

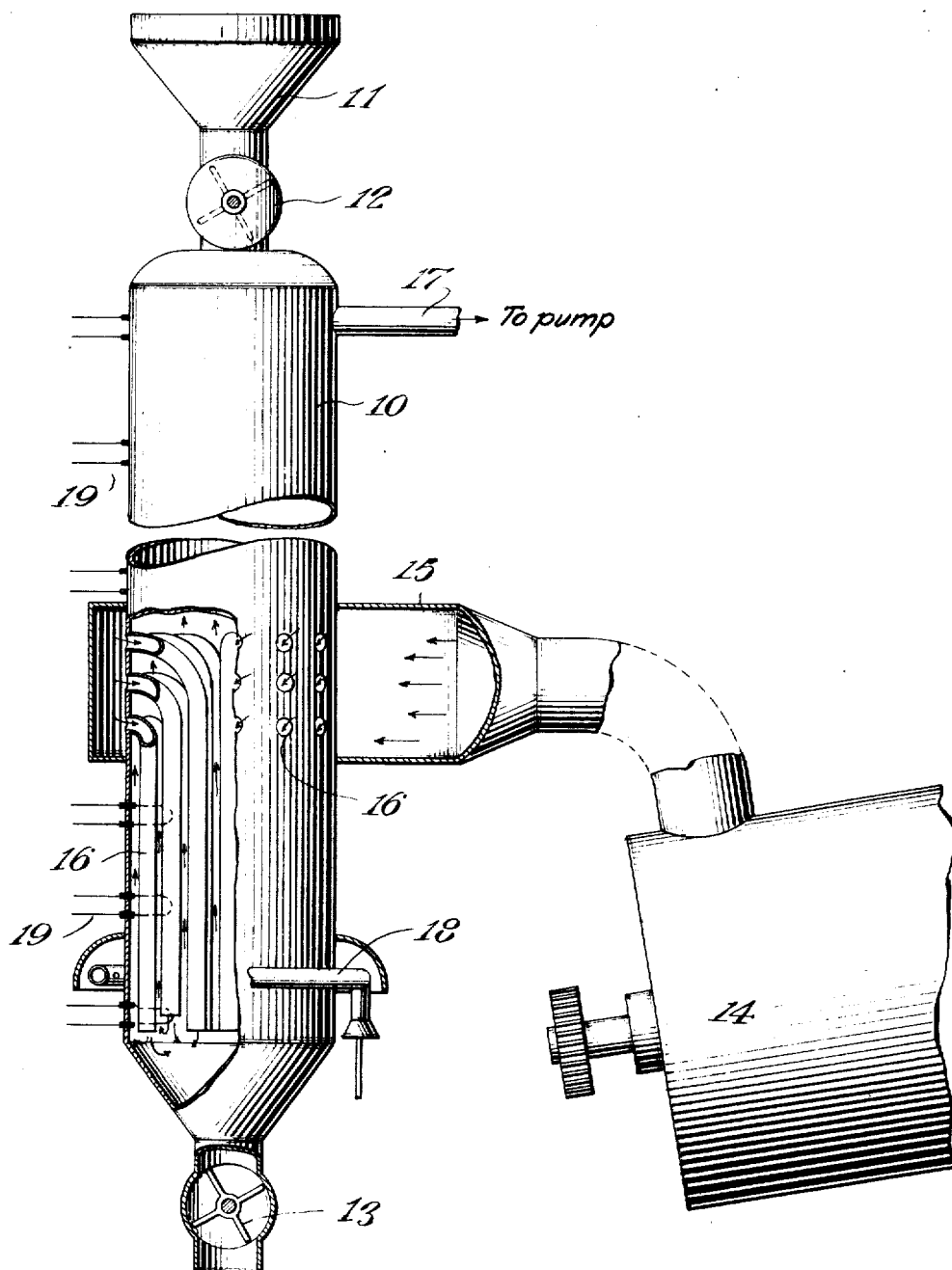
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METHOD OF MANUFACTURING FLUORIDE MATERIALS

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METHOD OF MANUFACTURING FLUORIDE MATERIALS

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This invention relates to the manufacture of metallic compounds containing fluorin, particularly aluminum and sodium fluorides, and the complex sodium-aluminum compound, or artificial cryolite so-called.

Heretofore the industry has known but one process for the purpose, which process, as universally practiced, comprises the preparation of an aqueous solution of hydrofluoric acid gas, the subsequent neutralization of this solution with suitable compounds containing the metal the fluoride of which it is desired to obtain, and finally, the separation and drying of the resultant fluoride product. Such processes are not advantageous in large scale operation, as the number of separate operations involved, the large volume of solutions which have to be handled, the necessity for lead-lined and expensive equipment which will resist the action of the acid solutions, and the inefficiency of the process as regards utilization of the fluorin, present almost insuperable obstacles to low cost operation. Notwithstanding such well known disadvantages, no improvements in the process have been made since the inception of the art except in the direction of refinement of details; and this in the face of the fact that fluorin-containing compounds are employed in many arts, where they are utilized for many and diverse purposes. Also, the purity of the compounds is an important requisite, one of the exceptions being that for some purposes the compounds may contain as an impurity, without affecting their value, the oxid of the metal which forms the fluoride. While compounds of high purity may be obtained by the prior process, they are obtained only as a result of carefully controlled manipulation and are not the natural result of the process. Furthermore, as in the case of aluminum fluoride, a fluorin-containing compound of low residual water content is often desirable but can not be obtained with the prior process except by further and additional heating or calcining of the product, with concurrent loss of fluorin.

We have therefore been led to devise our present invention, which has for its chief object to provide a simple and efficient process in which the disadvantages of the prior method outlined above are entirely avoided and by which the desired fluorin compounds can be produced at low cost on any desired scale. Another object is to provide a process which can be carried on in a continuous manner and be largely automatic in operation, requiring practically nothing

more than regular feeding of the materials to a reaction zone and withdrawal of the product therefrom. To these and other ends the invention comprises the novel features hereinafter described. In its broader aspects the invention consists in bringing gaseous fluorin, or preferably, a gaseous fluorin compound, as for example hydrofluoric or hydrofluosilicic acid gas, directly from the source of production into contact with the material which is to be converted, under conditions which will bring about the desired conversion by direct reaction.

The invention may be carried out in a variety of ways. For example, the metallic compound, say a carbonate, which is to be converted into fluoride, may be charged dry into a closed vessel and the gas introduced at a rate which will maintain the reaction (which is in general exothermic) without excessive evolution of heat. If agitation is necessary or desirable, as is usually the case when the solid material is powdered, the vessel may be rotated so as to tumble the material. Where the vessel is large and well filled the radiation surface may not be extensive enough to keep the temperature of the reacting materials down to an efficient point, in which case the vessel may be cooled by an air blast or by means of a simple water jacket. In another method of practicing the process, especially advantageous when the solid material is powdery in nature, the solid material is supplied to one end of a rotating drum and the gas is admitted at the other end, at which latter end the reaction product is discharged from time to time by means of any suitable valve mechanism.

In the preferred method, however, we establish a reaction zone in the lower part of an upright converter of the shaft or tubular type, filled, at least to a substantial height above the reaction zone, with the dry oxid, hydrate, carbonate, or other suitable compound of the metal the fluoride of which is to be produced. Below the reaction zone the converter is provided with a valved opening for continuous or periodic discharge of the product, and at the top is a valved hopper for supplying the carbonate, oxid, or other compound. The gas is delivered in contact with the solid material at a point above the valved outlet, and rises through the material, which, in order to avoid the necessity of agitation, is in lump or granular form. Preferably the supply of gas and solid material, and the withdrawal of the reaction product, are so related that all the gas is consumed in the reaction zone; it being understood, however, that the upper end of the reac-

tion zone is not sharply defined but shades off more or less gradually into the material above.

In the accompanying drawing we have shown in elevation, partly in section, an apparatus of the shaft or tower type which may be employed for carrying out the invention in the manner outlined above. The illustration is diagrammatic in character, as the precise nature of the mechanical details is immaterial.

In the drawing, 10 is an upright shaft or tower provided at the top with a feed hopper 11 for feeding the solid material into the tower, the feed being effected through any suitable valve means, as for example a star valve 12. A similar valve 13 at the bottom is provided for discharge of the product. These valves may be rotated continuously or intermittently, having due regard to the rate at which the reaction product is formed.

The hydrofluoric acid gas needed for the conversion may be generated in a still 14 by the well known reaction of calcium fluoride (fluorspar) and sulfuric acid. The apparatus and process of Fickes Patent No. 1,316,569, issued September 23, 1919, have been found highly satisfactory but the invention is not limited to any particular method or apparatus for producing the gas. It is desirable, however, that the supply of gas be substantially uniform and constant in amount. This is readily obtained in the Fickes process referred to, by maintaining proper heating of the still and a uniform supply of spar and acid to the still.

From the still the gas passes to a manifold 15 surrounding the tower 10 at a convenient height above the bottom. From the manifold the gas passes downwardly through pipes 16 and is discharged from the latter at a suitable point above the bottom of the tower. The tower being filled with the granular material to a height well above the manifold the pipes are surrounded by the reacting material, and as the reaction is exothermic the gas flowing down through the pipes is preheated.

Rising through the granular or lump material through which the preheating pipes extend, the gas comes into contact with the material over a large surface. As before stated, it is desirable to have the gas all consumed at a point well below the top of the column of material, so that no acid will be lost with the gaseous products of the reaction, consisting chiefly of steam, or steam and carbon dioxide, when, as is preferred, the solid material which is to be converted is an oxide or a carbonate. These gaseous products escape from the tower at the top thereof by way of the outlet pipe 17. A pump or suction fan (not shown) may be connected with the pipe to create a partial vacuum in the tower and thus facilitate the flow of gas from the still and through the material in the tower.

To start the reaction, heat may be applied in any convenient way, as by preheating the gas initially or by heating the starting charge. In cases where external heat is needed to start the reaction or to keep up the reaction or maintain a desired reaction velocity, the contents of the reaction vessel may be heated by a gas flame from a suitable burner, as for example the annular burner 18 surrounding the tower 10 at the reaction zone; or the gas may be heated by any convenient means, not shown, between the generating still and the reaction chamber. In such cases the use of the preheating tubes 16 is advantageous in utilizing heat that might otherwise be wasted. Of course where the reaction is

sufficiently exothermic no external heating means is needed and the preheating tube may be dispensed with. Where it is found necessary to control the temperature in the reaction zone to prevent its becoming too high the necessary control may be obtained by pre-cooling the gas, or by an air blast or water spray directed upon the reaction chamber, or by passing water or other cooling fluid through a water jacket around the chamber or through pipes inside of the same. Devices for the purpose being well known we deem it unnecessary to illustrate the same. The temperature at various points in the reaction vessel can be ascertained by means of suitably spaced pyrometers, indicated diagrammatically at 19, 19.

To avoid packing it is desirable to have the solid material in lump or granular form, preferably about three-fourths of an inch in size but not smaller than would pass through a screen having eight meshes to the inch. Where, however, the material available is not suitably granular it may be converted into lump form in any convenient way, as for example by briquetting by pressure. In such case the briquettes are preferably made porous so as to expose a large surface to the gas.

The reaction chamber or vessel may be made of any suitable material, but we prefer mild steel as we have found that it is lasting and, contrary to expectation, does not introduce any appreciable amount of iron impurity into the product.

In the manufacture of aluminum fluoride we use the vertical or tower type of reaction vessel. With such a tower two feet six inches in diameter with its cylindrical portion sixteen feet in height, and with continuous operation, a production of 5,000 to 6,000 pounds of aluminum fluoride per day is easily obtainable. As aluminous material we use preferably an aluminum-oxygen compound, as oxide or hydrate. Both are readily available, and the gaseous product of their reaction with fluorine or hydrogen fluoride (hydrofluoric acid gas) is water vapor, which escapes from the tower without contaminating the product. The preferred form of aluminum is trihydrate which has been calcined at a temperature between about 575° and 1575° F. The material is thus made adsorptive, and we have found that when hydrogen fluoride gas is passed over it, the adsorption of the gas promotes the reaction therebetween to such an extent that it is unnecessary to initially supply heat from an external source in order to start the reaction. From a commercial viewpoint, this discovery is of particular importance since, although the reaction between hydrogen fluoride and non-absorbent aluminum trihydrate is exothermic in character, an initial amount of heat must normally be applied to start the reaction. Thus calcining the aluminum trihydrate, in accordance with our preferred practice, is an important step in eliminating expense in the production of aluminum fluoride. While calcining all the aluminum hydrate is desirable, it is not necessary, and in order to initiate the reaction it is sufficient, where the reaction is carried out in vertical reaction vessels, to place in the bottom of the vessel a layer of calcined hydrate, the reaction between which and the incoming gas will be sufficient to produce an initiating heat to start the exothermic reaction which will then continue whether or not the remaining material entering the reaction zone be initially calcined.

The size of the aluminum compound which is

fed into the vertical reaction vessel is important only in that particles which are too small in size will tend to pack under their own weight to such extent that the fluorin-containing gas will not pass readily throughout the mass. If an agitating type of reaction vessel is used, the size of the material contained therein is not, in general, important. However, in manufacturing aluminum fluoride in a vertical reaction vessel in accordance with preferred practice, it is preferable to use particles of aluminum hydrate of a size of an eighth or a quarter of an inch or larger, and where such particles are not available, we have found that smaller particles of aluminum hydrate may be briquetted together to form aggregates of a size preventing any material "packing" in the reaction vessel. In making such briquettes, we have found that they should be porous to some extent so as to allow free permeation by the gas throughout the briquette structure.

In manufacturing aluminum fluoride according to the methods above outlined and in quantities as large as 30,000 pounds per day, we have produced a product containing from 80 to 90 per cent of aluminum fluoride, about 0.2 per cent of silica, about 0.15 per cent of iron oxid, and about 0.5 per cent of residual water, the balance being Al_2O_3 which, in the ordinary uses of aluminum fluoride, such as in the manufacture of aluminum, is not a harmful impurity. The aluminum fluoride content averaged about 85 per cent.

In obtaining such a product, we have found that loss of fluorin introduced into the process will be negligible,—on an average about 1.3 per cent,—if the fluorin-containing gas is fed to the reaction in a quantity somewhat less than that theoretically required by the chemical reaction taking place between the gas and the aluminous substance. The importance of this feature of our invention will be appreciated when it is remembered that in the prior processes the fluorin loss is about 15 per cent.

In making aluminum fluoride we have found that for satisfactory results the upper limit of working temperature in the reaction zone is about 1300° F. or say about 700° C. At about this temperature the fluoride begins to volatilize and there is also a tendency for the alumina or aluminum hydroxid to undergo a change of physical state and become corundum. In the former case recovery of the volatilized product is difficult and in the latter case the reaction is slowed down. As for the lower limit the temperature should not be much below about 750° F., or 400° C., if good efficiency is desired.

It is in general necessary to control the temperature of reaction in order to maintain it at the preferred temperature. While this may be done by any of several methods, as for instance by artificially cooling the material in the reaction zone as before described, we prefer to mix in the aluminum compound charged into the vessel a suitable amount of aluminum fluoride product of the reaction which serves to dilute the charge and absorb part of the heat of the reaction.

The invention can be employed with marked advantage for the commercial manufacture of the fluorides of various other elements, as for example zinc fluoride, barium fluoride, magnesium fluoride, sodium fluoride, sodium bifluoride, and sodium-aluminum fluoride. We prepare the latter compound (sometimes called artificial cryolite) by treating a mixture of the aluminum and sodium compounds, preferably aluminum oxid

or hydrate and sodium carbonate or soda ash, with hydrofluoric acid gas in a tumbling barrel type of apparatus, operating preferably at a temperature between about 750° and 950° F., or 400° and 510° C., and feeding the gas in at one end and the solid material at the other, the product thus obtained being approximately neutral and containing about 95 per cent pure sodium-aluminum fluoride.

It is to be understood that the invention is not limited to the specific features and procedures herein described but can be carried out in other ways without departing from its spirit as defined by the following claims.

We claim:

1. The method of making fluorin compounds of aluminum which comprises treating with fluorin-containing gas material containing an aluminum compound capable of reacting with the gas, the reacting substances being free of water in the liquid state.

2. The method of making fluorin compounds of aluminum which comprises treating with gaseous hydrofluoric acid material containing an aluminum compound capable of reacting with hydrofluoric acid, the reacting substances being free of water in the liquid state.

3. The method of making aluminum fluoride which comprises passing fluorin-containing gas through material comprising an aluminum compound capable of reacting with the gas, the reacting substances being free of water in the liquid state.

4. The method of making aluminum fluoride which comprises treating aluminum trihydrate with fluorin-containing gas, the reacting substances being free of water in the liquid state.

5. The method of making fluorin compounds of aluminum which comprises passing fluorin-containing gas through material containing an aluminum compound capable of reacting with said gas, and maintaining the material being so treated at a temperature below a point at which any material quantity of aluminum-containing substance present would undergo conversion to corundum, the reacting substances being free of water in the liquid state.

6. The method of making fluorin compounds of aluminum which comprises treating with gaseous hydrogen fluoride material containing an aluminum compound capable of reacting with hydrogen fluoride, and controlling the heat generated by the said treatment, to maintain a temperature below the point at which any aluminum-containing substance present would in appreciable quantity undergo conversion to corundum, the reacting substances being free of water in the liquid state.

7. The method of making fluorin compounds of aluminum which comprises treating with fluorin-containing gas material containing an aluminum compound to react with the gas, and maintaining the substances in reaction at a temperature less than about 700° C., the reacting substances being free of water in the liquid state.

8. The method of making fluorin compounds of aluminum which comprises passing fluorin-containing gas through material containing combined aluminum to react with the gas, and maintaining the substances in reaction at a temperature above about 400° C. and below about 700° C., the reacting substances being free of water in the liquid state.

9. The method of making aluminum fluoride which comprises treating with gaseous hydro-

fluoric acid an aluminum compound capable of reacting with hydrofluoric acid, and controlling the heat of reaction to maintain a temperature between about 400° C. and 700° C., the reacting substances being free of water in the liquid state.

10. The method of making aluminum fluoride which comprises passing fluorin-containing gas through material comprising an aluminum compound capable of reacting with the gas, and maintaining the temperature of reaction above about 400° C. and below a temperature at which any appreciable quantity of aluminum-containing substance present would undergo conversion to corundum, the reacting substances being free of water in the liquid state.

11. The method of making aluminum fluoride which comprises passing gaseous hydrofluoric acid through material comprising an aluminum compound to react with the hydrofluoric acid, the reacting substances being free of water in the liquid state; and maintaining the temperature of reaction below a point at which any appreciable quantity of aluminum-containing substance would undergo conversion to corundum.

12. A process of producing aluminum fluoride, which comprises passing fluorin-containing gas through material comprising aluminum in combined form capable of reacting with the gas, the said material containing calcined aluminum trihydrate capable of adsorbing a quantity of the gas on the initial passage of same through the material, whereby heat is generated to facilitate further reaction of the material with the gas, the reacting substances being free of water in the liquid state.

13. A process of producing compounds of aluminum with fluorin, which comprises admitting a fluorin compound in gaseous form to a vessel enclosing particles of material containing an aluminum compound capable of reacting with the fluorin compound; causing the gas to permeate substantially all portions of the material for thorough reaction therewith; maintaining the reacting substances in the vessel at a temperature above the volatilization point of non-fluorin-containing products of the reaction, and below about 700° C.; and withdrawing from the vessel the said non-fluorin-containing products therein volatilized, the reacting substances being free of water in the liquid state.

14. The method of making fluorides of aluminum which comprises treating with a fluorin compound in gaseous form material containing an aluminum compound capable of reacting with the fluorin compound, the reacting substances being free of water in the liquid state; and maintaining the reacting substances at a temperature between 400° C. and 700° C.

15. The method of making fluorides of aluminum which comprises passing gaseous hydrogen fluoride through material containing a hydrate of aluminum, the reacting substances being free of water in the liquid state.

16. The method of making fluorides of aluminum which comprises treating material containing a hydrate of aluminum with a fluorin-containing acid in gaseous form, whereby reaction of the gas with the material is self-promoted by heat generated exothermically; and maintaining the reacting substances at a temperature below about 700° C., the reacting substances being free of water in the liquid state.

17. In a process of producing compounds of aluminum with fluorin by admitting fluorin-containing gas to a vessel enclosing material con-

taining an aluminum compound capable of reacting with the gas, the step of introducing in the vessel calcined aluminum trihydrate capable of adsorbing a quantity of the gas on the initial admission of the latter to the vessel, whereby heat is generated to facilitate further reaction of the gas with substances in the vessel, the reacting substances being free of water in the liquid state.

18. A process of producing fluorin compounds of aluminum, which comprises admitting fluorin-containing gas into a chamber near one end thereof, said chamber enclosing material containing an aluminum compound capable of reacting with the gas; causing gases containing non-aluminum-bearing products of reaction to flow to the opposite end of the chamber, for withdrawal therefrom; and maintaining the quantity of said material in the chamber greater than necessary to react with all of the supply of gas admitted thereto whereby a zone of greatest reaction is established in the material near the gas-admitting end of the chamber, and the fluorin content of gases arriving at the opposite end of the chamber is rendered inappreciable, the reacting substances being free of water in the liquid state.

19. A process of producing fluorin compounds of aluminum which comprises admitting fluorin-containing gas into an upright chamber, near the lower end thereof, said chamber enclosing particles of material containing combined aluminum to react with the gas; withdrawing solid products of reaction at the lower end of the chamber, and introducing further quantities of material containing combined aluminum through characteristic means at the upper end of the chamber; and maintaining in the chamber a body of said material greater than necessary to react with all of the supply of gas admitted thereto, whereby a zone of reaction is established near the lower end of the chamber, and escape of an appreciable quantity of fluorin-containing gas on introduction of material through the aforesaid introducing means is prevented, the reacting substances being free of water in the liquid state.

20. A process of producing fluorides of aluminum which comprises admitting a flow of gas comprising a fluorin-containing acid into an upright converter near the lower end thereof, said converter enclosing particles of material containing an aluminum compound capable of reacting with the fluorin-containing acid; withdrawing solid products of reaction at the lower end of the converter; and introducing through the upper end of the converter further quantities of the aforesaid material to maintain in the converter a body of material greater than necessary to react with all of the supply of gas admitted thereto, whereby a zone of reaction is maintained near the lower end of the converter and the escape of any appreciable quantity of fluorin containing gas through the upper surface of the body of material in the converter is prevented, the reacting substances being free of water in the liquid state.

21. The method of making a fluorin compound of aluminum and sodium which comprises treating with fluorin-containing gas material containing aluminum and sodium compounds capable of reacting with the gas, the reacting substances being free of water in a liquid state.

22. The method of making sodium-aluminum fluoride which comprises treating with gaseous hydrofluoric acid, material containing aluminum

and sodium compounds capable of reacting with the hydrofluoric acid, the reacting substances being free of water in a liquid state.

23. The method of making sodium-aluminum fluoride which comprises treating with gaseous hydrogen fluoride a mixture of aluminum hydrate

and sodium carbonate, and maintaining the temperature of the reacting materials below about 700° C., the reacting substances being free of water in the liquid state.

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