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PROCESS FOR PRODUCING HYDROFLUORIC ACID.

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1,316,569.

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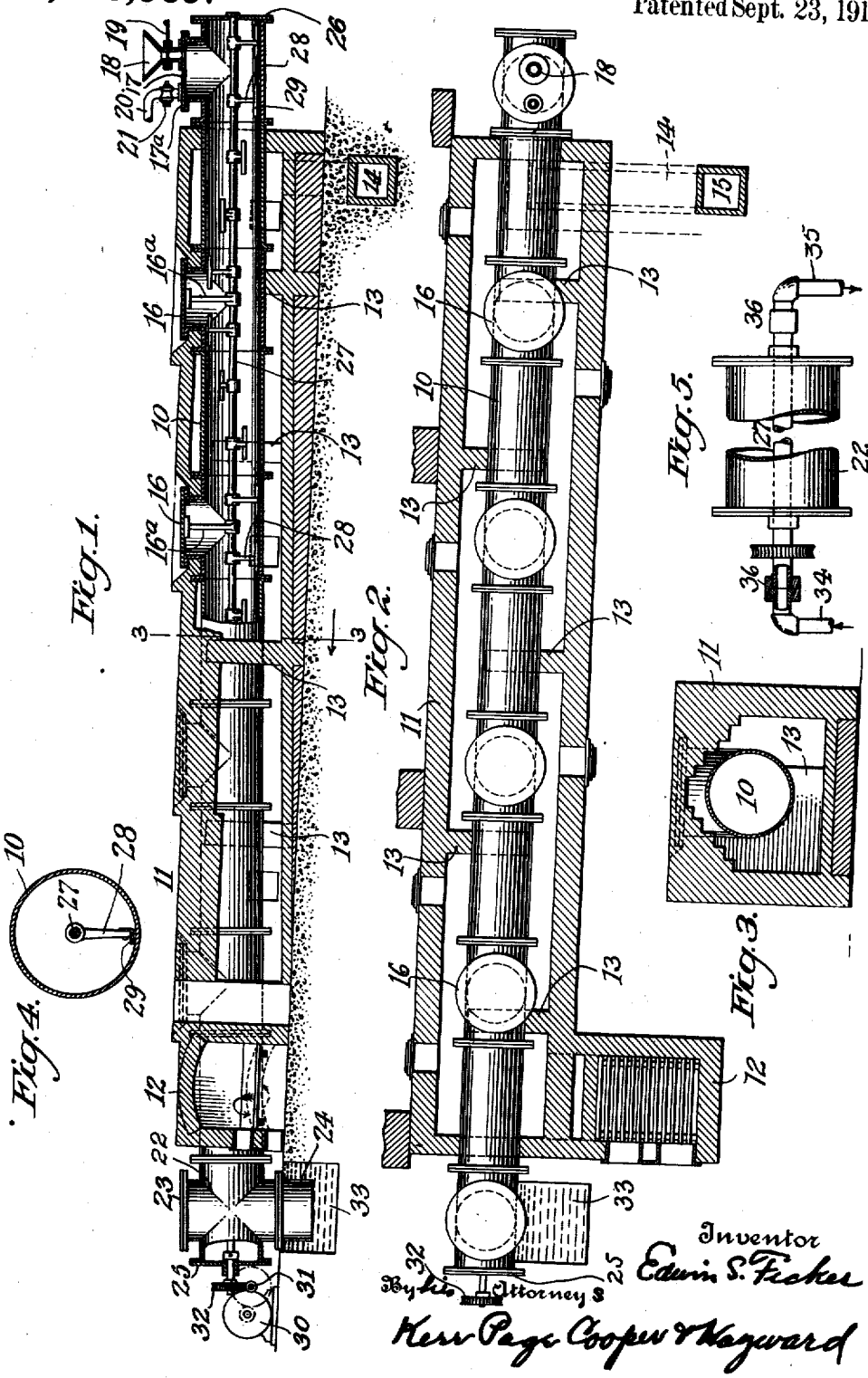


Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

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PROCESS FOR PRODUCING HYDROFLUORIC ACID.

1,316,569. Specification of Letters Patent. Patented Sept. 23, 1919.

Original application filed March 31, 1914, Serial No. 828,436. Divided and this application filed October 8, 1918. Serial No. 257,329.

To all whom it may concern:

Be it known that I, EDWIN S. FICKES, a citizen of the United States, residing at Pittsburgh, in the county of Allegheny and State of Pennsylvania, have invented certain new and useful Improvements in Processes for Producing Hydrofluoric Acid, of which the following is a full, clear, and exact description.

The invention which constitutes the subject matter of this application is a division of my copending application, Serial No. 828,436, filed March 31, 1914, and relates to a method for the production of hydrofluoric acid continuously, more rapidly, and more economically on a commercial scale than has heretofore been possible.

Broadly speaking the process consists in feeding the material through an elongated stationary retort, agitating it and subjecting the same continuously to the action of heat which increases gradually in temperature in the direction of the movement of the material through the retort and taking off the hydrofluoric acid as fast as formed. The reagents, which are fluorspar and sulfuric acid, may be fed to the retort at one end thereof either intermittently or continuously and the residue ($CaSO_4$) may be removed from the opposite end in like manner. I have found that in employing a stationary retort provided with a continuous agitator comprising paddles or scrapers, a very thorough mixing of the reagents may be accomplished, and this in conjunction with the action of the heat, which increases gradually in temperature in the direction of movement of the material, not only enables the latter to gradually stiffen as it moves along the retort, but very effectively prevents said material from baking into a hard mass or from sticking to the side of the retort. The paddles also serve to expose any undecomposed fluorspar to the action of heat and also keep the latter continuously scraped off the walls of the retort. Furthermore by employing a stationary retort it is a very simple matter to maintain the walls thereof fluid tight, thereby preventing the escape of any hydrofluoric acid fumes into the air or into the furnace gases, the detrimental and obnoxious effects of which are very well understood. A better understanding of the process may be had by a specific description of one form of apparatus by which the process is carried out in practice, as illustrated in the accompanying drawing, in which—

Figure 1 is a longitudinal vertical section.

Fig. 2 is a sectional plan view.

Fig. 3 is a cross section on line 3—3 of Fig. 1, omitting the agitator or mixer with which the apparatus is preferably equipped.

Fig. 4 is a detail cross section, on a larger scale, of the tubular retort, showing the agitator.

Fig. 5 is a detail view showing means for cooling the shaft of the agitator or mixer.

The still illustrated consists, in general, of a long, tubular, stationary retort 10, inclosed in a suitable housing or setting 11, by which a gaseous heating medium is passed along the retort, which medium may be the hot products of combustion from a furnace or fire chamber 12. Vertical baffles 13, extending alternately from opposite sides of the setting cause the smoke and gases to take a more or less tortuous course, thereby giving a more efficient utilization of the heat. At the end opposite the fire chamber the products of combustion flow downwardly and laterally through a flue 14 to the stack, shown in horizontal section at 15, Fig. 2.

In the present instance, the retort 10, preferably inclined downward toward the fire chamber, for example at an angle giving about a half-inch fall per foot of length, is formed of cast iron pipe-sections, the straight sections alternating with the T sections. The latter are turned up, and are provided with suitable closures, as 16, removably secured by any convenient means not shown. These lids or closures 16 may also be used to support hangers 16^a for the shaft of the agitator, described hereinafter. The closure 17^a on the T 17 at the upper end of the retort, is provided with means for supplying the necessary acid producing material, continuously or intermittently. In the drawing I have shown a simple hopper 18, with a gate valve 19, by which convenient quantities of material can be delivered into the retort at proper intervals. The closure 17^a also has an outlet pipe 20 to carry off the hydrofluoric acid vapor and conduct the same to a suitable condenser, not shown. The pipe, which is preferably made of lead or lined with lead, is provided with a valve 21 to regulate the rate of outflow.

At its lower end the retort terminates in a cross 22, having at the top a removable

closure 23 and at the bottom a pipe 24 extending below the surface of the water in the pit 33, forming a water-seal. Any other form of seal may be provided. Journaled in the end closures 25, 26, is a shaft 27 extending through the retort at the axis thereof and provided with helically arranged radial arms 28 equipped at their ends with paddles or scrapers 29 close to, but preferably not touching, the walls of the retort. At the lower end the shaft is connected with suitable driving mechanism, as for example an electric motor 30, by means of a worm 31 and worm gear 32.

Fluorspar and sulfuric acid in suitable proportions, are fed into the hot stationary still or retort at the upper end through the hopper 18. In the retort it is thoroughly mixed by the revolving paddles 29, and gradually stiffens as it moves slowly down into the hotter parts. Finally it breaks up, part into powder and part into small balls or rounded lumps. Meanwhile, the reaction between the calcium fluorid and the sulfuric acid goes on, yielding hydrofluoric acid (hydrogen fluorid, HF) in the form of vapor, and calcium sulfate ($CaSO_4$) as a solid residue. The former goes off through the lead pipe 20; while the residue, as fast as it reaches the cross 22, falls into the pit 33 and is removed from time to time in any convenient way. If necessary to push the residue out, the lid 23 may be removed for the purpose.

The proportions of calcium fluorid and sulfuric acid may vary widely in practice. Theoretically they should be in equal parts (by weight) but as natural calcium fluorid (fluorspar) is always impure, equal parts would involve more or less waste of the sulfuric acid, as a part of the latter would simply volatilize and escape. More definite proportions cannot be given, since different lots of fluorspar vary greatly in impurity content, but the most economical proportions can easily be determined by analysis or trial or by both.

The temperature inside the retort or still at the hottest parts should not be less than about 315° C. (600° F.), but may be increased to any degree which will not injure the retort or soften the agitator shaft so as to cause it to twist, bend, or spring. To prevent overheating of the shaft and permit higher temperatures to be used, the shaft may be hollow, as in Fig. 5, for the purpose, if desired, of carrying water or other cooling medium supplied to the lower end by a pipe 34 and discharged at the upper end by a pipe 35. The couplings 36 are of any suitable kind, permitting the shaft to turn. This shaft should, in most cases, revolve quite slowly. If the rate of progress is too fast the mixture is heated too rapidly and causes volatilization of the sulfuric acid, thus resulting in a loss of fluorin and giving a considerable amount of sulfuric acid in hydrofluoric acid condensed. If the retort is inclined, with the inlet for the fluorspar and sulfuric acid at the higher end, the axis of the retort, as the inclination of paddles or scrapers 29 may be parallel to the latter, together with the agitation produced by the paddles, will cause the material to move through the retort at a fast enough rate.

The hydrofluoric acid being given off gradually as the mixture progresses, the process is in effect continuous even when the raw material is supplied intermittently.

Actual use of the invention has demonstrated its superiority over any processes known at the present time employed for the same purpose.

What I claim is:

1. The process for the production of hydrofluoric acid which consists in continuously moving fluorspar and sulfuric acid in a substantially horizontal direction through a stationary elongated retort, continuously heating and agitating the same in their passage through the retort, and taking off the hydrofluoric acid vapors as fast as formed.

2. The process for the production of hydrofluoric acid which consists in simultaneously agitating and continuously moving fluorspar and sulfuric acid in a substantially horizontal direction through a stationary elongated retort, heating the same as they are passing through the retort, taking off the hydrofluoric acid vapors as fast as formed, and discharging the residue from said retort.

3. The process for the production of hydrofluoric acid which consists in simultaneously agitating and continuously moving fluorspar and sulfuric acid through a stationary elongated retort, continuously heating the same in their passage through the retort, and taking off the hydrofluoric acid vapors as fast as formed.

4. The process for the production of hydrofluoric acid which consists in supplying the raw material at one end of a stationary elongated retort, continuously moving and agitating the same along the length of the retort, taking off the hydrofluoric acid vapors as fast as formed, and discharging the residue at the other end of the retort.

5. The process for the production of hydrofluoric acid which consists in supplying the raw material at one end of a stationary elongated retort, continuously moving and agitating the same along the length of the retort while subjecting the same to heat increasing in temperature in the direction of the flow of the material, taking off the hydrofluoric acid vapors as fast as formed, and discharging the residue at the other end of the retort.

6. The process for the production of hydrofluoric acid which consists in moving fluorspar and sulfuric acid in a substantially horizontal direction through an elongated retort, continuously heating and stirring the same in their passage through the retort, and taking off the hydrofluoric acid vapors as fast as formed.

7. The process for the production of hydrofluoric acid which consists in moving fluorspar and sulfuric acid continuously through an elongated retort, heating the material during its passage through said retort, simultaneously stirring the material to keep the same stripped from the walls of the retort and to give the heat freedom of action upon substantially all portions of the material, and taking off the hydrofluoric acid vapors as fast as formed.

8. The process for the continuous production of hydrofluoric acid which consists in moving fluorspar and sulfuric acid in a substantially horizontal direction through an elongated retort, heating the material during its passage through the retort, constantly stirring the material in its passage to prevent its baking into hard masses, continuously stripping from the inner walls of the retort any material adhering thereto to enable a free transfer of the heat to any undecomposed fluorspar, and taking off the hydrofluoric acid as fast as formed.

9. The process for the continuous production of hydrofluoric acid which consists in continuously moving fluorspar and sulfuric acid in a substantially horizontal direction through an elongated retort, subjecting the material in the retort to heat increasing in temperature in the direction of movement of the material, constantly stirring the material in its passage to prevent its baking into hard masses, continuously stripping from the inner wall of the retort any material tending to adhere thereto to enable a free transfer of the heat to any undecomposed fluorspar, and taking off the hydrofluoric acid vapors as fast as formed.

In testimony whereof I hereunto affix my signature.

EDWIN S. FICKES.

Correction in Letters Patent No. 1,316,569.

It is hereby certified that in Letters Patent No. 1,316,569, granted September 23, 1919, upon the application of Edwin S. Fickes, of Pittsburgh, Pennsylvania, an error appears in the printed specification requiring correction as follows: Page 2, transpose lines 71 and 72 as now numbered; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 21st day of October, A. D., 1919.

[SEAL.]

M. H. COULSTON,

Acting Commissioner of Patents.

Cl. 23—1.