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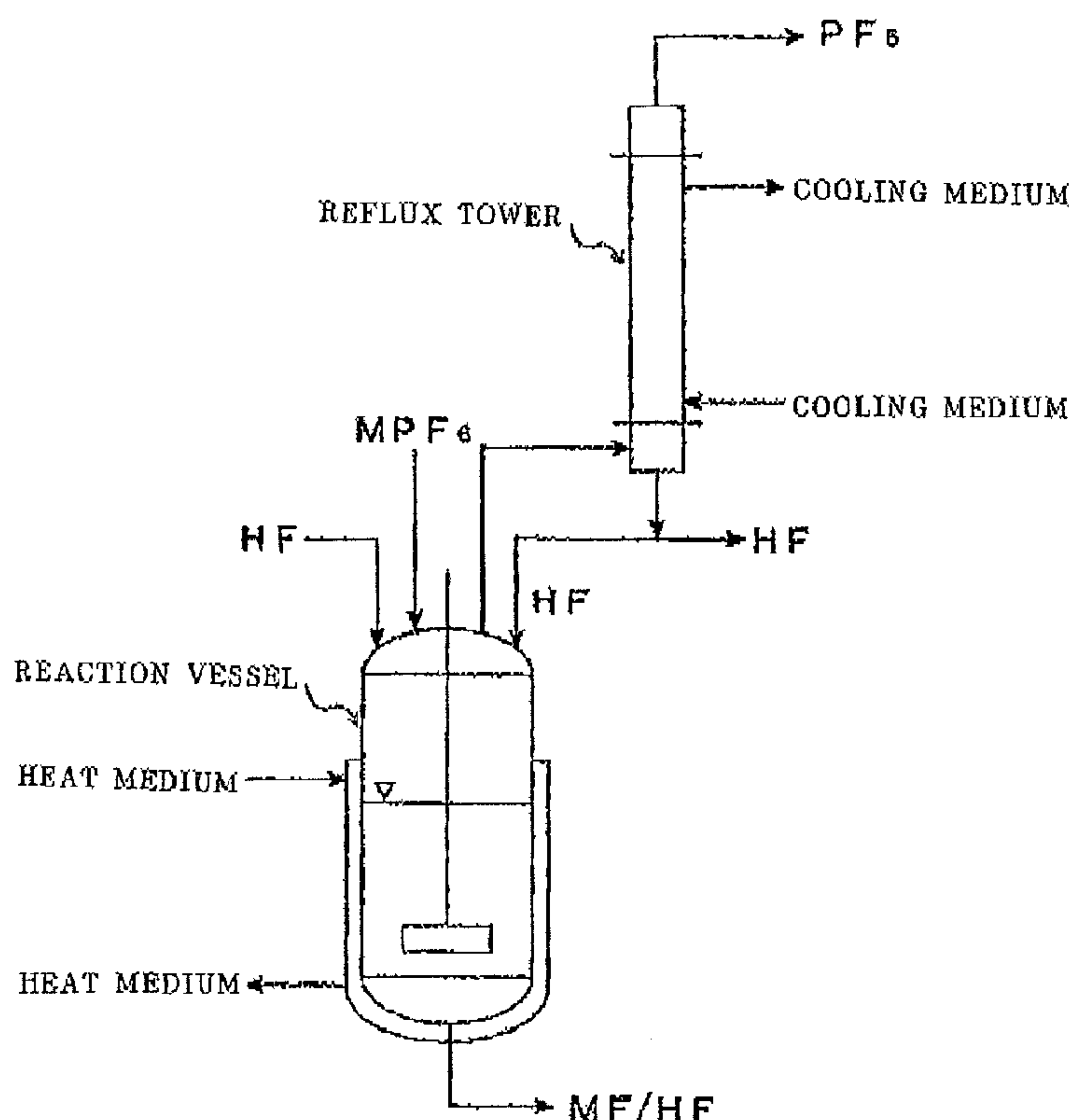
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(54) Titre : PROCÉDES DE PRODUCTION DE PENTAFLUORURE PHOSPHOREUX ET D'HEXAFLUOROPHOSPHATE

(54) Title: METHOD OF MANUFACTURING PHOSPHOROUS PENTAFLUORIDE AND HEXAFLUOROPHOSPHATE



(57) Abrégé/Abstract:

A process for phosphorus pentafluoride production by which high-purity phosphorus pentafluoride can be produced by a simple and economical procedure without the need of a large-scale purification apparatus or high-pressure apparatus and without

(57) **Abrégé(suite)/Abstract(continued):**

generating a large amount of a by-product gas requiring a special discharge-gas treatment. The process for phosphorus pentafluoride production is characterized by introducing hydrogen fluoride and a hexafluorophosphate (MPF_6) into a vessel and reacting them according to the reaction shown by the scheme (1) to yield phosphorus pentafluoride. $\text{MPF}_6 + u\text{HF} \rightarrow \text{PF}_5 + \text{MF}_r(\text{HF})$ (Scheme 1) In the scheme, M is at least any one of Li, Na, K, Rb, Cs, NH_4 , and Ag; $0 \leq r \leq u$; and the HF is used in an amount not smaller than the stoichiometric amount.

ABSTRACT

A process for phosphorus pentafluoride production by which high-purity phosphorus pentafluoride can be produced by a simple and economical procedure without the need of a large-scale purification apparatus or high-pressure apparatus and without generating a large amount of a by-product gas requiring a special discharge-gas treatment. The process for phosphorus pentafluoride production is characterized by introducing hydrogen fluoride and a hexafluorophosphate (MPF_6) into a vessel and reacting them according to the reaction shown by the scheme (1) to yield phosphorus pentafluoride. $\text{MPF}_6 + u\text{HF} \rightarrow \text{PF}_5 + \text{MF}_r(\text{HF})$ (Scheme 1) In the scheme, M is at least any one of Li, Na, K, Rb, Cs, NH_4 , and Ag; $0 \leq r \leq u$; and the HF is used in an amount not smaller than the stoichiometric amount.

DESCRIPTION

METHOD OF MANUFACTURING PHOSPHOROUS PENTAFLUORIDE AND
HEXAFLUOROPHOSPHATE

5 TECHNICAL FIELD

[0001]

The present invention relates to a method of manufacturing phosphorous pentafluoride and a hexafluorophosphate. More particularly, the present invention relates to a method of
10 manufacturing a hexafluorophosphate that is useful as an electrolyte for a battery, a catalyst for an organic synthesis reaction, and the like, and a method of manufacturing phosphorous pentafluoride that is used as a starting raw material in manufacturing a hexafluorophosphate.

15

BACKGROUND ART

[0002]

Phosphorous pentafluoride (PF_5) is a substance that is gaseous at room temperature and is used as a fluorinating agent
20 in various chemical reactions in the electronics industries, and it is especially a starting material of manufacturing a hexafluorophosphate DPF_6 ($\text{D} = \text{Li}, \text{Na}, \text{K}, \text{or the like}$) that is used in the electrolytic liquid of a battery. Among these, in the case of $\text{D} = \text{Li}$, lithium hexafluorophosphate is an important
25 substance as the electrolyte of a lithium battery. Lithium

hexafluorophosphate has extremely high safety, has excellent physical properties, is considered to be an indispensable substance particularly in a lithium secondary battery, and is greatly expected for the utilization in a hybrid car in the future.

5 [0003]

Further, in the case of $D = Ag$, it being paid attention to as a counter ion that generates an acid that is necessary for an initiation and growth reaction in photo polymerization. Furthermore, in the case of $D = NH_4$, it is useful as a raw material that is used in the manufacture of an intermediate of medicine.

10 [0004]

This lithium hexafluorophosphate is conventionally manufactured by dissolving lithium chloride into hydrogen fluoride and adding phosphorous pentachloride into the solution (Non-Patent Document 1: [Fluorine Chemistry Vol. 1 (1950)]).

15 Further, it is also manufactured by a reaction of lithium fluoride and phosphorous pentafluoride (for example, Patent Documents 1 and 2).

[0005]

20 As such, phosphorous pentafluoride is a very important compound in order to manufacture a high purity hexafluorophosphate (DPF_6 : D is a metal) such as lithium hexafluorophosphate or potassium hexafluorophosphate or a hexafluorophosphoric acid compound such as

25 triethylmethylammonium hexafluorophosphate or

tetraethylammonium hexafluorophosphate. However, when manufacturing such a substance using PF_5 , there is a common problem that the manufacturing cost becomes high because high purity PF_5 is extremely expensive.

5 [0006]

Methods of manufacturing PF_5 are described in various documents, and especially the following documents can be mentioned.

[0007]

10 The thermal decomposition described in Patent Document 3 (thermal decomposition of LiPF_6) follows the following chemical reaction formula a. However, in the case of LiPF_6 , the decomposition slightly occurs around 120°C and LiPF_6 decomposes completely around 200 to 250°C to give a LiF powder remained.
 15 Furthermore, in other cases, it is difficult to decompose LiPF_6 if the decomposition is not carried out a very high temperature such as about 250°C in the case of NH_4PF_6 , about 400°C in the case of NaPF_6 , and 600°C to 700°C in the case of KPF_6 and CsPF_6 , and it is hard to say that such decomposition is industrially
 20 suitable in the aspect of facilities.

[0008]



[0009]

The reactions described in Non-Patent Document 2
 25 (fluorination of phosphorous using ClF_3 in a liquid HF medium),

Patent Document 4, and Non-Patent Document 5 (fluorination of phosphorous using a fluorine gas) have a problem that it is very difficult to control the reactions because the reaction speeds are high and the reactions proceed explosively. Furthermore, because an expensive fluorine-based gas is used, as a matter of course, phosphorous pentafluoride that is obtained is also expensive.

[0010]

The reaction yield in Patent Document 5 (a reaction of fluorspar and phosphoric acid in the existence of sulfuric trioxide) reaches only 12%.

[0011]

In the reaction of Patent Document 6 (fluorination of phosphoryl trifluoride (POF_3) using hydrogen fluoride in the existence of sulfuric trioxide), the yield is low, sulfuric acid is produced, and corrosiveness is extremely high in the existence of HF.

[0012]

Furthermore, in the reaction of Patent Document 7 (by heating of calcium fluoride (CaF_2), phosphoric acid or monofluoro-phosphoric acid, and sulfur trioxide), $\text{HPF}_6 \cdot 2\text{H}_2\text{O}$ and CaSO_4 are produced in addition to PF_5 , and a problem of separation and disposal of a large amount of calcium sulfate are problems that have to be coped with in this method.

[0013]

Similarly to Patent Document 6, in the reaction of Patent Document 8 (a method of reacting hexafluorophosphoric acid (HPF_6) with a sulfur-based acid under high pressure), sulfuric acid is produced, corrosiveness is extremely high in the existence
5 of HF , and water in the system and fluorosulfuric acid (HSO_3F) react with PF_5 even when oleum is used, and the produced PF_5 is decomposed into POF_3 .

[0014]

In the halogen exchange method and the chlorofluorination
10 method of Non-Patent Document 3 (fluorination of phosphorous pentachloride (PCl_5) using arsenic trifluoride), Patent Document 9 (chlorination of phosphorous trifluoride), and Patent Document 10 (chlorination and fluorination of phosphorous trichloride), a large scale apparatus is necessary to separate
15 hybrid halides (PClF_4 and PCl_2F_3) and HCl especially from phosphorous pentafluoride that is the desired final product.

[0015]

In addition, in the reaction of Patent Document 11 (fluorination of phosphorous pentachloride (PCl_5) using calcium
20 fluoride), the reaction has to be performed at a very high temperature of 250°C to 300°C , and consequently there is a problem that a reaction with members of the furnace proceeds, and any of these reactions are industrially unsuitable.

[0016]

25 Furthermore, in the methods described in Patent Document

12 (fluorination of phosphorous pentachloride (PCl_5) using
liquid phase and/or gas phase HF), Patent Document 13 (a method
of manufacturing a high purity hexafluorophosphoric acid
compound), and Patent Document 14 (a method of manufacturing
5 a hexafluorophosphate by reacting phosphorous pentachloride and
a hydrogen fluoride gas at a temperature of 60 to 165°C and
introducing the obtained phosphorous pentafluoride into an
anhydrous hydrofluoric acid solution of an alkaline metal
fluoride), handling of phosphorous pentachloride is difficult
10 because it is a solid having high moisture absorption
characteristics, and especially the workability is poor when
the raw materials are placed into the manufacturing facilities,
and there is a problem that it is difficult to attempt
mechanization. Further, because phosphorous pentachloride
15 easily reacts with moisture in the atmosphere, a toxic hydrogen
chloride gas is often generated during the work to deteriorate
the work environment.

[0017]

Further, moisture that is contained in phosphorous
20 pentachloride is mixed into the reaction system, the moisture
that is mixed reacts with a part of the produced phosphorous
pentafluoride, and phosphorous oxyfluoride such as POF_3 or PO_2F
is produced as a by-product. As a result, a hexafluorophosphate
(for example, in the case of lithium) becomes an
25 oxyfluorophosphoric acid compound such as LiPOF_4 or LiPO_2F_2 ,

contaminates the product, and deteriorates the productivity of LiPF_6 in the end. Further, in the case of using this oxyfluorophosphoric acid compound as the electrolyte of a lithium battery, a problem occurs such that the characteristics of the
5 battery are deteriorated.

[0018]

In order to alleviate this problem, some methods have been proposed. For example, there is a method of reacting phosphorous pentachloride and anhydrous hydrogen fluoride, separating
10 phosphorous oxyfluoride by cooling a mixed gas of the produced phosphorus pentafluoride and hydrogen chloride to a temperature that is the boiling point of phosphorous oxyfluoride or lower and the boiling point of phosphorous pentafluoride or higher, for example -40°C to -84°C , and then reacting the mixed gas with
15 lithium fluoride that is dissolved into anhydrous hydrogen fluoride (Patent Document 15 (a method of manufacturing lithium hexafluorophosphate)). However, in this method, since a small amount of phosphorus oxyfluoride is separated from the mixed gas of large excess hydrogen chloride and phosphorus
20 pentafluoride, this separation operation is extremely difficult, and phosphorus oxyfluoride cannot be separated completely. Further, because the boiling point and the coagulating point of phosphorus oxyfluoride, for example, POF_3 are close to each other, there is a worry that the collection apparatus may occlude
25 and this method cannot be said to be a method that is to be

industrially sufficiently accepted.

[0019]

Further, not only in this method, in the case of using a chloride (for example, phosphorous trichloride or phosphorus pentachloride) as a phosphorous raw material, hydrogen chloride
5 is mixed into the produced phosphorus pentafluoride.

Furthermore, because the boiling point of hydrochloric acid is -84.9°C while the boiling point of phosphorus pentafluoride is -84.8°C , it is impossible to separate hydrogen chloride from
10 phosphorous pentafluoride by a simple method (Patent Document 16 (a method of manufacturing lithium hexafluorophosphate)).

[0020]

On the other hand, disaggregation of KPF_6 is investigated in Non-Patent Document 4 [J. Inorg. Nucl. Chem., 1961, Vol. 20,
15 pp. 147-154]. However, because the document is negative on generation of a PF_6 gas, conditions of the generation of the PF_6 gas and the like are not described at all.

[0021]

Furthermore, when moisture is contained in the final
20 product, in the case of $\text{M} = \text{Li}$, LiPF_6 is decomposed into LiF , HF , and PF_5 by the moisture. Because these substances are transferred in a gas state, an inner pressure is formed in the battery, and especially, HF not only reacts with an organic solvent, but also influences the corrosion of the case wrapping
25 the battery. Therefore, it has a bad influence on the stability

of the battery as a whole. From such reasons, LiPF_6 that is used as the electrolyte strictly limits the standards of purity, moisture, metal content, free hydrofluoric acid, and the like. [0022]

5 Naturally enough, the most economical method for obtaining phosphorous pentafluoride is a method utilizing the most inexpensive substance as the starting raw material. However, the method of manufacturing phosphorous pentafluoride is complicated as described above. Moreover, because there is a
10 necessity to refine the produced phosphorous pentafluoride even when the manufacture is started from an inexpensive raw material, the manufacturing cost of phosphorous pentafluoride becomes high, which makes a hexafluorophosphate as the electrolyte expensive. [0023]

15 Therefore, in order to manufacture a high purity hexafluorophosphate (DPF_6 : D is a metal element) or a high purity hexafluorophosphoric acid compound at a low price, the manufacturing cost of phosphorous pentafluoride is the most important. That is, it is necessary to suppress the bad influence
20 due to mixing-in of moisture, and it is also necessary to adopt a method utilizing as a starting material in which an (anhydrous) oxide raw material such as phosphorous pentaoxide or a raw material of which a chloride or bromide raw material having high moisture absorption characteristics are not used, in the case
25 of considering the work environment.

[0024]

Patent Document 1: U.S. Patent No. 3,607,020

Patent Document 2: Japanese Patent Application Laid-Open

No. 64-72901

5 Patent Document 3: Japanese Patent Application Laid-Open

No. 2000-154009

Patent Document 4: Japanese Patent Application Laid-Open

No. 2001-122605

Patent Document 5: French Patent No. 2,086,704

10 Patent Document 6: French Patent No. 2,082,502

Patent Document 7: U.S. Patent No. 3,634,034

Patent Document 8: Japanese Patent Application National

Publication (Laid-Open) No. 2005-507849

Patent Document 9: U.S. Patent No. 3,584,999

15 Patent Document 10: Japanese Patent No. 3494343

Patent Document 11: German Patent No. 290,889

Patent Document 12: Japanese Patent Application Laid-Open

No. 60-251109

Patent Document 13: Japanese Patent Application Laid-Open

20 No. 04-175216

Patent Document 14: Japanese Patent Application Laid-Open

No. 06-056413

Patent Document 15: Japanese Patent Application Laid-Open

No. 5-279003

25 Patent Document 16: Japanese Patent Application Laid-Open

No. 11-92135

Non-Patent Document 1: Fluorine Chemistry Vol. 1 (1950)

Non-Patent Document 2: "Fluorination of Phosphorous Using
ClF₃ in Liquid HF Medium": Clifford, Beachell, and Jack, Inorg.
5 Nucl. Chem (1957), 5, 76-78

Non-Patent Document 3: "Fluorination of Phosphorous
Pentachloride (PCl₅) Using Arsenic Trifluoride": Ruff Die
Chemie des Fluoros (1920), p. 239

Non-Patent Document 4: [J. Inorg. Nucl. Chem., 1961, Vol.
10 20, p. 147-154]

Non-Patent Document 5: Gros, Hayman, and Stuart, Trans.
Faraday Soc. (1966), 62 (10), 2716-18

BRIEF DESCRIPTION OF THE DRAWING

15 [0025]

Fig. 1 is a schematic drawing of an apparatus used in the
examples.

DISCLOSURE OF THE INVENTION

20 PROBLEMS TO BE SOLVED BY THE INVENTION

[0026]

An object of the present invention is to provide a method
of manufacturing phosphorus pentafluoride that can provide
phosphorous pentafluoride having high purity by a simple and
25 economical procedure without the need for a large-scale refining

apparatus or a high pressure apparatus, and on top of that, that
 can manufacture phosphorous pentafluoride having high purity
 without generating a large amount of by-product gas that requires
 a special exhaust gas treatment in the case that phosphorus
 5 pentafluoride is generated.

Another object is to provide a method of manufacturing
 a hexafluorophosphate that can manufacture a
 hexafluorophosphate having high purity and low moisture content
 simply and at a low price.

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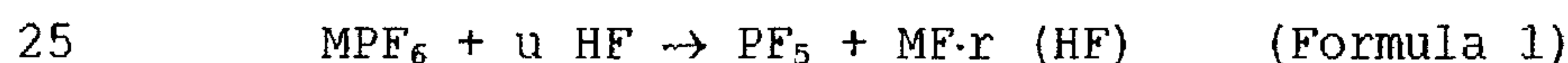
MEANS FOR SOLVING THE PROBLEMS

[0027]

In order to solve the above-described problems, the present
 inventors performed a devoted investigation, and as a result,
 15 found that a hexafluorophosphate having high purity and low
 moisture content is manufactured simply and at an inexpensive
 price by using phosphorous pentafluoride that is manufactured
 from a hexafluorophosphoric acid compound and hydrogen fluoride,
 and achieved the present invention.

20 [0028]

The present invention provides a method of manufacturing
 phosphorous pentafluoride in which phosphorus pentafluoride is
 produced according to the reaction of Formula 1 by introducing
 hydrogen fluoride and a hexafluorophosphate (MPF_6) a container:

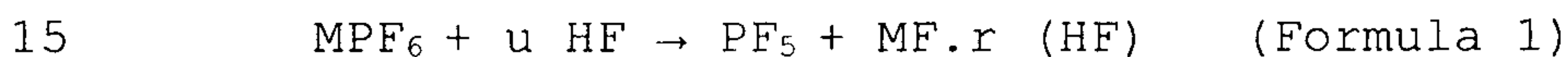


wherein M is any one or more of Li, Na, K, Rb, Cs, NH₄, and Ag,

$0 \leq r \leq u$, and

wherein HF is used in the stoichiometric amount or
5 more.

According to one aspect of the invention there is provided a method of manufacturing phosphorous pentafluoride, wherein hydrogen fluoride and a hexafluorophosphate MPF₆ are introduced into a container,
10 and phosphorus pentafluoride is produced in a state in which hydrogen fluoride accompanied with the phosphorus pentafluoride is refluxed or hydrogen fluoride is supplied into the container according to the reaction of Formula 1:



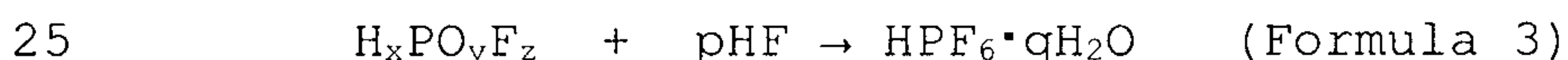
wherein:

M is Li, Na, K, Rb, Cs, NH₄, Ag, or any combination thereof;

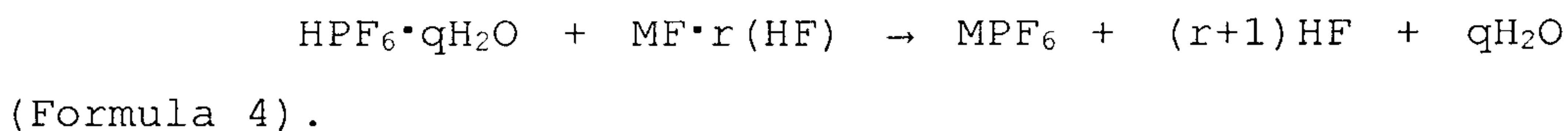
$0 \leq r \leq 6$, $u > 0$; and

20 HF is used in the stoichiometric amount or more.

According to a further aspect of the invention there is provided the method of manufacturing phosphorous pentafluoride as described herein, wherein MPF₆ is synthesized by the reaction of Formulas 3 and 4:

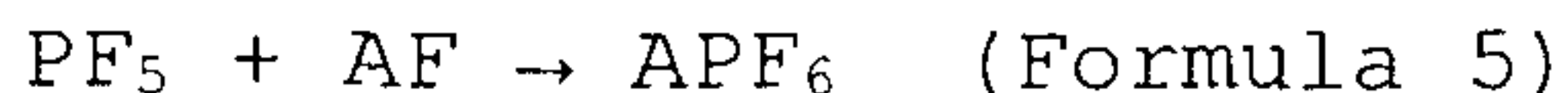


wherein $q \geq 1$, $p > 0$, and $p+z > 6$; and



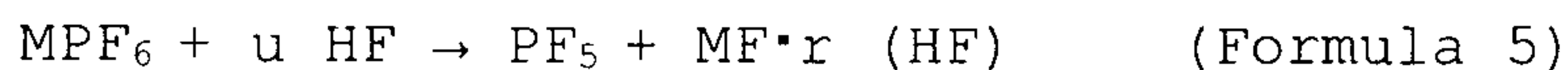
[0029]

30 Further, the present invention provides a method of manufacturing a hexafluorophosphate in which a hexafluorophosphate (APF₆) having high purity and low moisture concentration is produced according to the reaction of Formula 5 using a fluoride (AF) and
35 phosphorous pentafluoride that is obtained by the method:



wherein A is any one or more of Li, Na, K, Rb, Cs, NH₄, and Ag.

According to another aspect of the invention there is provided a method of manufacturing a hexafluorophosphate, wherein a hexafluorophosphate APF₆ is produced according to the reaction of Formula 6 using a fluoride AF and phosphorous pentafluoride that is obtained according to the reaction of Formula 5 by introducing hydrogen fluoride and a hexafluorophosphate MPF₆ in a container in a state in which hydrogen fluoride accompanied with the phosphorus pentafluoride is refluxed or hydrogen fluoride is supplied into the container:

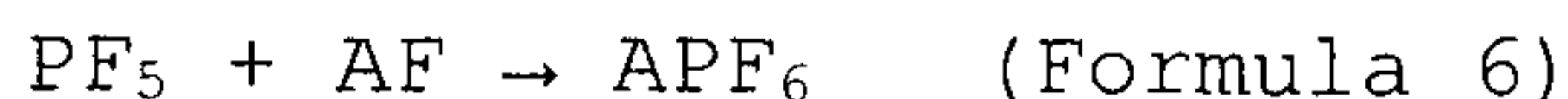


wherein:

M is Li, Na, K, Rb, Cs, NH₄, Ag, or any combination thereof;

$$0 \leq r \leq 6, \quad u > 0; \text{ and}$$

HF is used in the stoichiometric amount or more; and



wherein A is Li, Na, K, Rb, Cs, NH₄, Ag, or any combination thereof.

[0030]

The method of manufacturing a hexafluorophosphate may be any of a method of reacting a gaseous phosphorous pentafluoride with a solid fluoride or an acidic fluoride, a method of reacting gaseous phosphorous pentafluoride with a fluoride that is dissolved into anhydrous hydrogen fluoride as a solvent or an acidic fluoride, and a method of reacting gaseous phosphorus pentafluoride with a fluoride or an acidic fluoride in an organic solvent.

EFFECT OF THE INVENTION

[0031]

In the present invention, it is possible to generate phosphorous pentafluoride even at the outside of a high temperature region (less than 120°C), and a hydrogen chloride
5 gas, a hydrogen bromide gas, and the like are not generated because a chloride and a bromide are not used.

[0032]

Furthermore, according to the present invention, because the operation is simple, a hexafluorophosphate APF_6 (A = Li,
10 Na, K, Rb, or Cs) can be synthesized at a low price, and it can be used in the electrolyte of a battery whose further development for a hybrid car is expected in the future.

BEST MODE FOR CARRYING OUT THE INVENTION

15 [0033]

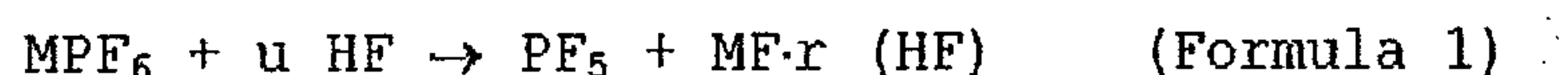
The present invention provides a method of manufacturing APF_6 (A = any one or more of Li, Na, K, Rb, Cs, NH_4 , and Ag) having high purity without using a phosphorous halide of chlorine, bromine, or the like other than fluorine and an (anhydrous) oxide
20 raw material, by an industrially safe method, and at a relatively low temperature.

[0034]

More specifically, the present invention provides a method of manufacturing phosphorous pentafluoride in which phosphorus
25 pentafluoride is produced according to the reaction of the

following chemical reaction formula 1 by introducing a hexafluorophosphate (MPF_6) and hydrogen fluoride into a container and heating the inside of the reaction system to the boiling point of the reaction mixture or higher. However, M
 5 is any one or more of Li, Na, K, Rb, Cs, NH_4 , and Ag, and it does not have to necessarily be a high purity product.

[0035]

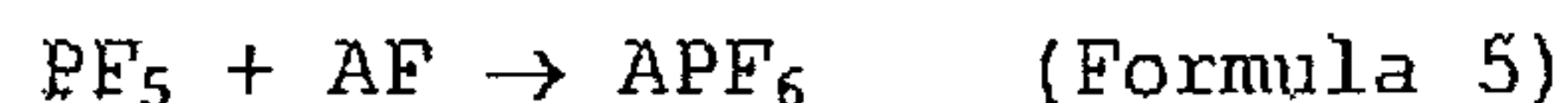


$0 \leq r \leq u$, and in the formula, HF is used in the stoichiometric
 10 amount or more.

[0036]

Furthermore, the present invention provides a method of manufacturing a hexafluorophosphate in which a hexafluorophosphate (APF_6) having high purity and low moisture
 15 concentration is produced according to the reaction of the following chemical reaction formula 5 using phosphorous pentafluoride that is obtained by the above method and a fluoride (AF). However, A is any one or more of Li, Na, K, Rb, Cs, NH_4 , and Ag.

20 [0037]



[0038]

Furthermore, MPF_6 is synthesized by the reaction of the following chemical reaction formula 2.

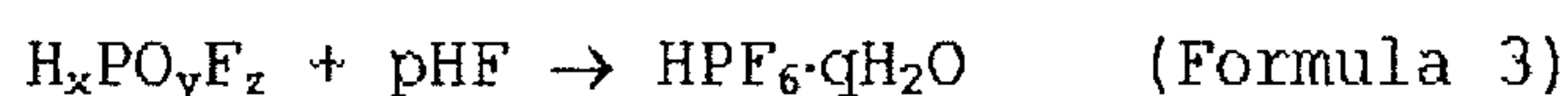


However, $r \geq 0$, $0 \leq x \leq 3$, $1 \leq y \leq 4$, $0 \leq z \leq 6$, and among these preferably $0 \leq z \leq 5$ and especially preferably $0 \leq z \leq 3$, and in the formula, HF is used in the stoichiometric amount or more.

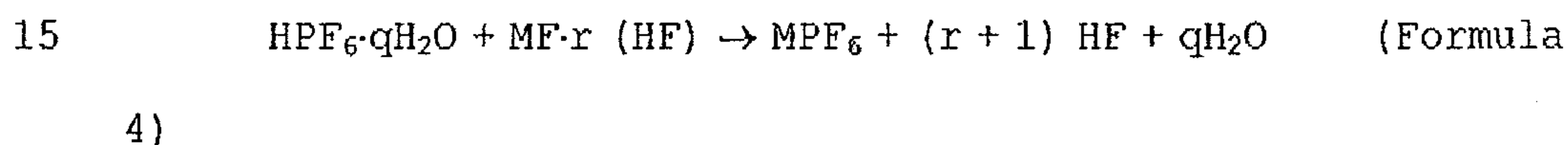
5 [0039]

Further, MPF_6 is synthesized by the reaction of the following chemical reaction formulas 3 and 4. Specifically, MPF_6 is synthesized by reacting an aqueous $\text{H}_x\text{PO}_y\text{F}_z$ solution and an aqueous hydrofluoric acid solution according to Formula 3, extracting a hexafluorophosphoric acid hydrate crystal

10 $(\text{HPF}_6 \cdot q\text{H}_2\text{O})$ as a solid once, and then reacting the extracted $\text{HPF}_6 \cdot q\text{H}_2\text{O}$ and $\text{MF} \cdot r$ (HF) according to Formula 4.



(wherein $q \geq 1$)



[0040]

Moreover, there is no problem when the ratio of added HF to $\text{H}_x\text{PO}_y\text{F}_z$ in the following chemical reaction formulas 2 to 4 is 1 equivalent or more. However, in the case that the ratio of addition is small, the concentration of hydrofluoric acid after the reaction becomes low, and therefore the ratio of addition is preferably 1.5 equivalent or more. Furthermore, when the ratio of addition is increased, the concentration of

25 hydrofluoric acid after the reaction can be increased. However,

because an increase in the ratio of addition is industrially uneconomical, the ratio of addition is preferably less than 10 equivalents. On the other hand, because the solubility of the produced MPF_6 decreases as the HF concentration increases, it is possible to increase the yield. However, because the amount of dissolved MPF_6 increases due to a large HF amount even if the solubility is low and the yield decreases, the ratio of addition is especially preferably 2 equivalents or more and 7.5 equivalents or less.

10 [0041]

Further, $\text{MF}\cdot\text{r}$ (HF) that is produced by the chemical reaction formula 1 is reused in the chemical reaction formula 2 or 4.

[0042]

In addition, M is any of Na, K, Rb, Cs, and NH_4 , and A is Li. Furthermore, the P-containing gas that flows out during the APF_6 manufacture is recovered and reused by Formulas 2 to 4 using an absorption liquid containing at least one of water, hydrofluoric acid, and $\text{MF}\cdot\text{r}$ (HF) (M is any one or more of Li, Na, K, Rb, Cs, NH_4 , and Ag).

20 [0043]

More specifically, a PF_5 gas is generated according to the chemical reaction formula 1 by introducing MPF_6 and HF into the reaction vessel and heating an MPF_6 /HF liquid to 20°C to lower than 120°C . Furthermore, after that, by reacting a metal fluoride (AF) or an acidic metal fluoride ($\text{AF}\cdot\text{r}$ (HF)) and the

PF₅ gas that is generated by the present invention according to the reaction of the chemical reaction formula 5, a hexafluorophosphate (APF₆) having high purity and low moisture content (moisture concentration: 50 ppm by weight or less).

5 However, M and A may be the same or may be different.

[0044]

MPF₆ that is used in the reaction may be synthesized by a known method. Furthermore, MPF₆ having low purity (for example, having a large amount of metal impurities) may be used.

10 Furthermore, MPF₆ may be a mother liquid containing MPF₆ that is produced in the synthesis process.

[0045]

Here, M may be any of Li, Na, K, Rb, Cs, NH₄, and Ag. Among these, M is preferably an aqueous solution system and a compound with which the synthesis of a hexafluorophosphate having a moisture concentration 1000 ppm by weight or less is easy with the above-described chemical reaction formula 2 or 4.

[0046]

However, in the case of M = Li or Ag in the above-described chemical formula 2 or 4, because the synthesis in an aqueous solution system is relatively difficult, at least one or more of NaPF₆, KPF₆, RbPF₆, CsPF₆, and NH₄PF₆ that can be easily synthesized in the above-described chemical formula 2 or 4 is preferable. Furthermore, KPF₆ is especially preferable from the respect that the synthesis is easy also by a technique of

synthesizing KPF_6 by the reaction of a potassium compound of phosphoric acid and hydrofluoric acid described in Japanese Patent Application Publication No. 5-72324 in addition to the above-described chemical formulas 2 to 4, in the respect that

5 KPF_6 has low moisture absorption characteristics, and in the respect that the raw materials can be obtained easily at a low price. However, in Japanese Patent Application Publication No. 5-72324, potassium hexafluorophosphate is synthesized using 60 to 97% by weight of hydrofluoric acid by reacting the acid with

10 a potassium compound of phosphoric acid (potassium monophosphate or potassium polyphosphate) without using anhydrous hydrogen fluoride. However, it is described that in this method, although the reaction is not so intense as in the case of phosphorous pentaoxide, the temperature of the solution rapidly increases

15 as the reaction proceeds when adding a potassium salt into hydrofluoric acid. Furthermore, it may be possible to synthesize rubidium hexafluorophosphate and cesium hexafluorophosphate by this method. However, in this case, the method of the present invention is preferable because rubidium

20 monophosphate, cesium monophosphate, rubidium polyphosphate, and cesium polyphosphate cannot be obtained easily.

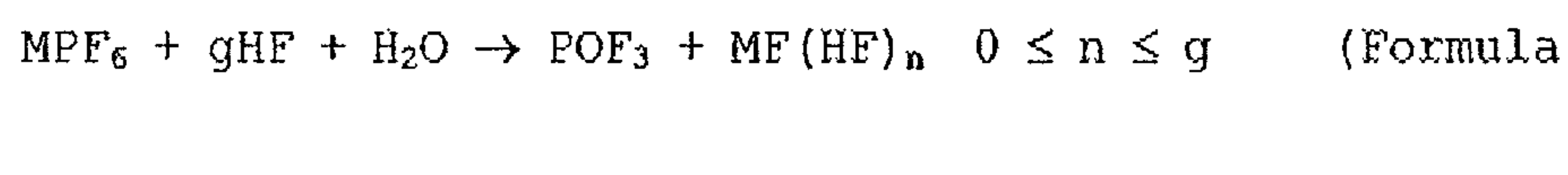
[0047]

LiPF_6 , NaPF_6 , KPF_6 , RbPF_6 , CsPF_6 , NH_4PF_6 , and AgPF_6 that are synthesized in an aqueous solution by the methods in the

25 above-described chemical reaction formulas 2 to 4 contain a

little moisture because they are synthesized in an aqueous solution system. Because the thermal decomposition temperature of NaPF_6 , KPF_6 , RbPF_6 , CsPF_6 , NH_4PF_6 , and AgPF_6 is considerably high, it is possible to decrease the amount of moisture by drying at a temperature lower than 120°C (moisture content of 1000 ppm by weight or less). However, because partial thermal decomposition starts at 120°C for LiPF_6 , LiPF_6 inevitably contains about 1000 ppm by weight of moisture. However, because the content of moisture entering into the reaction system is extremely small (about 1000 ppm) compared to the method using moisture absorbable phosphorous pentachloride (the content of moisture entering into is 1 to 10% by weight), it is difficult for the reaction of the following chemical reaction formula 6 to occur, and it becomes possible to increase the yield.

15 [0048]



[0049]

On the other hand, A is contrary to the above, and may be any of Li, Na, K, Rb, Cs, NH_4 , and Ag. However, Li, Na, NH_4 , and Ag are preferable, and among these, Li and Ag whose synthesis in an aqueous solution system is relatively difficult are more preferable. Furthermore, Li that is a substance necessary in recent lithium secondary batteries is especially preferable.

25 [0050]

There is no problem if the amount of hydrogen fluoride is 95% by weight or more. However, because the generated PF_5 becomes POF_3 due to the moisture existing in the system as in the above-described chemical reaction formula 5, the amount of hydrogen fluoride is preferably 97% by weight or more and especially preferably 99% by weight or more. Furthermore, the moisture in hydrogen fluoride may be removed by adding concentrated sulfuric acid into hydrogen fluoride. As such, even high purity hydrogen fluoride normally containing about 10 ppm of moisture may be used as it is. Furthermore, if necessary, the moisture can be further removed by performing rectification.

[0051]

The feeding method of the raw materials is not especially limited, and hydrogen fluoride may be fed after putting a hexafluorophosphate (MPF_6) in the reaction vessel, or MPF_6 may be fed after feeding hydrogen fluoride into the reaction vessel in advance. The case of reacting phosphorous halide, for example phosphorous pentafluoride, and hydrogen fluoride is not preferable because the reaction heat is extremely larger than the amount of heat in dissolving, control of the reaction is difficult, the reaction liquid boils due to the reaction heat, and phosphorous pentafluoride, hydrogen fluoride, and a hydrogen chloride gas spout from the feeding port. This phenomenon is the same for the case of (anhydrous) phosphorous pentaoxide.

However, because heat is hardly generated even when MPF_6 is

dissolved into HF, the control of the reaction is easy and such a case is excellent industrially.

[0052]

Hydrogen fluoride that is used in the generation of
5 phosphorous pentafluoride is used in a liquid state in an amount such that the concentration of MPF_6 becomes 1% by weight to 50% by weight. MPF_6 does not have to necessarily be dissolved in hydrogen fluoride completely, and may be in a suspended state. However, because the reaction vessel needs to be large when MPF_6
10 is too dilute, the concentration of MPF_6 is preferably 2.5% by weight to 40% by weight.

[0053]

Further, the solubility of MPF_6 is in inverse proportion to the cation size, and the solubility is the highest in the
15 case of lithium which has the smallest cation size. Therefore, in order to increase the solubility, a liquid may be used in which at least one of $\text{M}'\text{F}$ and $\text{M}'\text{F}\cdot\text{r}$ (HF) (however, M' is one type or more) having the smaller cation size than M is added and a salt exchange is performed. Further, the liquid after
20 the salt exchange is performed may be used as it is. However, it is also possible to take out and use only the dissolved liquid. Furthermore, if necessary, the operation can be carried out in the existence of one or a plurality of catalysts.

[0054]

25 In a reaction of generating phosphorous pentafluoride,

hydrogen fluoride accompanies the generated phosphorous
pentafluoride. However, there is no necessity to perform reflux
by cooling and condensing hydrogen fluoride, and phosphorous
pentafluoride and hydrogen fluoride may be used in the next
5 reaction as they are. However, because it is difficult for the
reaction to proceed when the amount of hydrogen fluoride in the
reaction system is small, hydrogen fluoride is supplied into
the reaction vessel on a timely basis in the case of not performing
the reflux. In the case of performing the reflux, there is no
10 problem if the temperature of the reflux tower is the boiling
point of hydrogen fluoride (+19.5°C in the case of 1 atmospheric
pressure) or lower. However, to trap more hydrogen fluoride,
the temperature is +10°C to -50°C, preferably +5°C to -25°C, and
more preferably 0°C to -10°C. Because the effect hardly changes
15 even when operating the reflux tower at a temperature lower than
-50°C, there is no necessity to use a reflux apparatus at an
extremely low temperature. Nevertheless, in the case of using
phosphorous halide such as phosphorous pentachloride as a PF_5
raw material, because it is a solid having strong moisture
20 absorption characteristics, a considerable amount of moisture
is entered into the reaction system, and a POF_3 gas is generated
from a decomposed part of the generated PF_5 gas. Together,
because hydrogen halide that is a by-product of the reaction
is generated and the POF_3 gas and the hydrogen halide accompany
25 a large amount of hydrogen fluoride as a carrier gas, a large

amount of hydrogen fluoride is extracted from the reaction system.

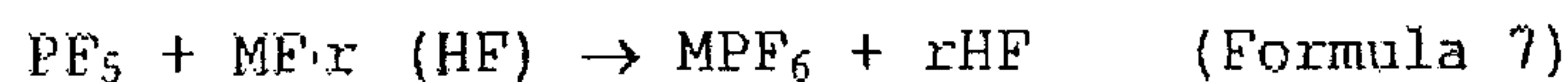
In order to trap and recover hydrogen fluoride from these accompanying gases, it is preferable to cool the gases to an extremely low temperature of -50°C or less, and a significantly
5 large cost is needed for an extremely low temperature generating apparatus or the like and its operation. Contrary to that, in the present invention, there is no necessity for an extremely low temperature of -50°C or less when performing the reflux operation and the cost can be reduced.

10 [0055]

Because $\text{MF}\cdot\text{r}(\text{HF})$ increases as the reaction proceeds, the following chemical reaction formula 7 occurs that is a reverse reaction of the above-described chemical reaction formula 1. Because of this, it becomes difficult for the generation of the
15 PF_5 gas to occur as the reaction proceeds. In order to suppress this, the $\text{MF}\cdot\text{r}(\text{HF})$ may be extracted from the reaction system whenever necessary. In the case of extracting the $\text{MF}\cdot\text{r}(\text{HF})$, the method may be any of a method of extracting the $\text{MF}\cdot\text{r}(\text{HF})$ that is deposited as a solid, a method of extracting an HF solution
20 in which the $\text{MF}\cdot\text{r}(\text{HF})$ is dissolved whenever necessary, and the like. Further, a small amount of HPF_6 is contained in the refluxed HF. This HPF_6 is unstable in anhydrous HF, and reacts again with $\text{MF}(\text{HF})\text{r}$ by returning to the reaction vessel to be stable MPF_6 . Because of this, a PF_5 gas may be generated by putting
25 the reflux liquid into a different reaction vessel without

returning it directly to the reaction vessel.

[0056]



[0057]

5 The pressure during the reaction in the chemical reaction
formula 1 is not especially limited. However, when the pressure
is set to too high a pressure or too much a reduced pressure,
because there is a large load in the aspect of facilities, the
reaction is preferably performed at a normal pressure. However,
10 in the case that it is desired, the reaction may be performed
at an increased pressure or a reduced pressure.

[0058]

Furthermore, reaction members and reflux tower members
in the chemical reaction formula 1 can be selected from members
15 made of stainless steel or a stainless steel alloy, especially
a chromium/nickel/iron/copper alloy such as trade names Inconel
(registered trademark), Monel (registered trademark), and
Hastelloy (registered trademark), members made of a fluorine
resin (Polytetrafluoroethylene: "PTFE"), members made of a PFA
20 resin (a tetrafluoroethylene perfluoroalkylvinylether
copolymer), and apparatus members coated with these fluorine
resins.

[0059]

However, in the case of using phosphorous pentachloride
25 or phosphorous trichloride and a halide of chlorine or the like

as a raw material for the generation of phosphorous pentafluoride,
because high-quality members have to be used that can deal with
all of the moisture that is brought-in by the raw materials
themselves, HCl that is produced as a by-product, and HF in the
5 reaction system, the members that can be used are limited.
Therefore, it leads to an increase in the facility cost. However,
by the method of the present invention, because the amount of
the moisture that is brought-in is small (1000 ppm by weight
or less) and hydrogen halide such as HCl is not produced as a
10 by-product, it is possible to use any member as long as it is
made of materials that are only durable to hydrogen fluoride.
[0060]

Further, because a PF_5 gas is generated indirectly and
sent to the reaction vessel of the chemical reaction formula
15 5 in this method, metal impurities in the container in the chemical
reaction formula 1 do not mix into the PF_5 gas. That is, because
there is no necessity to consider the problem of the metal
impurities that has been a problem when using phosphorus
pentachloride, the method leads to a cost reduction because even
20 raw materials having a high metal impurity concentration can
be used as long as the moisture content of MPF_6 that is used
is 1000 ppm by weight or less. Therefore, the PF_5 gas generated
by the method of the present invention can achieve a low price
while having high purity.

25 [0061]

Furthermore, the temperature of the reaction system of the chemical reaction formula 1 is preferably the boiling point of the reaction system. That is, the produced phosphorus pentafluoride can be taken out from the reaction system with hydrogen fluoride being a carrier gas that is generated upon boiling by operating the reaction at the boiling point of the reaction system that is determined by the operating pressure, the concentration of MPF_6 in the reaction system, and the concentration of the produced $\text{MF}\cdot\text{r}$ (HF), and it is difficult for the reaction in the chemical reaction formula 1 to proceed at the boiling point of the reaction system or lower, and it is difficult to generate phosphorous pentafluoride. For example, in the case of 1 atmospheric pressure, the boiling point is determined in the range of 19.5°C to less than 50°C depending on the concentration of MPF_6 and the concentration of $\text{MF}\cdot\text{r}$ (HF) in the solution (the boiling point of hydrogen fluoride at 1 atmospheric pressure: $+19.5^\circ\text{C}$). Naturally enough, when the operating pressure is high, the boiling point is high, and when the operating pressure is reduced, the boiling point becomes low. When performing the operation at high temperature by increasing the pressure, the reaction speed becomes high. However, facilities that are durable to high pressure are required. When performing the operation at low temperature by decreasing the pressure, the reaction speed becomes low.

25 [0062]

Then, when economics is evaluated by taking factors such as the temperature of the reaction system, the pressure-resistant strength of materials that constitutes the reactor, and the reaction speed, the operation is preferably performed at a
5 temperature of the reaction system of 0°C to 50°C and a pressure in the absolute pressure being in the range of 0.5 atm to 10 atm, 15°C to 35°C, and above all, the operation is more preferably carried out in the range of 0.8 atm to 1.5 atm and at a reaction temperature in the reaction system of 20°C to 30°C.

10 [0063]

A heat medium that is used to warm the reaction system is not especially limited as long as the boiling point thereof is the boiling point of the reaction system or higher, and steam or the like can be used. However, in the case of a temperature
15 higher than 120°C, troubles occur such that the incidental facilities and running costs become expensive, and therefore, it is preferable to add a heat source from outside so that the temperature becomes lower than 120°C.

[0064]

20 Furthermore, the reaction in the chemical reaction formula 1 can be performed by either of a batch method and a continuous method. Furthermore, the reaction time is not especially limited. However, when considering the production efficiency, in the case of the batch method, it is preferable to generate
25 the product within 24 hours.

[0065]

Further, in order to promote the effect of extracting the generated phosphorous pentafluoride out of the reaction system, dry air or an inert gas such as N_2 or Ar that does not have an interaction with the reaction system can be used in an appropriate amount as a carrier gas. However, in this case, using a large amount of the inert gas is not preferable because of the economical problem, or because it increases the amount of accompanying hydrogen fluoride.

10 [0066]

Because a MPF_6 raw material having a moisture content of 1000 ppm by weight or less is used in the PF_5 that is generated in the present invention, an oxy product such as POF_3 is not produced. Therefore, there is no necessity of refining.

15 Further, because no halide raw material is used, there is no problem at all such that hydrogen halide is mixed in.

[0067]

Furthermore, because MF_r (HF) that is produced by the chemical reaction formula 1 can be circulated by reusing the MF_r (HF) in the chemical reaction formula 2 or 4, the method of the present invention is excellent.

[0068]

The method of manufacturing a hexafluorophosphate (especially preferably lithium hexafluorophosphate; $LiPF_6$) (the chemical reaction formula 5) may be any of a method of reacting

gaseous phosphorous pentafluoride that is obtained by the present invention with a solid fluoride: AF (especially preferably lithium fluoride: LiF), a method of reacting gaseous phosphorous pentafluoride that is obtained by the present invention with
5 a fluoride: AF (especially preferably lithium fluoride: LiF) that is dissolved into anhydrous hydrogen fluoride as a solvent, and a method of reacting gaseous phosphorous pentafluoride that is obtained by the present invention with a fluoride: AF (especially preferably lithium fluoride: LiF) in an organic
10 solvent. Moreover, in the case of using anhydrous hydrogen fluoride as a solvent, it is preferable to perform the reaction at the boiling point or lower (for example, 19.5°C or lower) by performing a treatment such as cooling in order to suppress the reaction of the chemical reaction formula 5.

15 [0069]

Any material that is durable to anhydrous hydrofluoric acid (HF) can be used for the reaction vessel of the chemical reaction formula 5. However, if there are problems during the step, that is, the cases of leakage or exposure to the air, there
20 is a fear that the material reacts with concentrated hydrofluoric acid and is corroded. If the reactor is corroded, the product is inevitably contaminated with the corroded substances, and these contaminated substances act as a cause for increasing the content of the metal components in the product. From these points,
25 the apparatus, piping and the like that are configured are

preferably coated with a fluorine resin (for example, PTFE or PFA) for the management of the metal component.

[0070]

Because a hexafluorophosphate (DPF_6 : D is a metal element) that is in a salt state is more stable in anhydrous HF, it does not easily dissociate, and it is difficult to generate a PF_6 gas. On the other hand, hexafluorophosphoric acid (HPF_6) that is in an acid state cannot exist stably as HPF_6 in anhydrous HF, and easily dissociates and gasifies. This agrees with a known matter that PF_5 is hardly absorbed or is not absorbed at all into anhydrous HF and an HPF_6 complex is not formed under non-existence of water.

[0071]

Furthermore, during the reaction in the formula 5, an excess amount of PF_5 gas is reacted to a fluoride (AF) for the purposes of manufacturing a product having higher purity, of increasing the yield more, or the like. However, excess PF_5 flows out of the reaction system and invites a decrease in the yield of phosphorous.

20 [0072]

In order to reduce this loss of the phosphorous source, a gas that is originated from the excess PF_5 that flows out of the reaction system is absorbed into 0 to 80% by weight of water or an aqueous hydrofluoric acid solution, or into 0 to 80% by weight of water or an aqueous hydrofluoric acid solution in which

an M salt (the M salt is any one or more of carbonates, hydroxides,
and halides of any one or more of Li, Na, K, Rb, Cs, NH₄, and
Ag) is dissolved, and is recovered as MPF₆ or H_xPO_yF_z ($0 \leq x \leq 3$, $1 \leq y \leq 4$, $0 \leq z \leq 6$). Furthermore, among those, especially
5 preferably, the gas that is originated from the excess PF₅ that
flows out of the reaction system is absorbed into 0 to 80% by
weight of water or an aqueous hydrofluoric acid solution in which
a fluoride of MF_r (HF) is dissolved, and is recovered as MPF₆
or HPF₆. Here, MF_r (HF) may be obtained by a reaction of
10 hydrofluoric acid with the above-described M salt.

[0073]

Here, this flowed-out gas may be absorbed into water or
an aqueous hydrofluoric acid solution once and supplied to the
reaction of Formula 2 or 3. However, it is preferable that the
15 M salt (the M salt is any one or more of carbonates, hydroxides,
and halides of any one or more of Li, Na, K, Rb, Cs, NH₄, and
Ag) is added to the aqueous HF solution in advance because the
phosphorus source can be absorbed efficiently. Furthermore,
among these, MF_r (HF) ($r \geq 0$) is especially preferable. Further,
20 a fluoride salt of K, Rb, Cs, or NH₄ is preferable of which the
solubility of MF_r (HF) that is added is high and the solubility
of MPF₆ is low, and that is easily separated from the reaction
system. Furthermore, among those, Na and K are the most
preferable when considering that the raw materials can be
25 obtained easily and considering problems such as draining.

Moreover, the absorption method is not especially limited, and the absorption is performed by a known method using a packed tower, a multistage tower, a spray tower, or the like.

[0074]

5 By performing the reaction in such a manner, a circulation type manufacture can be performed, and the loss of the raw materials becomes is extremely reduced. Furthermore, phosphorous pentafluoride and a hexafluorophosphate that is obtained by the present invention can be manufactured at a low
10 price while having a moisture content of 50 ppm by weight or less and a free acid concentration of 50 ppm by weight or less.

EXAMPLES

[0075]

15 In the following, preferred examples of the present invention are explained in detail for the purpose of exemplification. However, the materials, the compounding amounts, and the like that are described in these examples are not for the purpose of limiting the scope of the present invention
20 as long as there is no particular limitative description, and they are just explanatory examples.

All of the examples and comparative examples were performed at atmospheric pressure.

[0076]

25 (Example 1)

The following operations were performed using an apparatus shown in Fig. 1.

50 g of potassium hexafluorophosphate (KPF_6) and 2000 g of anhydrous hydrogen fluoride (HF) from the market were placed in a 5 L reaction vessel made of a fluorine resin (PFA) together with a rotator, and the reaction vessel was connected to a reflux tower (20 mm ϕ x 2 m) made of SUS 316. The PFA reaction vessel was warmed with a water bath so that the temperature outside the reaction vessel became 45°C, and at the same time, the reflux tower was cooled with a brine of -50°C. Furthermore, the reaction liquid was stirred with a magnetic stirrer. As the bath temperature increased, the reflux of HF started. The HF temperature inside at that time was 21°C.

[0077]

After 5 minutes, a gas started to generate from the reflux tower. The analysis of this gas was performed with FTIR. As a result, it was confirmed that the gas was PF_5 and a small amount of HF.

[0078]

(Example 2)

330 g of lithium hexafluorophosphate (LiPF_6) and 2000 g of anhydrous HF were placed in a 5 L PFA reaction vessel together with a rotator, and the reaction vessel was connected to a reflux tower (20 mm ϕ x 2 m) made of SUS 316. The PFA reaction vessel was warmed with a water bath to 80°C, and at the same time, the

reflux tower was cooled with a brine of 0°C. Furthermore, the reaction liquid was stirred with a magnetic stirrer. As the bath temperature increased, the reflux of HF started. The HF temperature inside at that time was 30°C.

5 [0079]

The analysis of the gas that was generated from the reflux tower was performed with FTIR, and it was confirmed that it was PF₅ and a small amount of HF. At the same time, the generated gas was absorbed into pure water for 4 hours, and the P content
10 of the absorption liquid was measured. As a result, the weight of the PF₅ gas that was generated was calculated to be 205 g, and it was possible to generate 75% of the gas.

[0080]

(Example 3)

15 90 g of ammonium hexafluorophosphate (NH₄PF₆) and 2000 g of anhydrous HF were placed in a 5 L PFA reaction vessel together with a rotator, and the reaction liquid was stirred with a magnetic stirrer. Example 3 was performed without setting up the reflux tower. The generated gas was analyzed with FTIR, and at the
20 same time, it was absorbed into pure water. When the PFA reaction vessel was warmed with a water bath to 65°C, hydrogen fluoride evaporated and reacted vigorously with pure water as the absorption liquid. When the FTIR analysis was performed on the generated gas, it was confirmed that the gas was PF₅ and a large
25 amount of HF. The gas was absorbed into pure water for 6 hours,

and the P content of the absorption liquid was measured. As a result, the weight of the PF_5 gas that was generated was calculated to be 43 g, and it was possible to generate 62% of the gas.

5 [0081]

(Example 4)

1.5 kg of cesium hexafluorophosphate (CsPF_6), 140 g of lithium fluoride (LiF), and 18 kg of anhydrous hydrogen fluoride (HF) were placed in a 20 L PTFE reaction vessel together with a rotator, and the reaction vessel was connected to a reflux tower (20 mm ϕ x 2 m) made of SUS 316. Furthermore, separately, 210 g of silver fluoride (AgF) and 500 g of anhydrous HF were placed in a 3 L PFA reaction vessel together with a rotator and dissolved, and the outlet of the reflux tower was connected to the 3 L PFA reaction vessel so that the generated gas can be absorbed in the 3 L PFA reaction vessel. The 20 L PFA reaction vessel was warmed with a water bath to 70°C, and the 3 L PFA reaction vessel was cooled with an ice bath. The reflux tower was cooled with a brine of 0°C. Stirring was performed in each of the two reaction vessels.

[0082]

The temperature of the 20 L PFA reaction vessel gradually increased, the internal temperature became 23°C, and the reflux of HF started. At almost the same time as that, the temperature of the 3 L PFA reaction vessel increased from 0°C to 5°C. After

the reaction was performed for 6 hours, the 3 L PFA reaction vessel was removed from the reflux tower, cooled to -40°C , and crystallization was performed for 48 hours. Next, the supernatant liquid in the 3 L PFA reaction vessel was slowly
5 taken out, and solid-liquid separation was performed. After the separation, N_2 was introduced into a bottle at 3 L/min, and dried by air. Furthermore, after that, drying was performed in a dryer at 85°C for 3 hours, and 395 g of a crystal was obtained.
[0083]

10 The obtained crystal was analyzed with XRD, and it was found that the crystal belongs to silver hexafluorophosphate (AgPF_6). Further, the moisture content was 50 ppm by weight or less, and the concentration of free hydrofluoric acid was 50 ppm by weight or less. The moisture content was measured
15 with a moisture meter, and the concentration of free hydrofluoric acid was obtained by titration with sodium hydroxide.

[0084]

(Example 5)

[Step I]

20 1.2 kg of acidic potassium fluoride (KHF_2) was placed in a 10 L PTFE reaction vessel, and 5.25 kg of HF (semiconductor grade 75%) was slowly added while being cooled with an ice bath. Furthermore, 1.3 kg of 85% by weight phosphoric acid (H_3PO_4) was added over 30 minutes. Stirring was performed for 6 hours
25 with a water bath of $+20^{\circ}\text{C}$, and the reaction and the

crystallization were performed. Next, the obtained precipitate was filtered by suction filtration. The recovered crystal was washed with water, and then, dried for 6 hours at 105°C. The yielded amount of the obtained crystal was 1.35 kg (yield 65%).

5 Furthermore, XRD measurement was performed on the obtained crystal, and it was found that the crystal was KPF_6 . Because the yielded amount of the obtained crystal was 1.35 kg, the yield was 65%.

[0085]

10 [Step II]

1.2 kg of KPF_6 that was obtained above and 6 kg of anhydrous hydrogen fluoride (HF) were placed in a 10 L PTFE reaction vessel together with a rotator, and the reaction vessel was connected to a reflux tower (20 mmφ x 2 m) made of SUS 316. Furthermore, separately, 95 g of LiF and 1200 g of anhydrous HF were placed in a 2 L PTFE reaction vessel together with a rotator and dissolved, and the outlet of the reflux tower was connected to the 2 L PTFE reaction vessel so that the generated gas can be absorbed in the 2 L PTFE reaction vessel. Furthermore, in order to absorb exhaust gas, a 3 L PTFE reaction vessel was connected to the latter stage of the 2 L PTFE reaction apparatus. In this 3 L PTFE reaction vessel, a liquid was used in which 50 g of $\text{KF} \cdot (\text{HF})$ was dissolved into 2 kg of 50% by weight HF.

[0086]

25 The 10 L PTFE reaction vessel was heated with a water bath

of 85°C, and the 2 L PTFE reaction vessel and the 3 L PTFE reaction vessel were cooled with an ice bath. The reflux tower was cooled with a brine of 0°C. Stirring was performed in each of the three reaction vessels.

5 [0087]

The temperature of the 10 L PTFE reaction vessel gradually increased, the internal temperature became 25°C, and the reflux of HF started. At almost the same time as that, the temperature of the 2 L PTFE reaction vessel increased from 0°C to 8°C, and
10 the solution gradually became cloudy.

[0088]

[Step III]

After the reaction was performed for 8 hours, the 2 L PTFE reaction vessel was removed from the reflux tower, and stirring
15 was performed for 4 hours while being cooled to -40°C. Solid-liquid separation was performed on the obtained crystal product by filtration and the resulting crystal was transferred to a 1 L PFA container, N₂ was introduced at a flow rate of 3 L/min at room temperature for 4 hours, and the crystal was dried
20 by air. After that, drying was performed on the 1 L PFA container at 85°C for 3 hours, and 480 g of a crystal was obtained.

[0089]

Analysis of the obtained crystal was performed, and it was found that the crystal belongs to LiPF₆, the moisture content
25 was 50 ppm by weight or less, and the concentration of free

hydrofluoric acid was 50 ppm by weight or less.

[0090]

[Step IV]

5 A liquid was taken out from the 3 L PTFE reaction vessel and ion chromatography analysis was performed on the liquid, and it was found that PF_6^- anions were detected. This shows that the exhaust gas can also be trapped and reused as a raw material.

[0091]

[Step V]

10 Furthermore, the 10 L PTFE reaction vessel after the reaction was removed from the reflux tower, the solution was concentrated by a water bath of 35°C, and the HF solution containing viscous $\text{KPF}_6/\text{KF}\cdot v(\text{HF})$ ($v \geq 0$) was recovered. It was possible to reuse this solution in step I.

15 [0092]

(Comparative Example 1)

200 g of KPF_6 and 2000 g of anhydrous HF were placed in a 5 L PFA reaction vessel together with a rotator, and the reaction vessel was connected to a reflux tower (20 mmφ x 2 m) made of SUS 316. Furthermore, the reflux tower was connected to an absorption vessel in which pure water was placed from the upper part of the reflux tower with a PFA pipe. The PFA reaction vessel was kept at 15°C with an ice bath, and at the same time, the reflux tower was cooled with a brine of 0°C. Furthermore, the
25 reaction liquid was stirred with a magnetic stirrer. The

internal temperature of the reaction vessel was 14.2°C, boiling of the reaction liquid did not occur in this condition, and reflux was not observed.

[0093]

5 After 4 hours, the analysis of P was performed on the absorption liquid of the absorption vessel with ICP-AES and the weight of the generated PF₅ gas was obtained. As a result, the weight was 0 g, and the PF₅ gas was not generated at all.

[0094]

10 (Conventional Example)

The present example is an example showing a conventional example described in Patent Document 8.

790 g (9.4 mol) of polyphosphoric acid was put in a 5 L PFA reaction vessel, and 1235 g (61.7 mol) of anhydrous HF was
15 added while stirring while keeping the temperature at 25°C by cooling. Furthermore, 150 g of anhydrous HF was added and 25% excess HF was obtained in the above-described solution. The reaction vessel was connected to a reflux tower (cooled to -50°C), the temperature was kept at 32°C, and 1781 g (14.5 mol) of fuming
20 sulfuric acid (65%SO₃) was added over 3 hours. The analysis was performed on the generated gas with FTIR. As a result, a very small amount of PF₅ was contained in POF₃.

[0095]

From the above result, it is possible to produce
25 phosphorous pentafluoride by reacting a hexafluorophosphate

(MPF₆) and hydrogen fluoride in a hydrogen fluoride solvent and heating the product to the boiling point of the reaction system or higher, and phosphorous pentafluoride can be easily generated even without a high temperature of 120°C or more. Furthermore, by reacting phosphorous pentafluoride that is obtained in the present invention and a fluoride (AF), a hexafluorophosphate (APF₆) having a low moisture content and high purity can be manufactured relatively easily and simply.

10 INDUSTRIAL APPLICABILITY

[0096]

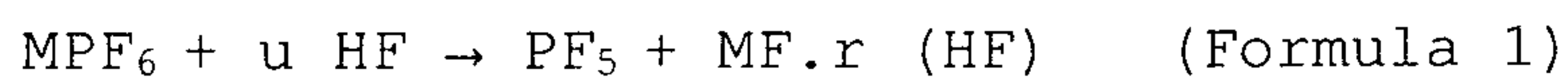
A hexafluorophosphate that is manufactured by the present invention is utilized as an electrolyte for a battery, a catalyst for an organic synthesis reaction, and the like.

15 [0097]

Among these, especially, a hexafluorophosphate (APF₆) (A = Li, Na, K, or the like) is used as an electrolyte for a battery such as for products related to a personal computer, for a portable phone, and for a hybrid car. Furthermore, in the case of A = Ag, it is used as a counter ion that generates an acid that is necessary for an initiation and growth reaction in photo polymerization. Furthermore, in the case of A = NH₄, it is useful as a raw material that is used in the manufacture of an intermediate of medicine.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of manufacturing phosphorous pentafluoride, wherein hydrogen fluoride and a hexafluorophosphate MPF_6 are introduced into a container, and phosphorus pentafluoride is produced in a state in which hydrogen fluoride accompanied with the phosphorus pentafluoride is refluxed or hydrogen fluoride is supplied into the container according to the reaction of Formula 1:



wherein:

M is Li, Na, K, Rb, Cs, NH_4 , Ag, or any combination thereof;

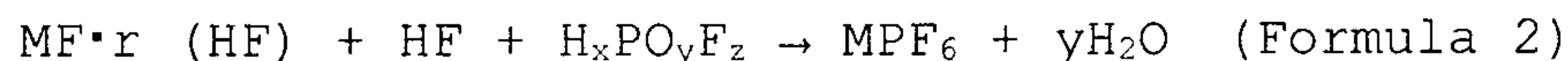
$$0 \leq r \leq 6, u > 0; \text{ and}$$

HF is used in the stoichiometric amount or more.

2. The method of manufacturing phosphorous pentafluoride according to claim 1, wherein the reaction of Formula 1 is warmed to the boiling point of the reaction mixture.

3. The method of manufacturing phosphorous pentafluoride according to claim 1, wherein a heat medium that is used in heating of the reaction system of Formula 1 is warmed to a temperature of 20 °C or more and less than 120 °C.

4. The method of manufacturing phosphorous pentafluoride according to claim 1, wherein MPF_6 is synthesized by the reaction of Formula 2:

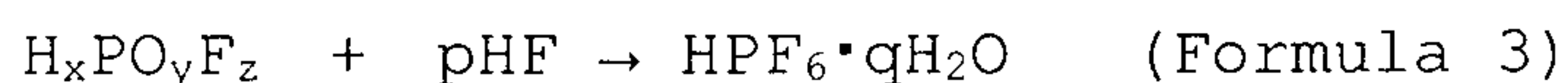


wherein:

$$r \geq 0, 0 \leq x \leq 3, 1 \leq y \leq 4, 0 \leq z \leq 6; \text{ and}$$

HF is used in the stoichiometric amount or more.

5. The method of manufacturing phosphorous pentafluoride according to claim 1, wherein MPF_6 is synthesized by the reaction of Formulas 3 and 4:



wherein $q \geq 1$, $p > 0$, and $p+z > 6$; and

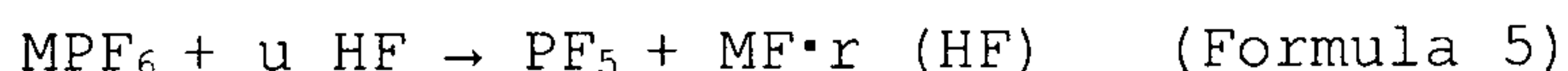


6. The method of manufacturing phosphorous pentafluoride according to any one of claims 1 to 4, wherein $\text{MF} \cdot r (\text{HF})$ that is produced by Formula 1 is reused in Formula 2.

7. The method of manufacturing phosphorous pentafluoride according to any one of claims 1 to 6, wherein M is Na, K, Rb, Cs, NH_4 , or any combination of thereof.

8. A method of manufacturing a hexafluorophosphate, wherein a hexafluorophosphate APF_6 is produced according to the reaction of Formula 6 using a fluoride AF and phosphorous pentafluoride that is obtained according to the reaction of Formula 5 by introducing

hydrogen fluoride and a hexafluorophosphate MPF_6 in a container in a state in which hydrogen fluoride accompanied with the phosphorus pentafluoride is refluxed or hydrogen fluoride is supplied into the container:

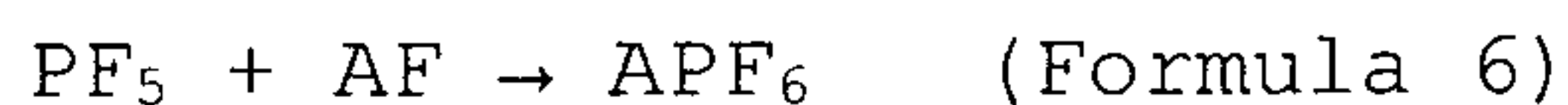


wherein:

M is Li, Na, K, Rb, Cs, NH_4 , Ag, or any combination thereof;

$$0 \leq r \leq 6, \quad u > 0; \text{ and}$$

HF is used in the stoichiometric amount or more; and



wherein A is Li, Na, K, Rb, Cs, NH_4 , Ag, or any combination thereof.

9. The method of manufacturing the hexafluorophosphate according to claim 8, wherein A is Li.

10. The method of manufacturing the hexafluorophosphate according to claim 8, wherein a P-containing gas that flows out when manufacturing APF_6 is recovered and reused using an absorption liquid containing at least one of water, hydrofluoric acid, and M salt, wherein M is Li, Na, K, Rb, Cs, NH_4 , Ag, or any combination thereof.

11. The method of manufacturing phosphorous pentafluoride according to claim 5, wherein $\text{MF} \cdot r \text{ (HF)}$ that is produced by Formula 1 is reused in Formula 4.

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Fig.1

