

MANUFACTURE OF VERY LOW ARSENIC HYDROGEN FLUORIDE

5 Field of the Invention

This invention relates to a process for the preparation of hydrogen fluoride having a very low arsenic level. More specifically, the invention provides a process in which industrial grade anhydrous hydrogen fluoride, or an intermediate product obtained during the hydrogen fluoride manufacturing process, is contacted with an oxidizer in order to oxidize the arsenic impurity to produce anhydrous hydrogen fluoride with a level of arsenic impurity that is at least less than two parts per billion, or aqueous hydrogen fluoride with a correspondingly low level of arsenic.

Background of the Invention

15 A generally employed method for manufacturing hydrogen fluoride involves heating a mixture of fluorspar and sulfuric acid. The initial crude hydrogen fluoride resulting from this process contains a variety of impurities that are removed by distillation to provide technical, or industrial, grade anhydrous hydrogen fluoride. This industrial grade anhydrous hydrogen fluoride still contains large quantities of impurities including arsenic. The amount of arsenic impurity, generally about 10 to 500 parts per million, depends on the arsenic impurity of the fluorspar from which the hydrogen fluoride was produced.

25 In the electronics industry, anhydrous hydrogen fluoride and aqueous hydrogen fluoride solutions are used as cleaning and etching agents for silicon wafers, circuit boards and high speed, high density chips for computers and optics. Arsenic impurity in the hydrogen fluoride deposits arsenic on the electronic component that may cause its failure. Currently, the industry requires aqueous hydrogen fluoride arsenic impurities of less than one part per billion. In the future,

it is anticipated that industry's arsenic impurity level requirements will be in the parts per trillion and parts per quadrillion range.

Several known processes provide for the removal of arsenic from industrial
5 grade hydrogen fluoride. United States Patent No. 4,929,435 to Boghean *et al.*
discloses the oxidation of volatile arsenic (III) compounds to nonvolatile arsenic
(V) compounds and separation of the arsenic (V) compounds from hydrogen
fluoride by distillation. The oxidation is accomplished by the addition of hydrogen
peroxide and a catalyst of a molybdenum or vanadium compound and a phosphate
10 compound. Similarly, US Patent No. 4,756,899 discloses contacting hydrogen
fluoride with hydrogen peroxide in the presence of a molybdenum or inorganic
molybdenum compound and a phosphate compound catalyst and distilling the
resultant arsenic (V) compound to provide purified anhydrous hydrogen fluoride.

15 The processes disclosed provide for the purification of hydrogen fluoride to
levels of only about 5 ppm. Even this low level of arsenic impurity, however, may
cause environmental or process problems and clearly does not meet industry's
current or future requirements. Therefore, a need exists for a process for
producing anhydrous hydrogen fluoride and aqueous hydrogen fluoride with very
20 low levels of arsenic impurity.

Description of the Invention and the Preferred Embodiments

The process of this invention involves, generally, contacting feed hydrogen
fluoride which may be industrial grade anhydrous hydrogen fluoride, or an
25 intermediate product obtained in the manufacturing process, with an effective
amount of an oxidizer and reacting the mixture under conditions suitable to oxidize
the arsenic impurity to produce a very low arsenic hydrogen fluoride product
stream and separating the product stream to produce a very low arsenic hydrogen
fluoride product. By "effective amount" of oxidizer is meant an amount effective

to oxidize the arsenic impurity in the feed hydrogen fluoride to produce very low arsenic hydrogen fluoride. By "very low arsenic hydrogen fluoride" is meant anhydrous hydrogen fluoride with arsenic levels of at least less than about 2 ppb or aqueous hydrogen fluoride with correspondingly low levels of arsenic. It has been
5 discovered that, with either multiple additions or a single sustained addition of oxidizer, hydrogen fluoride with very low levels of arsenic may be obtained.

In the process of this invention, feed hydrogen fluoride, which may be industrial grade anhydrous hydrogen fluoride, or an intermediate obtained in the
10 manufacture of anhydrous hydrogen fluoride, and an oxidizer are fed into a reactor to produce a very low arsenic hydrogen fluoride product stream. The product stream is fed into a distillation column in order to separate the resultant, very low arsenic hydrogen fluoride product from the waste. Optionally, the waste stream may be further treated to recover volatile hydrogen fluoride and the non-volatile
15 arsenic impurity separated and recovered as a useful product or discarded, as disclosed in United States Patent Nos. 5,089,241, 4,929,435 and 4,756,899 incorporated herein by reference. The process of this invention may be practiced in either batch or continuous mode, or a combination of these modes.

20 The hydrogen fluoride for use as feed hydrogen fluoride in the process of this invention may be hydrogen fluoride that is an intermediate product obtained during manufacture and is at least 95 % by weight hydrogen fluoride. Alternatively and preferably, the hydrogen fluoride feed material used is high purity anhydrous hydrogen fluoride that is at least 99.9 % hydrogen fluoride by weight. Generally,
25 the amount of arsenic impurity will be about 10 to about 500 ppm. For the process of this invention, preferably the arsenic impurity of the feed hydrogen fluoride is from about 1 to about 100 ppm. If the feed hydrogen fluoride contains arsenic impurities above the preferred range, preferably the feed hydrogen fluoride is first purified according to the process disclosed in US Patent No. 4,929,435 which is

incorporated by reference in its entirety herein and, subsequently, the process of this invention is employed.

Any suitable oxidizer may be used in the process of this invention. By
5 "oxidizer" is meant a compound or compounds capable of oxidizing volatile
arsenic (III) compounds to nonvolatile arsenic (V) compounds. Exemplary
oxidizers include, without limitation, potassium permanganate, fluorine, chlorine,
persulfuric acid and salts thereof, sulfuric acid, chromic oxide, chromate salts,
hydrogen peroxide, oxygen, ozone, and mixtures thereof with potassium fluoride,
10 metal fluoride salts, hydrogen chloride or methanol. Preferably, hydrogen peroxide
is used.

The hydrogen peroxide useful in the invention process may be either
reagent grade that is a pure compound with very little added stabilizer or
15 commercial grade that contains substantial quantities of stabilizers. Any
commercially available strength of hydrogen peroxide may be used. Preferably,
50% peroxide is used in order to limit the amount of water added to the process.

If hydrogen peroxide is used as the oxidizer, a catalyst may be added either
20 individually or in admixture with the peroxide. The amount of peroxide used, as
well as the nature and amount of the catalyst useful in the present invention are
disclosed fully in US Patent No. 4,929,435. Generally, from about 0.1 to about
1.5 weight percent peroxide is used based on 100% anhydrous hydrogen fluoride.
Preferably, from about 0.1 to about 0.5 weight percent is used.

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Suitable catalysts for use in this invention comprise a molybdenum
component or a vanadium component and a phosphate component. The
molybdenum component may include, without limitation, molybdenum metal, an
organic molybdenum compound such as molybdenum acetyl acetonate or an

inorganic molybdenum compound such as a mono- or polyalkali metal molybdate, a molybdenum oxide, or a mono- or polyammonium molybdate. Preferably, ammonium molybdate is used.

5 The vanadium component may include, without limitation, vanadium metal, an organic vanadium compound such as vanadyl acetate, or an inorganic vanadium compound such as mono- or polyalkali metal vanadate, a vanadium oxide, or mono- or polyammonium vanadate. The preferred vanadium component is sodium meta-vanadate, sodium orthovanadate, and ammonium vanadate.

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 Suitable phosphate components include, without limitation, phosphoric acid and inorganic phosphates such as mono- and polyalkali metal phosphates or polyphosphates and mono- and polyammonium phosphates or organic phosphonates used as stabilizers in peroxide. The preferred phosphate is sodium
15 tripolyphosphate. If commercial grade hydrogen peroxide is used containing phosphates or phosphate containing compounds, the need for the phosphate component of the catalyst may be eliminated.

 The amount of catalyst, including the proportions of components used, is
20 that amount effective to achieve satisfactory rates at which the volatile arsenic (III) impurities of the hydrogen fluoride are converted to nonvolatile arsenic (V) compounds. The particular amount and proportions will vary depending on the particular components chosen and are readily ascertainable by one of ordinary skill in the art.

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 Generally, at least about 3.7 ppm, based on 100 % hydrogen fluoride, of the metal component is required and at least about 3.5 ppm of the phosphate component is required. When the minimum amount of one of the catalyst components is used, the other component preferably is present in at least 3 to 4

times the amount. The preferred amount of the phosphate component is from about 25 to about 400 ppm, preferably from about 100 to about 400 ppm for phosphoric acid and from about 10 to about 55 for sodium tripolyphosphate.

5 It has been discovered that anhydrous hydrogen fluoride with arsenic levels of at least less than about 2 ppb, or aqueous hydrogen fluoride with correspondingly low arsenic levels, may be obtained using either multiple additions or a single sustained addition of oxidizer to the feed hydrogen fluoride. By "single sustained addition" is meant that the addition of the oxidizer occurs gradually over
10 the total reaction time. In the case of the hydrogen peroxide, it is believed, without being bound by this theory, that the multiple additions or single sustained addition permits sufficient time for the peroxide - arsenic (III) reaction, which is an extremely rapid reaction due to the rapid decomposition of peroxide, to proceed in order to produce hydrogen fluoride with very low levels of arsenic impurity.

15 If peroxide and catalyst are used, they may be added together to the feed hydrogen fluoride slowly in a single sustained addition. Alternatively and preferably, the peroxide and catalyst may be added in stages in a batch process or in multiple stages in a continuous process. If multiple additions are used for any of
20 the oxidizers, any number of additions may be made. Preferably and conveniently, at least two additions, more preferably four additions, are made. Further, when hydrogen peroxide and a catalyst are used, the catalyst need not be added with each addition of peroxide so long as the total amount of catalyst used is at least 3.7 ppm of the metal component and at least 3.5 ppm of the phosphate component
25 based on 100% hydrogen fluoride. Preferably, the catalyst is not added with each addition of peroxide because the addition of the catalyst adds water to the process. Also preferably, the catalyst is added before the peroxide to allow adequate mixing and performance of the catalytic function.

The product of this invention is very low arsenic hydrogen fluoride. The reaction time for the process of this invention is that time effective to produce the very low arsenic hydrogen fluoride product stream. Preferably, the total reaction time, generally, for either the single sustained addition or the multiple additions of the oxidizer is from about two minutes to about sixty minutes, preferably from about fifteen minutes to about sixty minutes.

The process of this invention may be carried out at a temperature from about 0° C to about 75° C, preferably from about 15° C to about 75° C. More preferably, the reaction is carried out at from about 40° C to about 65° C.

Organic contaminants of as little as 100 ppm can decrease the efficiency of the oxidation reaction. When an interfering amount of an organic contaminant is present, an organic oxidant such as nitric acid or nitric acid salts may be added in an amount of from about 2 to about 10 ppm for each 100 ppm of organic contaminant. The optimum amount is readily determinable by one ordinarily skilled in the art. The point of addition of the oxidizing agent is not critical, but preferably is to the feed hydrogen fluoride stream prior to the addition of catalyst.

The process of the invention must be conducted in equipment that is not attacked by anhydrous hydrogen fluoride in order to preclude contamination by material from the reactor or equipment. Accordingly, surfaces of the reactor, distillation column, column packing, condenser, and receiver that contact the hydrogen fluoride must be inert to hydrogen fluoride. Suitable inert materials include, without limitation, low carbon steel, stainless steel, nickel, nickel alloys, platinum, polyethylene, polyvinyl chloride, and fluorocarbon polymers. Preferably, fluorocarbon polymers are used if avoidance of metal impurities is desirable or the hydrogen fluoride will be diluted with water to make an aqueous product.

Because volatile arsenic (III) impurities are converted into nonvolatile arsenic (V) compounds, or residues with low volatility compared to hydrogen fluoride, elaborate fractionation is not necessary to purify the very low arsenic hydrogen fluoride product stream. Thus, any known method, including distillation at atmospheric pressure, may be used to separate the nonvolatile arsenic impurities to produce very low arsenic hydrogen fluoride product.

The invention will be clarified further by a consideration of the following examples, which are intended to be purely exemplary. Analysis of the volatile arsenic (III) was performed by the known method of arsine generation with absorption in silver diethyldithiocarbamate. Total arsenic analysis was accomplished by Graphite Furnace Atomic Adsorption Spectrometry ("GF-AAS"). The arsenic removal reactors were jacketed cylindrical mild steel or fluoropolymer lined 800 cc capacity reactors. Distillation and reflux equipment was made of fluoropolymer. A knitted PFA column packing was used. All water and ice used was 18 meg-ohm for purity. The anhydrous hydrogen fluoride feed material of the examples was at least 99.9% anhydrous hydrogen fluoride with an arsenic impurity of 2 to 10 ppm.

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Example 1

As a control, 200 g AHF were introduced into a jacketed circulation reactor cooled with ice water and the reactor and contents warmed to 55° C with hot water. Stabilized 50% hydrogen peroxide and aqueous reagent grade ammonium molybdate and aqueous sodium tripolyphosphate catalysts were then added as a mixture. An increase in pressure and temperature were observed. The reaction ran for about 30 minutes and the reactor was then cooled with ice water. The mixture in the reactor was sampled and analyzed for arsenic (III). It is known that arsenic (III) will be distributed evenly in the vapor and liquid phases and, thus,

no distillation was attempted. The reaction mixture was diluted to 50% HF for analysis and the results on a 100% HF basis are listed on Table 1.

Example 2

5 The procedure and equipment of Example 1 were modified in that two additions of hydrogen peroxide and catalyst mixtures were used. Additionally, during reactor cool down, a packed reflux column, reflux splitter and distillation column were attached. The reactor was vented through the reflux and distillation columns to avoid loss of AHF and to remove inert and other low boiling
10 substances such as phosphorous pentafluoride, phosphorous trifluoride, nitrogen and chlorine containing compounds, silicon tetrafluoride and oxygen from the peroxide composition. Heat was applied to the reactor and, at steady state, the reflux started and total reflux maintained for 1 hr. For purposes of atmospheric single distillation ("D-1"), the sample was collected in a PFA bottle packed in dry
15 ice to collect the AHF. The collected AHF was diluted to 50% HF for analysis and the results on a 100% HF basis are listed on Table 1

Example 3

400 g AHF were introduced into a jacketed reactor cooled with ice water
20 and the reactor and contents warmed to about 55° C with hot water. Stabilized 50% hydrogen peroxide was mixed with aqueous ammonium molybdate and sodium tripolyphosphate catalysts and added to the reactor. The reaction ran for 15 minutes. A second addition of the peroxide and catalyst was performed. After 15 minutes, peroxide alone was added and allowed to react for 15 minutes. A
25 fourth addition of peroxide alone was allowed to react for 15 minutes. The reactor was cooled with ice water and the reaction mixture distilled and analyzed as in Example 2. The results on a 100% HF basis are listed on Table 1.

Examples 4 and 5

For Examples 4 and 5, the procedure for Example 3 was followed except that a second atmospheric distillation ("D-2") was performed. The D-1 distilled AHF was sampled and then reintroduced into the clean reactor and distilled under the same conditions as for D-1. The distilled samples were analyzed as in Example 2 and the results on a 100% HF basis are listed on Table 1.

TABLE 1

Example	1	2	3	4	5
Reaction Time (min.)	30	30	15	15	15
Injections	1	2	4	4	4
% Peroxide	0.25	0.5	0.5	0.5	0.5
Molybdenum catalyst (ppm)	10	30	15	15	15
Phosphate catalyst (ppm)	10	50	25	25	25
Arsenic (III) (ppb)	62	-	-	-	-
D-1 (O/H total AS in ppb)	-	11	2	2	<2
D-2 (O/H total AS in ppb)	-	-	-	<2	<2

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Example 1 demonstrates that, although low levels of arsenic impurity can be achieved with the prior art method, very low levels cannot be attained.

Examples 3 through 5 illustrate that very low levels of arsenic can be attained by multiple additions of hydrogen peroxide and catalysts.

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Prospective Examples 1 - 5

The use of the oxidizers potassium permanganate, chromic oxide, chromate salts, persulfuric acid and persulfate are demonstrated in Prospective Examples 1 through 5, respectively, as follows. For each of the Prospective Examples 1 through 5, 400g anhydrous HF are introduced into a jacketed circulation reactor cooled with ice water and the reactor contents are warmed to about 25° C with hot water. 0.1 % of the oxidizer is added to the reactor. The reaction runs for 30 minutes and the reactor is then cooled with ice water. The reaction mixture is diluted to 50 % HF for analysis the results of which on a 100 % HF basis are < 2 ppb arsenic (III).

Prospective Examples 6 - 10

For each of the Prospective Examples 6 through 10, 400 g anhydrous HF are introduced into a jacketed circulation reactor cooled with ice water. 0.05 to 0.1 % of fluorine, chlorine, hydrogen chloride, oxygen and ozone are added for Prospective Examples 6 through 10, respectively. The reactor contents are warmed to about 25° C with hot water. The reaction runs for about 30 minutes and then the reactor is cooled with ice water. The reaction mixture is diluted to 50 % HF for analysis and the results on a 100 % HF basis indicate < 2 ppb arsenic (III).



What is claimed is:

1. A process for producing very low arsenic hydrogen fluoride comprising the steps of:
 - 5 (a) contacting a feed hydrogen fluoride with an effective amount of an oxidizer under conditions suitable to produce a very low arsenic hydrogen fluoride product stream; and
 - (b) separating the product stream of step (a) to produce a very low arsenic hydrogen fluoride product.
- 10 2. The process of claim 1 wherein the contacting of the feed hydrogen fluoride with the oxidizer is achieved by a single sustained addition of the oxidizer to the feed hydrogen fluoride.
- 15 3. The process of claim 1 wherein the contacting of the feed hydrogen fluoride with the oxidizer is achieved by at least two additions of the oxidizer to the feed hydrogen fluoride.
- 20 4. The process of claims 1, 2 or 3 wherein the oxidizer comprises hydrogen peroxide.
5. The process of claim 4 wherein the oxidizer further comprises an effective amount of a catalyst comprising:
 - (i) a component which is a molybdenum component or a vanadium
 - 25 component; and
 - (ii) a phosphate component.



6. The process of claim 5 wherein the component (i) is a molybdenum component selected from the group consisting of molybdenum metal, an organic molybdenum compound and an inorganic molybdenum compound.

- 5 7. The process of claim 5 wherein the component (i) is a vanadium component selected from the group consisting of vanadium metal, an organic vanadium compound and an inorganic vanadium compound.

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