air per minute per ton of acid may be required to establish the indicated stripping rate for the defluorination of the present invention.

Where operation of the apparatus depicted in attached FIG. 1 results in the formation of excessive foam at the gas-liquid interface, shut down of the reactor can generally be avoided by directing a stream of recycled acid from conduit 20 onto the acid surface.

An unexpected degree of inhibition of the defluorination is caused by failure to maintain the interior surfaces of the reactor dome at temperatures above the dew point of the effluent gas, i.e., above about 75° C. Where insufficiently high temperatures are achieved, the SiF_4 condenses on the reactor walls where it decomposes to SiO_2 and HF by reaction with water vapor. Heating of the reactor dome may be achieved by any convenient means as, for example, by electrical heating elements or by passage of hot gases through conduits provided within the reactor walls.

FIG. 2 illustrates another type of air-acid contacting vessel which may be utilized in the defluorination process of the present invention. In this apparatus, the wet process phosphoric acid to be defluorinated is charged through inlet 28 into holding tank 29. The acid is then delivered to the insulated reactor 25 through conduit 30 by gravity or pump means herein not shown.

When the reactor is filled to the desired level, acid delivery is ceased and agitation of the acid is begun. This is accomplished by actuating motor driven stirrer 31. To obtain satisfactory defluorination of the acid, the impeller of the stirrer will generally be rotated at a rate sufficient to produce an impeller tip speed of between about 2 and about 25 feet per second (fps) and preferably between about 8 and about 15 fps when the impeller diameter to tank diameter ratio is more than 0.2. Higher tip speeds are required if the ratio is less than 0.2. Acid is withdrawn from reactor 25 by actuating centrifugal pump 43 in the reactor exit line 42. The acid is thereby introduced through conduit 45 into heat exchanger 36 which is maintained at a temperature of between about 75° C. to about 121° C. to adjust the acid temperature from about 75° C. to about 105° C. The heated acid is then discharged onto the acid surface by way of conduit 35 which feeds the spray nozzles 32. Acid circulation rate is approximately 7 percent to 10 percent per minute of total acid tonnage being treated. Shorter defluorination time can be achieved by increasing the recycle rate. Recycle rates below 3 percent result in impractical high defluorination times.

Diatomaceous silica or spray dried silica gel, having a surface area of about 15 to about 30 sq. m/gram for the diatomaceous silica or about 320 to about 500 sq. m/gram for the silica gel is introduced through conduit 53 into vessel 52 which is equipped with a motor driven agitator 51. The vessel is then charged with phosphoric acid through conduit 50 connected to the acid recirculating line. The acid/silica mixture is pumped into reactor 25 either via conduit 49 through circulating pump 46, conduit 47, holding tank 29 and conduit 30 or through the circuit which includes conduit 45 and circulating pump 43, etc.

Silicon tetrafluoride is released from the acid in reactor 25 and the mixing vessel 52. It is then withdrawn from said vessels through the insulated and traced conduits 33, 55 to the gas scrubber inlet 56. The insulation and tracing prevent decomposition of SiF_4 on the walls of the exhaust conduit and refluxing of the fluorine into the acid. In the present system, approximately 2 to 16 cubic feet of air per minute per ton of acid is utilized for the air stripping. If the specific velocity of stripping gas drawn through the system is excessive acid mist is entrapped in the effluent gas and the fluorosilicic acid obtained by aqueous scrubbing of the gases is contaminated and valueless. Generally, about 20 cubic feet

per minute per ton of acid is the maximum flow which can be used in the present process without entraining acid mist with SiF_4 gases. SiF_4 vapors are passed through a scrubbing tower 57 with air scrubbed with an aqueous solution of fluorosilicic acid introduced through conduit 58 and sprayed over the gas stream by means of nozzles 59. The sprayed acid is recirculated from tower 57 via conduit 62 and holding tank 63, conduit 64, recirculating pump 65. The scrubbed exhaust gases exit through conduit 60 through port 61 into a second scrubbing tower 67. Therein, the gases are scrubbed with a stream of fresh water which enter the tower via conduit 68 and is sprayed over the gases with nozzles 69. The rescrubbed gases exit through conduit 70 with the assistance of exhaust fan 71, whereafter the purified exhaust gases are admitted into the atmosphere via exhaust port 72. The fluorosilicic acid scrubbing solution from the second tower is returned to holding tank 63 via conduit 73 whereafter it is recirculated through the first scrubbing tower 57. When the fluorosilicic acid concentration in the scrubbing unit reaches about 20 to about 25 percent, it is withdrawn from the system through conduit 66 by opening a valve therein (not shown). The acid withdrawn therefrom may be marketed as such or subject to further treatment.

Reaction temperature of the wet process phosphoric acid in vessel 25 is maintained by insulation 26 up to acid level. Decomposition of the SiF_4 is prevented by the heating means 27 such as electric tracing or conduits within the wall through which hot fluids or gases are passed in the reactor dome and gas exit lines. In the mixing vessel 52 heating means 54 are only required in the dome to prevent condensation or refluxing of the SiF_4 formed. The air inlet of the reaction vessel 74 may optionally be equipped with a heating means (unshown) to assist in maintaining the reaction temperature. As previously stated, the contents of the reaction vessel are primarily heated by the heat exchange 36. This can be done by passing steam through conduit 37 and valve 39 and out a steam exit conduit 38. Control of the steam flow and thus the reaction temperature can be automatically achieved by means of a temperature recording controlling device 40. This device can be positioned in conduit 34 which is adapted within the reaction vessel 25 to optionally permit the introduction of steam or an air stream into the reaction vessel by opening valve 39 and/or other valve means (unshown). The defluorinated acid can be supplied to a car loading station or storage vessel 48 by actuating pump 46 and opening a valve means (unshown) into vessel 48.

The present invention is further described by the following examples, which are not to be taken as limitative thereof. The percentages and parts in the above description and the following examples are in each case by weight, unless otherwise indicated.

EXAMPLE 1

A 4,000 gram sample of wet process phosphoric acid containing 1.46% Al_2O_3 and 0.85% F was defluorinated at 85° C. in an air sparged vessel, fitted with a 2 inch diameter turbine rotating at a speed of 350 RPM. A stoichiometric amount of diatomaceous earth was added. The air spraying rate was 0.5 liters per minute.

Defluorination kinetic data was collected as shown in Table I. The forward reaction rate constant k_1 was obtained from the defluorination kinetics of a separate run in which an extremely high stripping ratio was used. From the data of Table I, the values of dF/dt and $d^2 F/dt^2$ were calculated at time $t = 3$ hours.

Using Equations 3 and 4, the values of the stripping ratio mn/M and the reverse reaction rate constant k_3 were then calculated to be 1.54 and 12.2, respectively.

A simulated defluorination run was then carried out using an analog computer and the stripping ratio values and reverse rate constant obtained above. The comparison of the kinetic data from the experimental and simulated runs are shown in FIGS. 8 and 9, respectively.

TABLE I

Time, hrs. t	% Fluorine F	% Si^{++} X
0.0	0.85	0
0.5	0.76	—
1.0	0.63	0.0467
1.5	0.58	0.0373
2.0	0.49	0.028
3.0	0.39	0.0186
4.0	0.32	0.014
5.0	0.30	0.0093
6.0	0.26	0.00467
8.0	0.20	—

EXAMPLE 2

A defluorination run similar to the above was carried out at 105° C. using a wet process acid containing 1.48% Al_2O_3 and 1.03% F. From the defluorination kinetic data dF/dt and $d^2 F/dt^2$ at time $t = 1$ hour were calculated. The value of $k_1 = 1.45$ at 105° C. was obtained from a separately carried out defluorination run in which an extremely high stripping ratio was employed. From these data, the values of k_3 and mn/M were calculated to be 468 and 3.334, respectively.

A simulated run was carried out using the above values of k_3 and mn/M . The results of experimental and simulated defluorinations are shown in FIGS. 10 and 11. The data are in high accord.

A number of other simulated defluorination runs were carried out to investigate the effect of different stripping ratios at 85° C. and 105° C. From the results obtained, FIG. 12 was plotted. This plot shows the criticality of the stripping ratio and the ratio of F/Si in the acid, on the defluorination time.

EXAMPLE 3

FIG. 3 shows the defluorination kinetic data from several runs in which wet process phosphoric acid containing various Al_2O_3 concentrations was defluorinated at a stripping ratio of about 6 and a temperature of about 85° C.

The data clearly shows the retarding effect of dissolved aluminum concentration on defluorination rates. It also indicates that to achieve defluorination in same time period for acids of different Al_2O_3 content, an acid having higher dissolved aluminum concentration would require use of a higher stripping ratio.

EXAMPLE 4

FIG. 4 shows three simulated defluorinations carried out with the use of the analog computer as previously described for the acid compositions and operating conditions of Example 1, except that the stripping ratios were changed. Run A was carried out at a stripping ratio of 0.15; Run B at a stripping ratio of 0.5; and, Run C at a stripping ratio of 15.43. The defluorination times required to reduce the fluorine concentrations in the acids to 0.2 percent in Run C and Run B were 3.6 hours and 19 hours, respectively; whereas, the fluorine concentration of the acid at 20 hours time in Run A was still only 0.35 percent.

The dissolved silicon concentrations in the acid for Run A and Run C are shown in FIG. 5. These results again show the importance of maintaining low silicon concentrations in the acid for obtaining high defluorination rates.

EXAMPLE 5

This batch defluorination run using the process of the present invention was carried out to show the importance of dissolved silicon concentration levels on defluorination rates at two different stripping ratios. During the first 1.5 hours of the run, high stripping ratio of 25 was used. In the rest of the batch run, the stripping ratio was decreased to 0.3 by reducing the agitator speed from 1,800 RPM to 60 RPM.

In each case, the defluorination was carried out on a 4,000 gm. acid sample employing a 0.5 liter/min. air rate and a reaction temperature of 85° C. The Al_2O_3 concentration was 1.46 percent.

The results achieved are set forth in FIG. 6, which graphically shows how the decrease in rate of fluorine removal and increase in concentration of dissolved silicon is effected.

EXAMPLE 6

Experimental batch defluorination of 4,000 gms. of wet process acid carried out at 105° C. and different RPMs of a 2 inch diameter turbine and an air sparging of 0.5 liter/min. was carried out by the process of the present invention.

Stripping ratios were calculated with the use of Equations 3 and 4.

The effect of variations in stripping ratios achieved by varying the gas-liquid interface via turbine speed is graphically shown by the plot of data obtained, set forth in FIG. 7.

EXAMPLE 7

The following tests demonstrate the necessity for providing the reactor dome, etc. with an additional heating means to avoid condensation and decomposition of SiF_4 on the surfaces thereof.

In these tests acid having a P_2O_5 content of about 51 percent and containing 1.77 percent fluorine was placed in a flask and mixed with diatomaceous silica in an amount stoichiometrically equivalent to the fluorine present. Air was bubbled through the agitated acid at a

rate of 1 liter/minute/1,000 gm. of acid and the mixture was maintained at 85° C. $\pm 7^\circ$ C. during treatment. Data obtained show that after about eleven hours fluorine reduction is essentially halted even though 0.57% SiO_2 is still present in the acid. The results are set forth in Table II below.

TABLE II

Defluorination by Air Sparging¹ without Heating Mantle

P_2O_5 , %	F, %	P/F	Time, Hrs.
50.79	1.77	12.5	0
50.68	0.84	26.3	3
52.48	0.52	44.0	7
50.48	0.48	45.8	11
49.86	0.46	47.3	14
50.92	0.45	49.3	18

¹H₂O added to maintain approximately 50% P_2O_5

Following the procedure set forth above but placing a heating mantle over the surfaces of the reactor above the acid level produced defluorinated acid of greater than 100/1 P/F ratio. Data are given in Table III.

The series of runs were as follows:

1. 2 inch propeller $\times$ 1,750 RPM - air rate approximately 126 liters in 20 hours for 800 grams feed.
2. 3.4 inch propeller $\times$ 786 RPM - same air rate as above.
3. 3.4 inch propeller $\times$ 786 RPM - air rate equivalent to that 42 liters in 20 hours for 800 gm. feed.
4. Same agitator - same air rate, higher % F in feed.
5. Same as No. 4 except used 1.5X amount of silica.

TABLE III

Defluorination by Air Sparging with Heating Mantle

Components	Run No.				
	1	2	3	4	5
P_2O_5 %	51.47	50.76	49.90	47.03	49.03
F %	0.94	0.98	0.97	1.37	1.37
P/F	23.8	22.6	22.4	15.5	15.5
P_2O_5 %	55.93	58.66	57.84	57.58	56.73
F %	0.14	0.10	0.18	0.18	0.18
P/F	174	256	140	139	137
Time, Hours	14	14	13.5	21.25	30

EXAMPLE 8

Ten lbs. of wet-process phosphoric acid having 53.3% P_2O_5 , 0.64% F, 1.08% Al_2O_3 , 1.61% Fe_2O_3 , 2.00% SO_4 and 1.57% solids was put in a 4-liter container equipped with two baffles and a heating mantle covering the top of the container and exhaust system. Air was introduced under a four-bladed turbine impeller of 1.5 inch diameter revolving at 52.4 ft/sec tip

speed. Diatomaceous earth having about 25 sq.m./g. surface area was added to the acid in the amount of 1 gm. of diatomaceous earth per gm. of fluorine in the acid. When the temperature of the acid was 85° C. P/F weight ratio of somewhat greater than 100 was achieved in a period of about 5 hours.

Above experiment was repeated for 90° C. and 95° C. temperatures of the acid and respective defluorination times to reach P/F=100 were about 3 hours and 1.8 hours.

EXAMPLE 9

Effects of Air Rate and Tip-Speed of the Impeller on Defluorination

In the following tests 2.7 liters of wet process phosphoric acid, sp.g. 1.69, was placed in a 4-liter flask equipped with (1) an impeller driven by a variable speed motor, (2) an air sparger and (3) a heating mantle. The acid analyzed 53.3% P₂O₅, 0.64% F, 1.08% Al₂O₃, 1.61% Fe₂O₃, 2.00% SO₄ and contained 1.57 percent solids. The acid was heated in all tests to 85° C. and maintained at this temperature during treatments. Results obtained are set forth in Table IV below.

TABLE IV.

Air Rate Cu. ft./min/ton acid	Tip Speed ft./sec.	Time in hours to reach P/F=100
0.92	52.4	5.0
3.53	1.76	6.5
3.53	0.44	16.0
3.53	0.22	28.0
7.06	1.76	6.25

EXAMPLE 10

Defluorination experiments on larger scale were carried out using 400 to 500 gallons of wet-process acid. The agitator was a four-bladed turbine type with one horsepower motor. Diatomaceous earth was added in the amount of 1 lb. per lb. of fluorine in the acid. All experiments were carried out at 85° C. The agitator tip speed was 15 ft/sec. The results are set forth in Table V below.

TABLE V

Gallons of Acid	Air Rate cu. ft./mt or cu.ft./mt./ton		Time to Reach P/F=100 hours
400	10	3.6	9.0
400	5	1.8	5.0
500	5	1.4	7.0
500	10	2.8	8.0
400	2.5	0.8	14.0

EXAMPLE 11

Effect of Different Types of Silicon-Bearing Materials on Defluorination Rates

Different commercially available materials containing silica were tried for defluorination. The following table contains results of defluorination experiments and characteristics of different silica materials. All the experiments were carried out at 85° C. using 10 lbs. of wet process acid. The air volume used for sparging was 0.5 liters/minute. The amount of silica material added was equivalent to 1 gm. SiO₂ per gm. of fluorine in the acid. The results obtained are set forth in Table VI below.

TABLE VI

Effect of Type of Silica Material on Defluorination of Wet Process Acid

Silica Material	Characteristics of the Material	% F in the Acid	% F in the Acid	Elapsed Time to Reach Final fluorine hours
Diatomaceous Earth	21-23 sq.m./gm.			
Kenite 51 by Kenite Corp.		0.64	0.3	3.5
"		0.64	0.2	5.0
Diatomaceous Earth MN-35 by Johns-Manville Corp.	40 sq.m./gm.	0.64	0.2	6.0
Silica Gel	340 sq.m./gm.	0.64	0.3	4.0
"	Pore Vol. =2.4	0.64	0.2	5.0
Silica Gel	500 sq.m./gm.	0.64	0.3	5.0
"	Pore Vol. =1.0	0.64	0.2	6.0
Ground Sand	1.3 sq.m./gm.	0.64	0.56	7.0
"		0.64	0.55	10.0
Sodium Silicate Na ₂ SiO ₃ ·9H ₂ O		0.78	0.73	5.0
"		0.78	0.7	10.0
Talc	1.6 sq.m./gm.	0.64	0.52	4.0
"		0.64	0.51	6.0
Amorphous Silica	4.3 sq.m./gm.	0.64	0.60	10.0

From the above, it is evident (a) that diatomaceous silica and spray-dried silica gel are highly effective for defluorinating wet process acid when used in the process of the present invention and (b) that ground sand, sodium silicate and talc are only very poorly effective in this process.

EXAMPLE 12

In the following tests wet process phosphoric acid having from 0.64 percent to 1.33 percent fluorine, 1.08% to 2.66% Al₂O₃ and from 48.2% to 54.52% P₂O₅ was treated with a stoichiometric amount of silicic material selected from the group consisting of diatomaceous silica, amorphous silica, ground sand and sodium silicate. The mixtures were heated to about 85° C. and treated with (1) air sparged into the reactor beneath the acid surface, (2) air passed through the acid in a packed column or (3) by recirculating the acid from the reactor and spraying it as fine droplets over the surface of the acid in the reactor. The data obtained are given in Table VII and show that diatomaceous silica having a surface area of 10 sq.m./gm. used with air rates of 0.89 to 3.5 cu. ft./min. per ton of acid is effective for defluorinating acid maintained at 85° C. These data also show that silica having a surface area of less than 10 sq.m./gm. is ineffective for defluorinating phosphoric acid when used under the above stated conditions.

TABLE VII

Run No.	Acid Starting acid, percent				Surface area SiO ₂ , m. ² /gm.	Air rate, cu. ft./min. per ton acid	Temp., ° C.	Tip speed, ft./sec.	Time to reach P/F=100 hrs.	Product P ₂ O ₅	Recircu- lation, gal./min. spray nozzle
	wt., lbs.	F	Al ₂ O ₃	P ₂ O ₅							
1.....	100	0.64	1.08	53.3	Diatomaceous.....	10	3.5	85	13.1	5	-----
2.....	10	0.64	1.08	53.3	do.....	10	3.5	85	52.4	5.5	-----
3.....	10	0.64	1.08	53.3	do.....	10	1.6	85	52.4	5.5	-----
4.....	10	0.64	1.08	53.3	do.....	10	3.5	85	52.4	5.5	-----
5.....	10	0.64	1.62	53.3	do.....	10	3.5	85	52.4	7.0	-----
6.....	10	0.64	2.16	53.3	do.....	10	3.5	85	52.4	11.0	-----
7.....	10	0.64	2.66	53.3	do.....	10	3.5	85	52.4	14.0	-----
8.....	10	0.64	1.08	53.3	do.....	10	3.5	90	52.4	3.5	-----
9.....	10	0.64	1.08	53.3	do.....	10	3.5	95	52.4	2.0	-----
10.....	10	0.64	1.08	53.3	do.....	10	3.5	85	0.22	18.0	-----
11.....	10	0.64	1.08	53.3	do.....	10	3.5	85	0.44	16.0	-----
12.....	10	0.94	1.08	53.3	do.....	10	3.5	85	1.76	8.0	-----
13.....	5,600	0.88	1.2	54.52	do.....	10	3.5	85	-----	9.0	53.5 10
14.....	5,600	0.98	1.1	51.24	do.....	10	1.75	85	-----	5.2	53.3 10
15.....	7,000	0.96	1.12	53.0	do.....	10	2.85	84	-----	8.0	54.4 10
16.....	7,000	0.82	1.3	53.9	do.....	10	1.75	84	-----	7.0	----- 10
17.....	10	0.33	-----	53.9	Amorphous silica.....	4.3	3.5	86	52.4	-----	-----
18.....	10	0.64	1.08	53.9	Ground sand.....	1.3	3.5	85	52.4	-----	-----
19.....	5,600	0.97	1.33	53.4	Diatomaceous.....	0.89	0	86	-----	14.0	----- 10
20.....	5,600	0.88	1.50	55.6	do.....	0	0	85	-----	14.0	----- 10
21.....	5,600	0.83	1.43	53.9	do.....	0.89	0	85	-----	15.0	----- 10
22.....	10	0.64	1.08	53.3	do.....	10	3.5	105	52.4	1.0	-----
23.....	7,000	0.78	-----	49.5	do.....	10	300	85	-----	16	53.8 (1)
24.....	5,600	0.98	-----	48.8	do.....	10	300	85	-----	20	56.1 (2)

¹ 8%/min. of total acid.² 12.5%/min. of total acid.

We claim:

1. A process for the formation of phosphoric acid having a P/F weight ratio equal to or greater than 100 from wet process phosphoric acid containing an undesirable amount of fluorine as aluminum fluoride complexes, from about 0.8 percent by weight to about 2.2 percent by weight of dissolved aluminum and a P₂O₅ percent by weight of from about 45 percent to about 62 percent comprising the steps of

- admixing said wet process acid with an amount of silica at least about stoichiometrically equivalent to the fluorine to be removed therefrom;
- heating the mixture at a temperature in the range of from about 75°C. to about 105°C. but below the boiling point of said mixture;
- volatilizing the SiF₄ from the heated mixture into an inert gas effluent stream by intimately contacting said heated mixture with an inert gas wherein the gas-mixture interface is sufficient to establish a stripping ratio of the SiF₄ from about 0.5 to about 20;
- maintaining the temperature of said effluent stream above its dew point; and
- removing said effluent stream from the presence of the acid mixture.

2. A process according to claim 1 wherein volatilizing the SiF₄ is effected by acid spraying employing about 2 to 16 cubic feet of air per minute per ton of heated mixture.

3. A process according to claim 2 wherein the silica is selected from the group consisting of diatomaceous silica having a surface area of from about 15 to about 30 sq.m./gram and spray dried silica gel having a surface area of from about 320 to about 500 sq.m./gram.

4. A process according to claim 1 wherein the volatilizing of the SiF₄ is effected by air sparging employing from about 0.5 to about 10 cubic feet of air per minute per ton of heated mixture.

5. A process according to claim 1 wherein the volatilizing of the SiF₄ is effected by air sparging employing from about 1 to about 5 cubic feet of air per minute per ton of heated mixture.

6. A process according to claim 5 wherein about 1.1 pound of silica is employed per pound of fluorine contained in said heated mixture.

7. A process according to claim 6 wherein the silica is selected from the group consisting of diatomaceous silica or spray dried silica gel wherein the surface area of the silica is in the range of between 10 and 40 sq.m./gram.

8. A process according to claim 1 wherein the volatilizing of the SiF₄ is effected by a combination of acid spraying and air sparging.

9. A process according to claim 1 wherein the process is continuous.

10. A process for the defluorination of wet process phosphoric acid containing from about 0.3 percent to about 3 percent by weight of fluorine as aluminum fluoride complexes, from about 0.8 percent by weight to about 2.2 percent by weight of dissolved aluminum and a P₂O₅ percent by weight of from about 45 percent to about 62 percent comprising the steps of:

- admixing said wet process acid with an amount of silica at least about stoichiometrically equivalent to the fluorine to be removed therefrom;
- heating the mixture at a temperature in the range of from about 75° C. to about 105° C. but below the boiling point of said mixture;
- volatilizing the SiF₄ from the heated mixture into an inert gas effluent stream by intimately contacting said heated mixture with an inert gas wherein the gas-mixture interface is sufficient to establish a stripping ratio of the SiF₄ above about 1.5 and maintain the dissolved silicon concentration below about 0.05 percent by weight weight substantially throughout the defluorination;
- maintaining the temperature of said effluent stream above its dew point; and
- removing said effluent stream from the presence of the acid mixture.

11. A process according to claim 10 wherein the F/Si weight ratio is maintained above about 8 substantially throughout the defluorination.

* * * * *