No. 877,247. PATENTED JAN. 21, 1908.

E. A. SPERRY.

METHOD OF MAKING STANNIC CHLORID.

APPLICATION FILED MAR. 5, 1906.

4 SHEETS—SHEET 1.

Fig. 1.

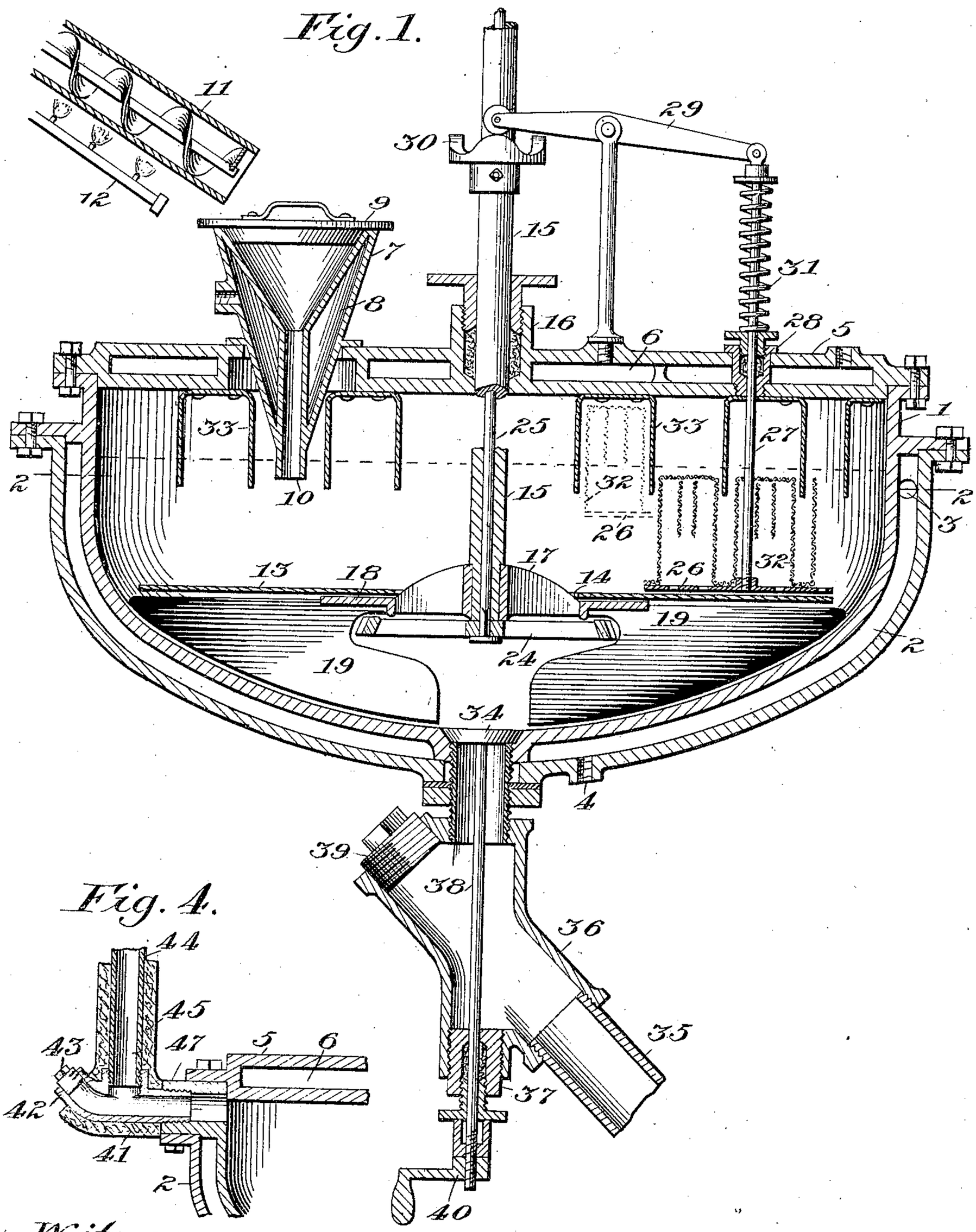

Fig. 4.

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4 SHEETS—SHEET 2.

Fig. 2.

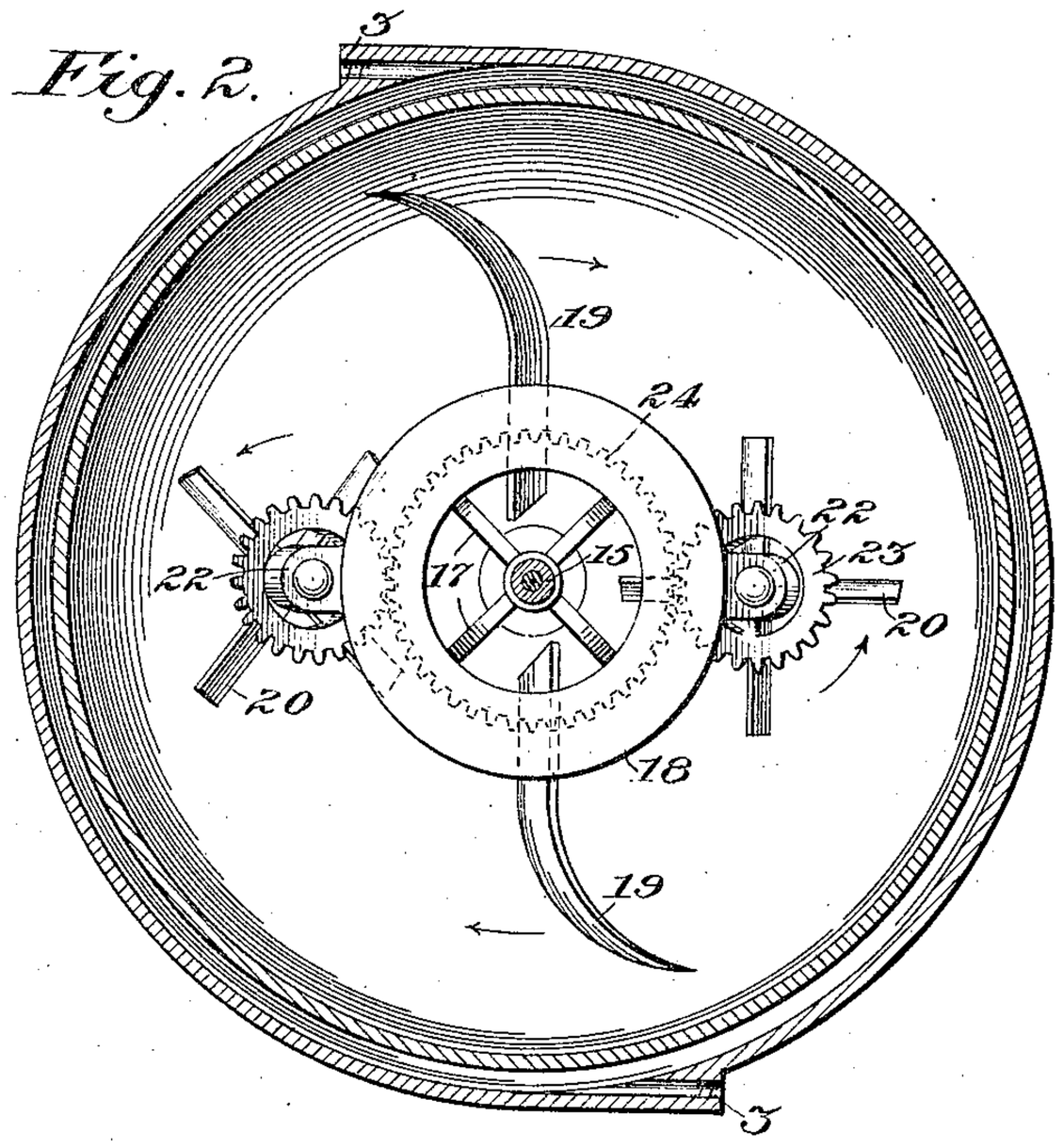
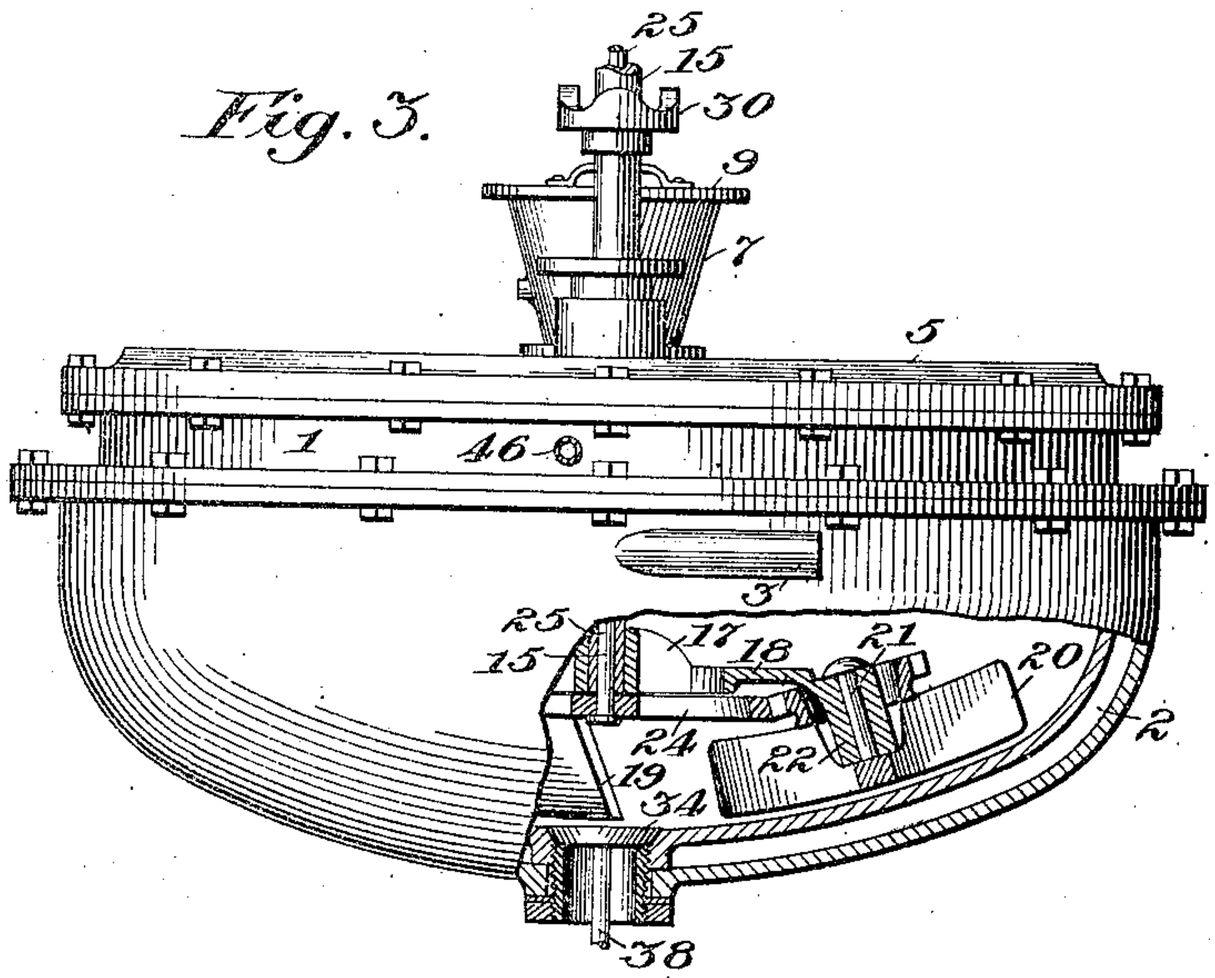


Fig. 3.



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4 SHEETS—SHEET 3.

Fig. 5.

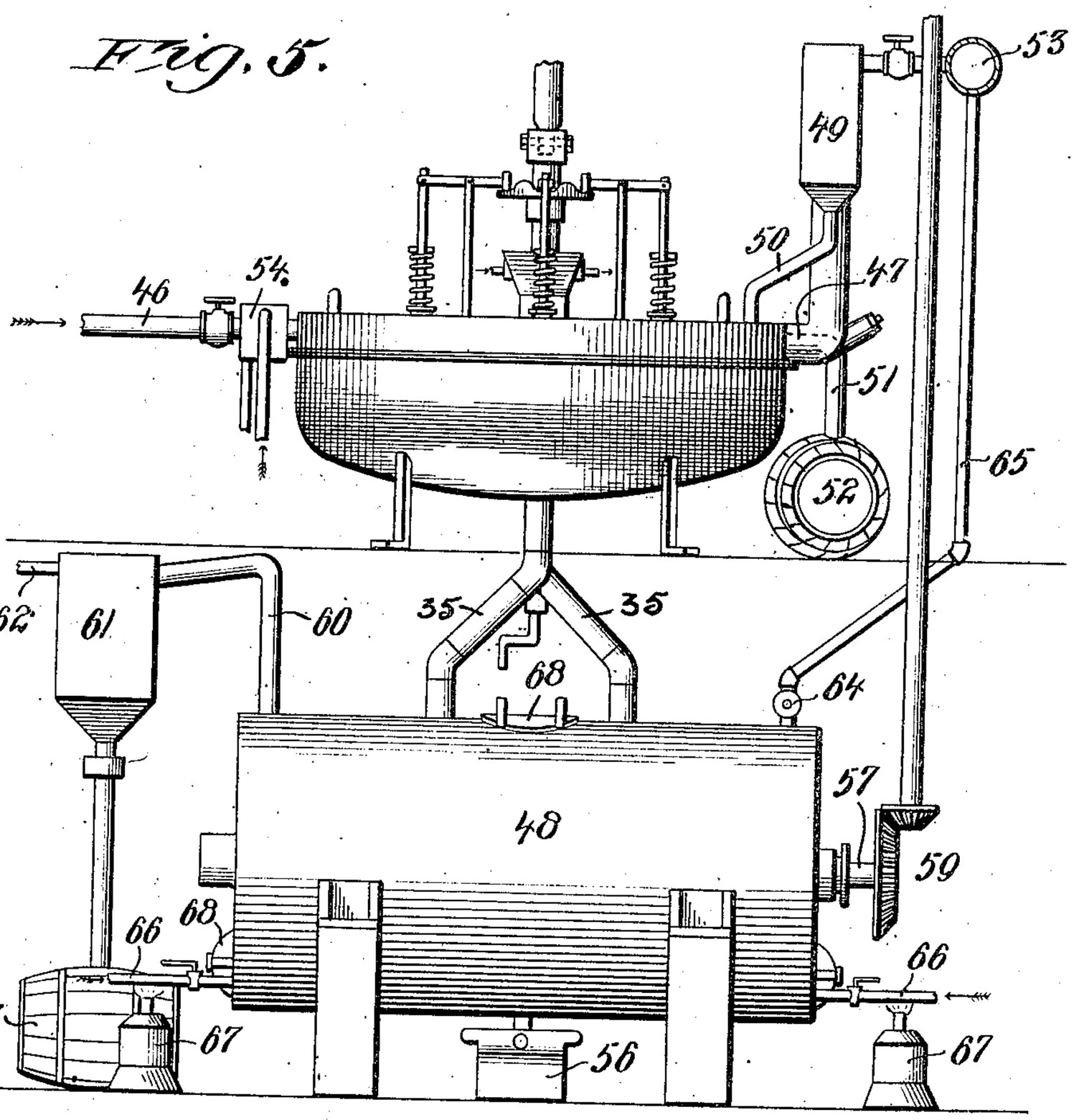
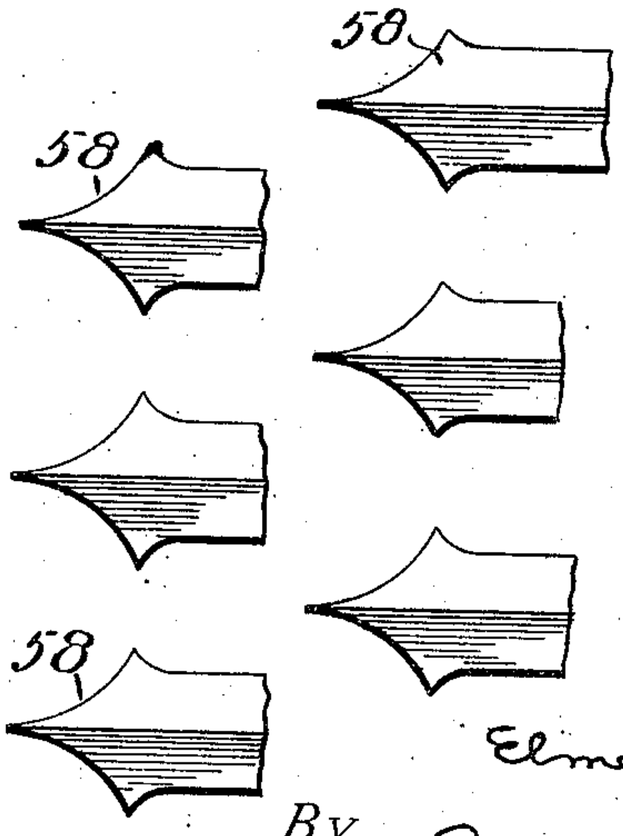


Fig. 8



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4 SHEETS—SHEET 4.

Fig. 6.

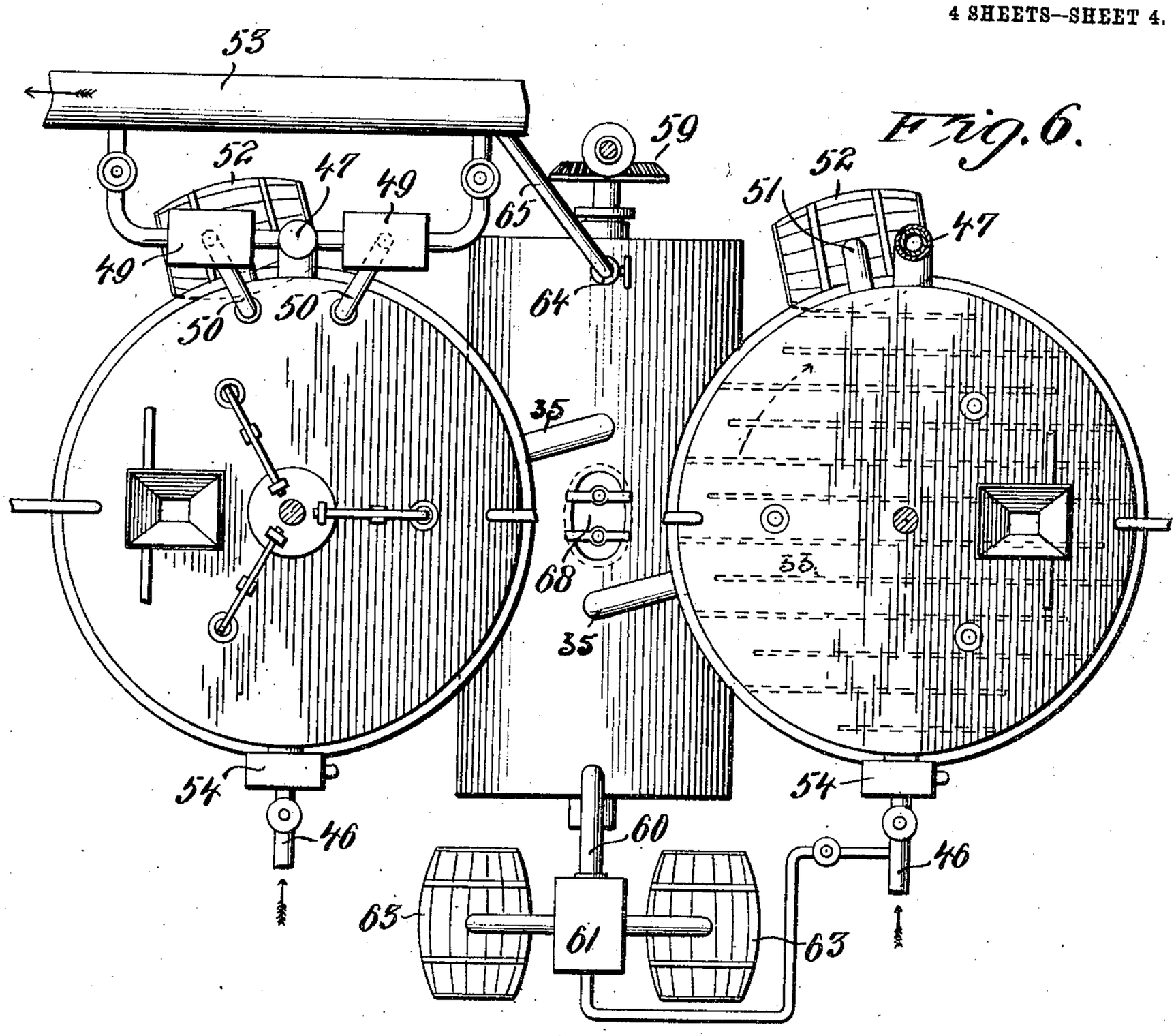
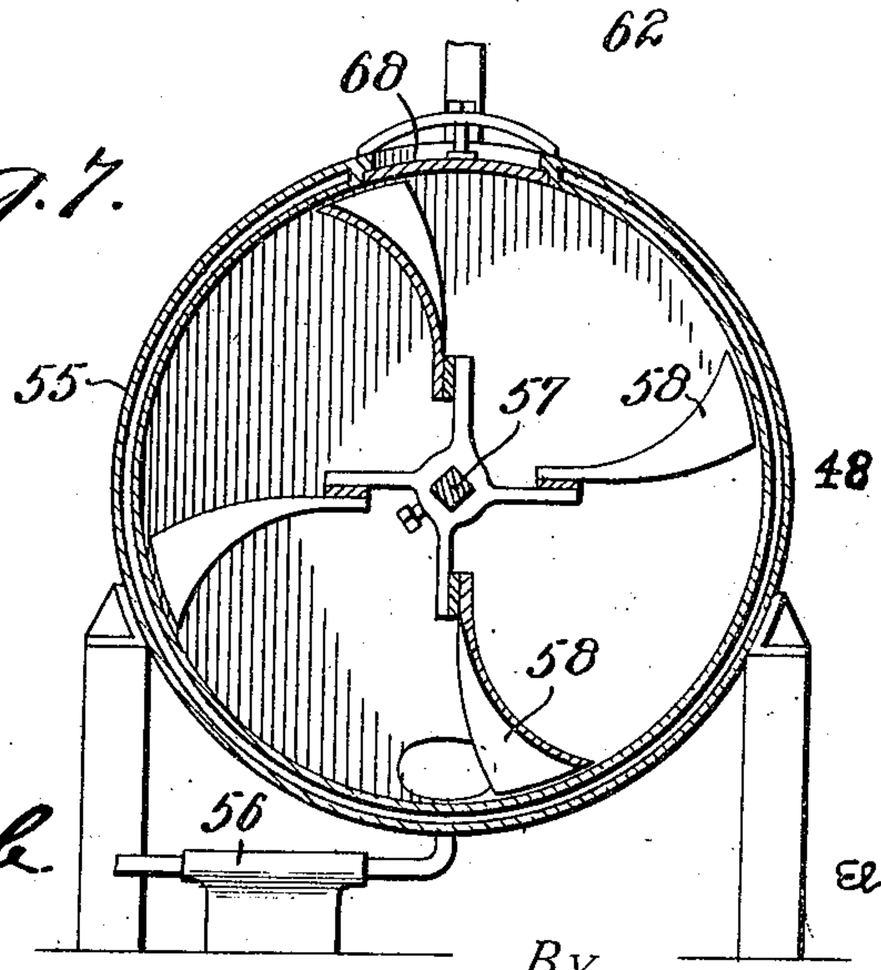


Fig. 7.



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UNITED STATES PATENT OFFICE.

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METHOD OF MAKING STANNIC CHLORID.

No. 877,247. Specification of Letters Patent. Patented Jan. 21, 1908.

Application filed March 5, 1906. Serial No. 304,328.

To all whom it may concern:

Be it known that I, ELMER A. SPERRY, a citizen of the United States, residing at Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in Methods of Making Stannic Chlorid, of which the following is a specification.

This invention is a method of making stannic chlorid by reaction between chlorin and metallic tin or a body containing the same.

According to my invention a material consisting wholly or in part of metallic tin, hereinafter referred to as a tin-bearing material, is brought into contact with liquid stannic chlorid and preferably is maintained in suspension therein, said liquid stannic chlorid being exposed to contact with chlorin under conditions favorable to the absorption of the gas. The stannic chlorid is preferably circulated in contact with the chlorin; portions of the same may be exposed as films to the gas; and those portions at which the gas absorption occurs are preferably mantained at a lower temperature than the region of reaction for the purpose of promoting the gas absorption. For this purpose I may provide divided but communicating bodies of stannic chlorid, which may be located in a single reaction vessel, and to effect a rapid interchange of liquid between said bodies.

For a full understanding of my invention reference is made to the accompanying drawings, wherein;

Figure 1 is a central longitudinal section of a form of reaction vessel for carrying my method into effect; Fig. 2 is a horizontal section of the same on a somewhat smaller scale on line 2—2 of Fig. 1, the septum and reciprocating devices being removed; Fig. 3 is a side elevation on the same scale as Fig. 2, parts being broken away, and the septum and disk-reciprocating devices removed; Fig. 4 is a detail section of one of the gas connections; Fig. 5 is a side elevation of a plant for the production of stannic chlorid, in accordance with my process; Fig. 6 is a plan view of the same; Fig. 7 is a vertical transverse section of the still; and Fig. 8 is a diagrammatic view illustrating the arrangement of lifting blades in the still.

1 represents a relatively shallow vessel which may be constructed of cast-iron or lead, or which may be constructed of or lined with any material adapted to resist chlorin and stannic chlorid. I have observed that iron is especially suited for this purpose, and shows no evidences of attack even when the chlorin supplied contains moisture. The body of the vessel is provided with a jacket 2 having tangential inlets 3, 3 for steam or water, and an outlet 4, this arrangement being found to insure a substantially even heating or cooling effect. The cover 5 is removable, and is provided with interior passages 6 for a temperature controlling medium. The cover supports a removable hopper 7 jacketed as shown at 8 for heating the contents thereof; the hopper is provided with a cover 9 and depends into the vessel as shown at 10 to a sufficient depth to be sealed by the liquid therein. Charging means 11 located above the hopper are preferably provided with means, indicated at 12, for heating the incoming material.

13 is a septum, suitably supported within the vessel, and illustrated as a horizontal ring-shaped disk, spaced from the walls of the vessel at its periphery and having a central aperture 14. A hollow shaft 15 extends through a stuffing-box 16 in the cover and carries at its lower end arms 17 supporting an annular disk 18 to which are secured lifting and stirring blades 19. These blades are preferably two in number and are oppositely disposed, the effect of this arrangement, together with the conformation of the blades, being to produce a wave action at the surface of the liquid, the purpose of which is to expose an extended surface of the same as hereinafter more fully explained. The blades extend approximately to the bottom of the vessel and are forwardly inclined in the direction of movement in such manner as to exert a lifting action on its liquid or solid contents; the outer ends of the blades may be curved backward as shown, the design being such as to insure an equal distribution of the materials with which they come in contact. The blades serve to impart to the liquid contents of the vessel a movement of circulation which in the particular form of device illustrated is outward beneath the disk 13 and inward above the same. The disk 13 may be carried by the shaft 15 and rotate therewith if desired. Between the blades 19 I preferably mount agitating devices, the purpose of which is to maintain finely divided solid matter in suspension in the circulating liquid,

and to agitate it violently in contact therewith. As one form of agitating device I have shown inclined blades 20 mounted near the bottom of the vessel and adapted to the curvature of the same, carried by a shaft 21 supported in a bearing in a lug 22 on the disk 18. A gear 23 secured to the blades 20 meshes with a stationary gear 24 carried by a fixed shaft 25 disposed within the rotating shaft 15. As the agitating devices, of which two are shown, revolve with the disk 18 they rotate in their bearings 22 in the direction indicated by the arrows and thoroughly agitate the liquid and commingle the solids therewith. The effect of this arrangement is to maintain solids even when of relatively high specific gravity in suspension in the liquid.

Above the septum 13 I prefer to mount a perforated disk 26 and to provide means for reciprocating the same in a vertical direction, the means shown comprising a plurality of rods 27, of which one only is shown, secured to the disk 26 and extending through stuffing boxes 28 in the cover; downward movement is imparted to the disk by a lever 29 actuated by a cam 30 on the shaft 15; a spring 31 serves to return the disk to its upper position. The disk 26 serves to maintain the solids in suspension in the portion of the liquid above the septum 13, and further serves to support a plurality of strips or pieces of wire-gauze or equivalent fabric or suitable structure 32, the function of which is to lift the liquid above its normal level and to expose extended surfaces of the same to the action of the gas in the upper portion of the vessel. The character and material of the liquid-exposing devices 32 will depend upon the materials treated; they should be substantially unattacked by the gas or the solvent liquid, and should possess such structure as to be capable of retaining a film of the liquid, thereby exposing both surfaces thereof for absorption of the gas. Perforated sheets or fabrics, whether metallic or otherwise, may be available for this purpose, or any device which will carry the liquid into the gas space will fulfil this function.

In order to improve the intimacy of contact between gas and liquid I prefer to direct the former in a restricted path above the latter, and for this purpose I provide baffles or depending partitions 33 extending transversely across the vessel and adapted to be sealed by the liquid therein. The arrangement of the baffles is such as to direct the gas in a tortuous path between the inlet and outlet 46, 47. In addition to their function in directing the gas the partitions 33 coöperate with the circulating blades 19, in that they are in position to be wetted by the waves produced by these blades, thus exposing a constantly renewed liquid film or surface to the gas; during the reaction period stannic chlorid condenses on the under surface of the cover and flows down the deflectors 33 and the walls of the vessel, this furnishing another means for the renewal of this film.

34 represents a discharge valve closing the upper end of the discharge conduit 35; the latter is illustrated as of special construction, comprising an angular cross 36 of which the lower aperture carries a stuffing box 37 for the valve stem 38, while one of the lateral apertures carries a removable plug 39 for convenience in cleaning. The stem 38 may be reciprocated through the stuffing box for operating the valve, and carries at its lower end a handle 40 by means of which the valve may be rotated for the purpose of grinding it to its seat or for clearing it from matter which would interfere with its seating. This feature is of particular value in valves for the discharge of finely divided solid matters.

In Fig. 4 I have shown in detail a preferred form of gas connection, comprising a pipe 41 having an upwardly inclined outer end 42, a removable closure 43 therefor, and a branch pipe 44 for the gas. The purpose of the upward inclination of the ends is to permit inspection or cleaning of the pipe 41 without danger of loss of the liquid contents of the vessel. At 45 I have shown a heat-insulating covering which is applied to the gas outlet pipe and which serves to prevent condensation or separation therein of any volatile reaction products; by properly covering said pipe I find that I am enabled to substantially prevent clogging of the same, as, for instance, by the separation of hydrated stannic chlorid in the production of stannic chlorid as hereinafter referred to. The liquid outlet in a vessel provided with circulating and agitating means may be substantially similar in construction, except that a downward turned branch pipe is provided; such outlet may be located somewhat above the normal liquid level, the wave action above referred to being sufficient for the discharge of any accumulation of liquid.

In most cases it is desirable that the gas-absorbing surfaces of the liquid should be maintained at a lower temperature than the reaction zone where the absorbed gas is brought into contact with the solid matter, it being well understood that absorption or solution of the gas is more rapid at lower temperatures. In the present construction this is provided for by means of the water-cooled cover through which heat is abstracted not only from the gas chamber itself but from the partitions 33, which serve as above pointed out as supplemental surfaces for the exposure of films of liquid. By means of the jacket 2 such temperature is maintained in the region of reaction as is most favorable under the particular conditions.

Referring to Figs. 5–8 I have shown the general arrangement of a plant comprising two reaction vessels 1, 1 arranged to dis-

charge through their outlets 35 into a still 48. Chlorin enters the vessels at 46, passes therethrough in a tortuous path between baffles 33 indicated in dotted lines in Fig. 6, and escapes, together with any associated or entrained stannic chlorid, to the condensers 49. It is in part condensed therein and the liquid chlorid is permitted to flow back into the reaction vessel through pipes 50. 51 is an overflow for the chlorid, which may, as above stated, be somewhat above the normal liquid level, the stannic chlorid, together with some tin-bearing material or residue in suspension, being discharged through pipe 51 into a receptacle 52, from which it may be transferred to the still 48. The effect of the return-flow 50 and the overflow 51 is to maintain a substantially constant volume of material in the reaction vessel throughout the operation. When the reaction is complete the valve 34 is lifted to discharge the contents of the vessel into the still. Any chlorid which passes through the condensers 49 is permitted to pass through conduit 53 to a suitable scrubber in which it is absorbed by water or other solvent.

The chlorin may in practice contain considerable moisture, in which case a deposition of hydrated stannic chlorid is liable to occur in the inlet of pipe 46: to prevent clogging from this cause I prefer to provide heating means, as a steam jacket 54, near the point of entry of the gas. I have observed that even when moist chlorin is passed over the surface of liquid stannic chlorid as herein described, there is no accumulation of hydrated chlorid in the reaction vessel, but that such hydrated chlorid as is formed is entrained by the gases and passes therewith to the condensers 49 from which it is readily removed. The chlorid formed contains dissolved chlorin and suspended matter or residue, the latter usually consisting in case the original tin-bearing material was a crude metal-bearing powder such as is obtained by detinning scrap, of tin oxid associated with metallic iron, iron oxid and other impurities. The chlorid and residue are collected in the still 48. This still is provided with a steam jacket 55 having a trapped outlet 56. A shaft 57, carrying lifting blades or plows 58, is mounted for rotation therein, being driven by any suitable means shown as bevel gears 59. The blades 58 are mounted on the shaft in staggered relation as diagrammatically indicated in Fig. 8, so as to effectually lift all portions of the contents in the still. These moving blades are found to greatly expedite the separation of chlorin from the chlorid, the subsequent distillation of the latter, and also the separation of the chlorid from any residue in the still. This portion of my method is preferably conducted as follows: The stannic chlorid in the still, containing dissolved chlorin and usually a quantity of solid matter representing the residue of the reaction in vessel 1, is heated under conditions of agitation to expel chlorin which is permitted to pass through pipe 60, condenser 61, and thence by pipe 62 to the reaction vessel 1. Thereafter the stannic chlorid is distilled, liquefied in condenser 61, and collected in suitable receptacles 63, agitation of the contents of the still being preferably continued, and any uncondensed chlorid being returned to the system through pipe 62. When condensation has substantially ceased, cock 64 in the pipe 65 leading from the still to the conduit 53 may be opened, and air conducted to the still through pipes 66 in opposite ends of the same. This air is drawn into the still by a suction fan (not shown) operating in connection with the scrubber, and is preferably heated, heating means being indicated as torches 67. The effect of this admission of air, together with the agitation of the residue, is to accomplish the complete separation of stannic chlorid from the residue.

In case a crude tin-bearing material is treated the dry residue is removed from the still, in which suitable apertures 68 are provided, and is treated in accordance with its character. A residue derived from the treatment of tin powder from detinning operations, and containing in addition to other substances, metallic iron and tin oxid, is preferably first subjected to treatment, as by magnetic separation of the iron, to concentrate the tin-bearing portions; these portions are thereafter smelted and the metal suitably granulated or subdivided is returned to the reaction vessels for the conversion of the tin into stannic chlorid. This method of treating the residues is further advantageous because it renders it unnecessary to convert all of the metallic tin into stannic chlorid in the vessels 1 at a single operation, any unconverted portions being returned to the vessel with the smelted residue: it will be understood that toward the end of the reaction the combination proceeds less rapidly, and that this method of procedure involves a considerable saving of time.

I claim:—

1. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, and bringing chlorin into contact with said liquid.

2. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, and passing chlorin in an elongated path over the surface of the liquid.

3. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, agitating said liquid and bringing chlorin into contact therewith.

4. The method of making stannic chlorid

which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, agitating said liquid, and passing chlorin in an elongated path over the surface of the liquid.

5. The method of making stannic chlorid which consists in circulating a body of liquid stannic chlorid, maintaining a tin-bearing material in suspension in one portion thereof, and bringing chlorin into contact with another portion of said body.

6. The method of making stannic chlorid which consists in providing divided but communicating bodies of anhydrous stannic chlorid, a tin-bearing material being in contact therewith, establishing a circulation between said bodies, and bringing chlorin into contact therewith.

7. The method of making stannic chlorid which consists in providing divided but communicating bodies of liquid stannic chlorid, maintaining a tin-bearing material in suspension therein, establishing a circulation between said bodies, and bringing chlorin into contact therewith.

8. The method of making stannic chlorid which consists in circulating a body of liquid stannic chlorid, maintaining a tin-bearing material in suspension in the lower portion thereof, and bringing chlorin into contact with the upper portion of said body.

9. The method of making stannic chlorid which consists in circulating a body of liquid stannic chlorid, maintaining a tin-bearing material in suspension in one portion thereof, bringing chlorin into contact with another portion, and maintaining the portion in contact with the chlorin at a lower temperature than the portion in contact with the tin-bearing material, whereby absorption of the gas is promoted.

10. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, bringing chlorin into contact with said liquid, and removing the heat produced by reaction.

11. The method of making stannic chlorid which consists in heating chlorin and causing the same to react on a tin-bearing material in presence of anhydrous stannic chlorid.

12. The method of making stannic chlorid by means of chlorin containing moisture which consists in heating the chlorin to a temperature sufficient to prevent accumulation of hydrated stannic chlorids, and causing the heated chlorin to react on a tin-bearing material in presence of anhydrous stannic chlorid.

13. The method of making stannic chlorid which consists in heating a tin-bearing material and reacting on the same with chlorin in presence of anhydrous stannic chlorid.

14. The method of making chlorids of tin which consists in heating a tin-bearing material, introducing the heated material into a body of anhydrous stannic chlorid, and reacting on the same with chlorin.

15. The method of making stannic chlorid which consists in reacting with chlorin on a tin-bearing material in presence of a body of anhydrous stannic chlorid, condensing stannic chlorid vapors, and returning the same to said body.

16. The method of making stannic chlorid which consists in reacting with chlorin on a tin-bearing material in presence of a body of liquid stannic chlorid, conducting the stannic chlorid vapors from the reaction vessel, and retaining the heat in said vapors leaving said vessel, thereby preventing deposition of crystalline hydrated stannic chlorid in the vapor connections.

17. The method of making stannic chlorid which consists in reacting with chlorin on a tin-bearing material in presence of a body of anhydrous stannic chlorid, condensing stannic chlorid vapors and returning the same to said body, and continuously removing stannic chlorid to maintain the volume of the same.

18. The continuous method of making stannic chlorid which consists in supplying a tin-bearing material to a body of liquid stannic chlorid, maintaining it in suspension therein, continuously admitting chlorin into contact with said liquid, and withdrawing the stannic chlorid together with the residue of the reaction.

19. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, exposing a film of said liquid above the surface of the same, and bringing chlorin into contact with said film.

20. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, exposing and constantly renewing a film of said liquid above the surface of the same, and bringing chlorin into contact with said film.

21. The method of making stannic chlorid which consists in agitating a body of liquid stannic chlorid, maintaining a tin-bearing material in suspension therein, exposing a film of said liquid above the surface of the same, and bringing chlorin into contact with said film.

22. The method of making stannic chlorid which consists in agitating a body of liquid stannic chlorid, maintaining a tin-bearing material in suspension therein, exposing films of said liquid above the surface of the same, and directing chlorin in a tortuous path above the surface of the liquid in contact with said films.

23. In a method of making stannic chlorid, the step of separating stannic chlorid from the residue, which consists in preventing

cementing of the residue by agitating the same, and simultaneously expelling the chlorid by heat.

24. In a method of making stannic chlorid, the step of separating stannic chlorid from the residue, which consists in applying heat to said residue by a medium out of contact therewith and simultaneously subjecting the residue to a current of gas.

25. In a method of making stannic chlorid, the step of purifying anhydrous stannic chlorid from dissolved chlorin, which consists in agitating the liquid and simultaneously expelling chlorin therefrom.

26. In a method of making stannic chlorid, the step of purifying stannic chlorid from dissolved chlorin, which consists in agitating the liquid and simultaneously expelling chlorin therefrom, and then distilling the residual stannic chlorid and condensing it.

27. In a method of making stannic chlorid, the step of treating the residues which consists in removing stannic chlorid therefrom, concentrating the tin-bearing portions, and returning the concentrate to the process.

28. In a method of making stannic chlorid, the step of treating the residues which consists in removing stannic chlorid therefrom, smelting the remaining portions and returning the same to the process.

29. In a method of making stannic chlorid, the step of treating the residues which consists in removing stannic chlorid therefrom, concentrating the tin-bearing portions, smelting the concentrate and returning the same to the process.

30. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, bringing chlorid into contact with said liquid, purifying the stannic chlorid from chlorin by agitating it and simultaneously expelling chlorin by heat, then distilling the liquid stannic chlorid and condensing it, concentrating the tin-bearing portions of the residue, smelting the concentrate, and returning the same to the process.

31. The method of making stannic chlorid which consists in maintaining a tin-bearing material in suspension in liquid stannic chlorid, bringing chlorin into contact with said liquid, purifying the stannic chlorid from chlorin by agitating it and simultaneously expelling chlorin by heat, then distilling the liquid stannic chlorid and condensing it, agitating the residue and expelling the chlorid by heat, concentrating the tin-bearing portions of the residue, smelting the concentrate, and returning the same to the process.

In testimony whereof, I affix my signature in presence of two witnesses.

ELMER A. SPERRY.

Witnesses:
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C. P. TOWNSEND.