

Aug. 28, 1956

G. R. FINDLAY ET AL

2,760,858

PROCESS FOR PRODUCING METALS IN PURIFIED FORM

Filed Oct. 22, 1951

4 Sheets-Sheet 1

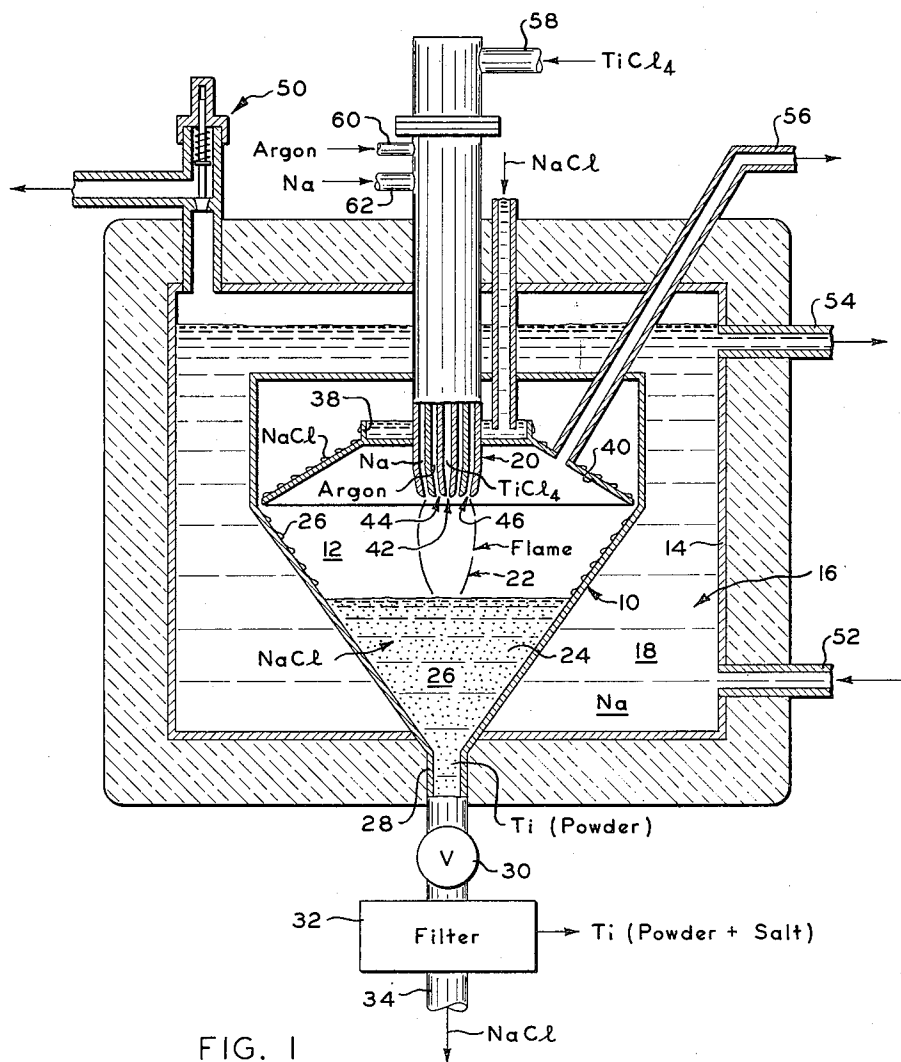


FIG. 1

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4 Sheets-Sheet 2

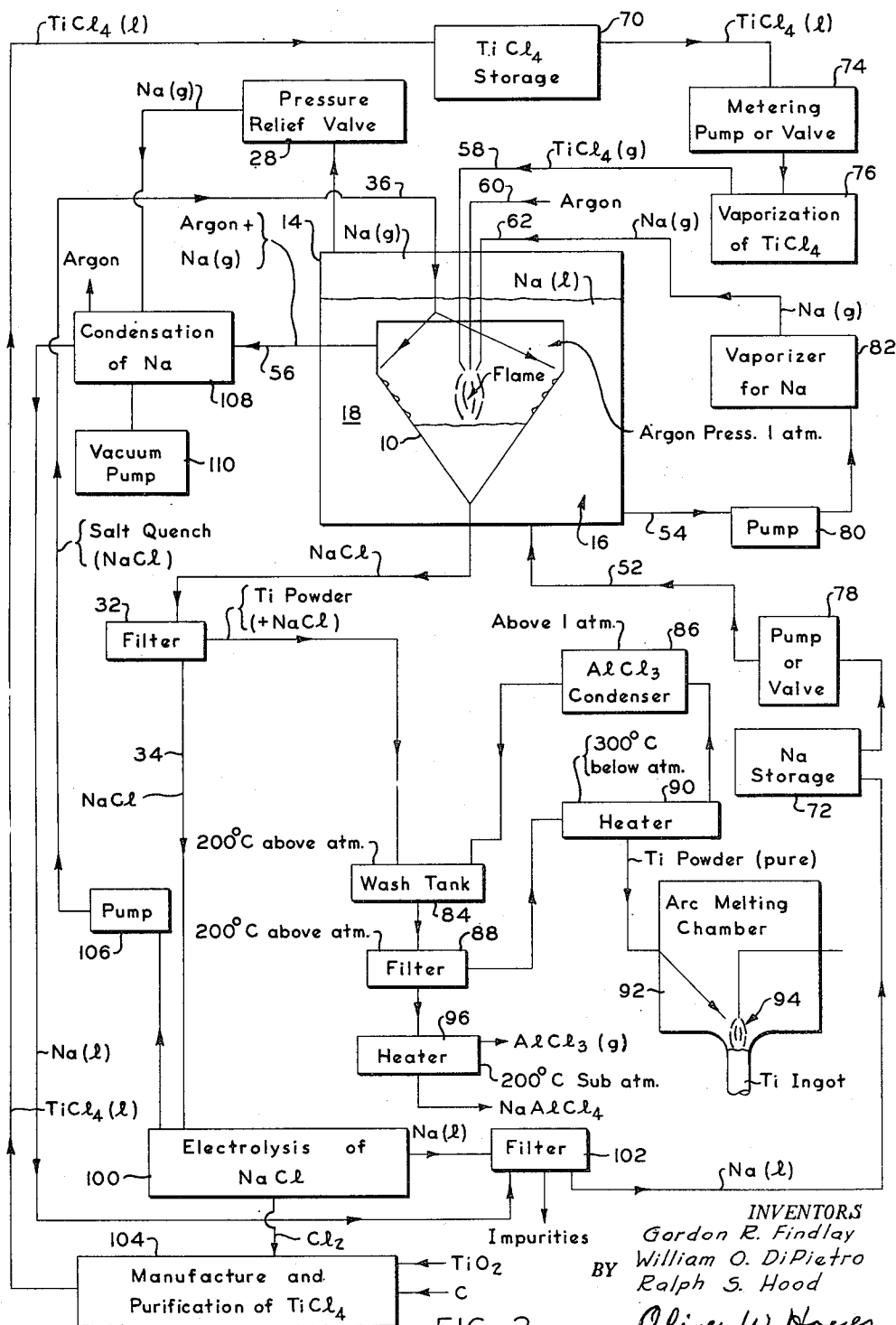
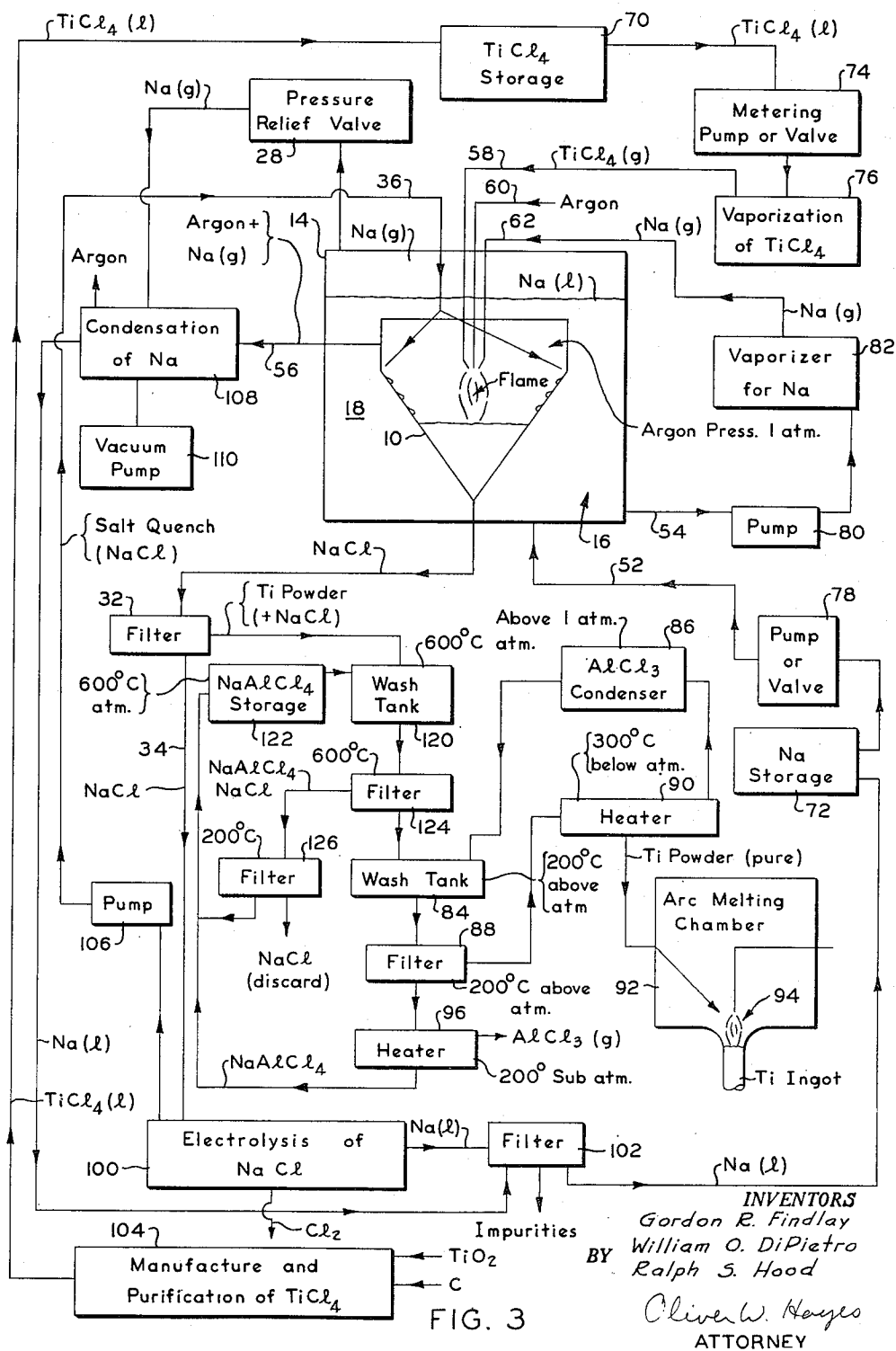


FIG. 2

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4 Sheets-Sheet 4

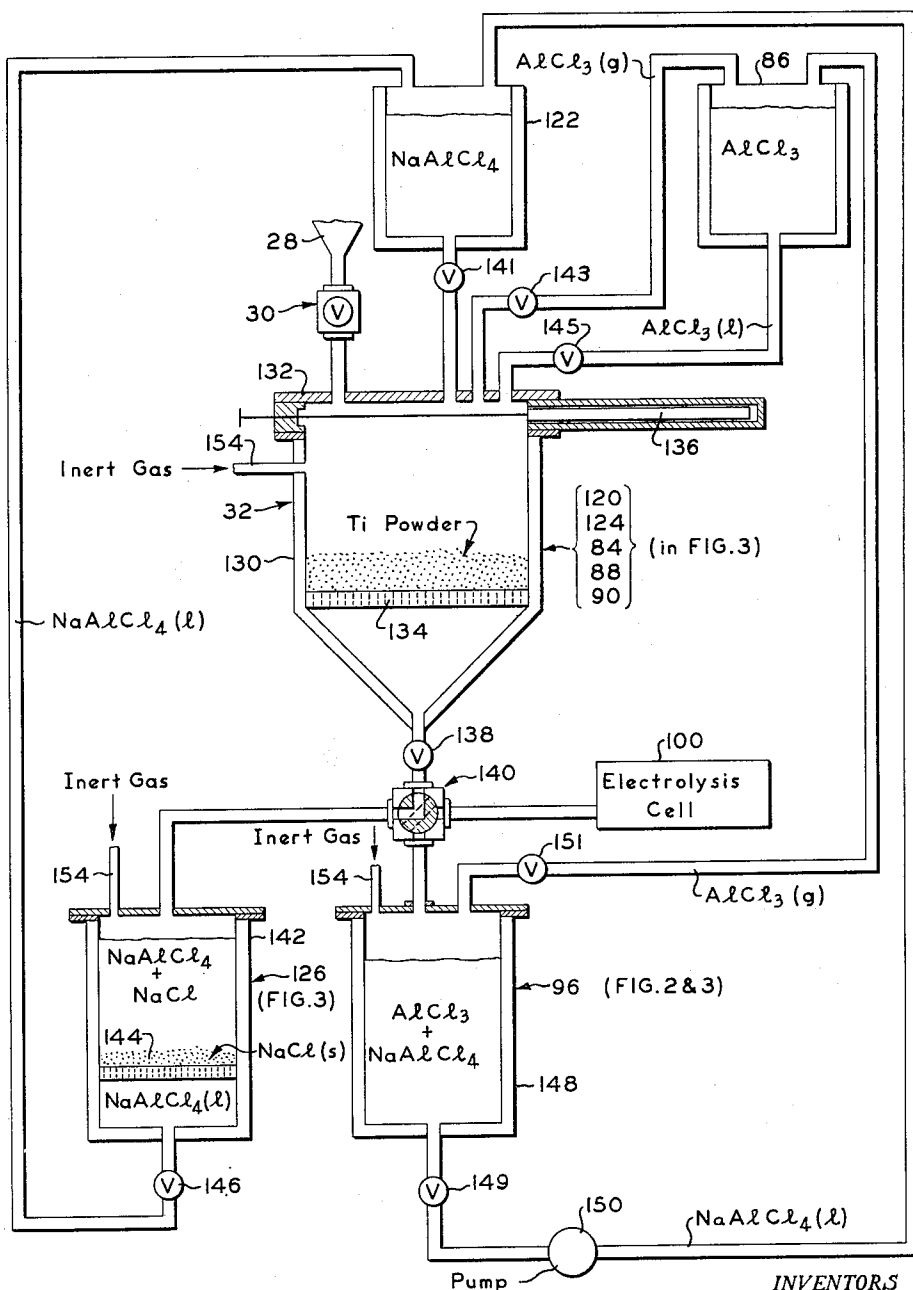


FIG. 4

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PROCESS FOR PRODUCING METALS IN PURIFIED FORM

Gordon R. Findlay, Bedford, William O. Di Pietro, Watertown, and Ralph S. Hood, Marblehead, Mass., said Hood assignor of one-third to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware, said Findlay and said Di Pietro assignors of two-thirds to National Research Corporation, Cambridge, Mass., a corporation of Massachusetts

Application October 22, 1951, Serial No. 252,564

11 Claims. (Cl. 75-84.5)

This invention relates to the production of metals in relatively pure form and more particularly to the separation of metals, such as titanium and the like, from a slurry of the metal powder in a fused salt.

A principal object of the present invention is to provide an improved process for obtaining, in relatively pure powdered form, metals such as titanium, zirconium and the like which are relatively easily contaminated by oxygen, carbon, and nitrogen.

Another object of the present invention is to obtain such metals in ingot or coalesced form free from oxides, nitrides, and carbides.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic, schematic, sectional view of one portion of an apparatus embodying the present invention;

Fig. 2 is a flow sheet showing one method of practicing the present invention;

Fig. 3 is a flow sheet showing an alternative method of practicing the present invention; and

Fig. 4 is a diagrammatic, schematic, sectional view of another portion of the apparatus of the present invention.

Many of the processes which have been proposed for producing metals, such as titanium, zirconium and the like, give the product metal in the form of a fine powder imbedded in a salt.

The Kroll process (U. S. Patent 2,205,854) and the various improvements thereon (e. g., U. S. Patent 2,564,337) produce titanium or zirconium powder or sponge suspended in a salt. In the prior art there have been numerous suggestions as to the treatment of such suspensions of titanium powder so as to remove the salt therefrom. Two principal methods have been employed. The first of these is vacuum leaching and the second is water leaching. Vacuum leaching is satisfactory from the standpoint of purity of the product, but the high cost thereof is undesirable. Water leaching tends to contaminate the product with oxygen, particularly when the particle size is less than 100 microns in diameter. In the present invention the advantages of vacuum leaching, from the standpoint of purity, are combined with the relatively low cost typical of water leaching.

The present invention will, for simplicity of illustration, be initially described in connection with the purification of a titanium powder suspended in sodium chloride, this product resulting from a gas phase reduction of titanium

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tetrachloride by sodium vapors. The superior results mentioned above, which are obtained by the present invention, are achieved by first mechanically separating the titanium powder from the bulk of the contaminating salt (i. e., sodium chloride in the specific embodiment under consideration). This is preferably accomplished by filtering a molten slurry of the sodium chloride carrying the suspended titanium powder. The thus purified titanium powder will contain about one-third to one-half of the total weight thereof in the form of the contaminating sodium chloride. The resultant partially purified titanium is then washed with a great excess of a wash salt which is liquid at relatively low temperatures. This wash salt is preferably one which is capable of substantially completely displacing the relatively high-melting, low vapor pressure contaminating salt (i. e., sodium chloride). In one embodiment of the invention (Fig. 2), this wash salt is one which has a high vapor pressure at a relatively low temperature and which also has a high solubility for the contaminating salt. In this case the wash salt may be an aluminum trihalide such as aluminum trichloride. In another embodiment of the invention (Fig. 3), the initial wash salt is a low-melting-point, complex salt such as sodium aluminum tetrachloride (NaAlCl_4 or $\text{NaCl} \cdot \text{AlCl}_3$). This sodium aluminum tetrachloride is utilized to dissolve the sodium chloride. The resultant slurry of titanium in the liquid aluminum tetrachloride is then filtered. The remaining sodium aluminum tetrachloride is then washed out of the titanium powder by using a large excess of a high vapor pressure salt such as aluminum trichloride.

In either case the bulk of the aluminum trichloride is separated from the titanium powder by filtration, and the residual aluminum trichloride is then evaporated from the titanium powder, preferably by heating to a relatively low temperature under subatmospheric pressure so that the aluminum trichloride is sublimed from the titanium. From the standpoint of simplicity, the washing step utilizing only the aluminum trichloride has the advantage that fewer operations are required. However, it does have the disadvantage that sodium chloride forms a compound with the aluminum trichloride which has a considerably lower vapor pressure than the aluminum trichloride. This compound is the sodium aluminum tetrachloride which is utilized as the initial wash salt in the second of the two alternative processes outlined above.

Referring now to Fig. 1 there is illustrated one preferred embodiment of a reactor for producing titanium in the form of a fine powder carried in a molten stream of a salt such as sodium chloride. In this figure, where like numbers refer to like elements in the other figures, the reaction vessel is indicated generally at 10 as defining an air-free reaction chamber 12. Surrounding the reaction vessel 10 there is an outer vessel 14 defining a space 16 with the reaction vessel 10. A heat-exchange liquid 18, preferably sodium, is provided in the space 16. The product titanium powder 24 is preferably produced in the reaction chamber by means of a "torch" 20 which serves to introduce the vapors of sodium and titanium tetrachloride, for example, into the reaction chamber so that they intermix and react with a highly exothermic reaction to form a flame generally indicated at 22. In this flame, titanium tetrachloride is reduced by the sodium to form molten titanium droplets 24 which are frozen in the form of a powder by a pool of molten salt 26 confined within the bottom part of the reaction chamber 12. This molten salt 26 may be the sodium chloride formed as a by-product of the reduction of titanium tetrachloride by sodium. The amount of this salt 26 may be increased, however, by introducing a quantity of molten sodium chloride into the reaction chamber so as to maintain the walls of the reaction chamber wet by this salt, and to protect these walls from the

high temperatures generated by the reaction. The molten salt, carrying the fine titanium powders in a suspension therein, is removed from the reaction chamber through a pipe 28 in the bottom thereof, the flow of molten salt from the reaction chamber being controlled by means of a valve 30. The molten salt and titanium powder passing through the valve 30 enter a filter 32 where most of the molten salt is separated from the titanium powder, this molten salt leaving the filter through the pipe 34.

In a preferred embodiment of the invention molten salt is fed into the reaction chamber to cool the walls of the reaction chamber and to quench the by-product sodium chloride vapors within the reaction chamber. This molten "quench" salt is preferably introduced through a pipe 36, the salt being distributed, by means of a weir 38, over a conical baffle 40 which guides the salt to the periphery of the wall of the reaction vessel 10 so that this wall is uniformly wet by the molten salt.

Titanium tetrachloride vapors are introduced through a central opening 42 in the "torch" 20 and the sodium vapors are introduced through an outer cylindrical opening 46 in the "torch." Argon is preferably introduced into the reaction chamber 12 between the points of introduction of the sodium and the titanium tetrachloride vapors, this argon entering through an intermediate cylindrical opening 44.

The temperature of the walls of the reaction vessel 10 is preferably maintained at above the melting point of sodium chloride by providing a suitable pressure relief valve 50 for controlling the vapor pressure of the heat-exchange liquid 18 surrounding the reaction vessel 10. As mentioned previously, this heat-exchange liquid is preferably sodium and the heat transferred to the sodium from the reaction vessel 10 may be utilized for preheating the sodium prior to vaporization thereof. The sodium is introduced into the space 16 by means of pipe 52, and is withdrawn therefrom through a pipe 54.

The reaction chamber 12 is also provided with a pipe 56 through which the reaction vessel 10 may be evacuated prior to commencement of a run, and through which any excess sodium vapors may be removed from the reaction chamber for condensation outside of the reaction chamber. Suitable pipes 58, 60 and 62 are provided for feeding, respectively, titanium tetrachloride, argon, and sodium into the "torch."

Referring now to Fig. 2 there is illustrated a schematic flow sheet which sets forth the various steps in one preferred embodiment of the process. This Fig. 2 also shows the auxiliary equipment preferably provided in connection with the reactor of Fig. 1. In this figure like numbers refer to like elements in the other figures. This Fig. 2 is directed to that embodiment of the invention where a single wash salt is employed for purifying the titanium powder. As illustrated, there is provided a storage tank 70 for holding titanium tetrachloride, and a storage tank 72 for holding liquid sodium. Liquid titanium tetrachloride is fed by means of a pump or metering valve 74 from the storage tank 70 to a titanium tetrachloride vaporizer 76. Liquid sodium is fed by means of a pump or valve 78 into the space 16 surrounding the reaction vessel 10, and is removed therefrom by means of a pump 80. From the pump 80 the sodium is fed into a vaporizer 82. The sodium vapors and the titanium tetrachloride vapors are fed into their respective openings in the "torch" through the pipes 62 and 58, respectively.

As mentioned previously, the titanium powder 24 and the by-product contaminating salt 26 (e. g., NaCl) are removed from the reactor by means of pipe 28 which leads into the filter 32. As the liquid sodium chloride passes through the filter 32 the titanium powder remains on the filter and is separated from the bulk of the sodium chloride. The titanium-free sodium chloride leaving the filter 32 then passes to an electrolysis chamber 100 where the sodium chloride is electrolyzed to sodium and chlo-

rine. Any very small titanium particles in the effluent sodium chloride leaving the filter 32 may be removed prior to reaching the electrolysis cell 100 by bubbling chlorine gas through the salt containing these titanium fines to convert the titanium to titanium tetrachloride.

The titanium powder leaving the filter 32 will be contaminated with from about one-half to one-third its total weight by sodium chloride depending upon the particle size. The titanium powder passes from filter 32 into a wash tank 84 where sodium chloride is washed from the titanium powder by means of liquid aluminum trichloride from an aluminum trichloride storage tank 86. The washing operation in the wash tank 84 preferably takes place at a relatively low temperature, on the order of several hundred degrees centigrade, and at a pressure above atmosphere so as to maintain the aluminum trichloride in a liquid phase. This washing is preferably a countercurrent washing and the sodium chloride-titanium powder mixture is preferably dumped into a relatively large batch of the aluminum trichloride liquid so that the titanium powder, with its contained sodium chloride, does not freeze into a solid mass from which the sodium chloride is difficultly dissolved. The aluminum trichloride will form sodium aluminum tetrachloride with the sodium chloride contaminating salt and thus remove the sodium chloride from the titanium powder. When the washing in the tank 84 is carried out in a countercurrent manner, a large excess of aluminum trichloride is used in the final wash so that the percentage of sodium aluminum tetrachloride in the final wash bath is extremely low, preferably on the order of less than 5%. The same is true when a series of batch washes is employed.

The washed titanium powder, suspended in aluminum trichloride, is then filtered by means of filter 88 so that the titanium powder is collected with perhaps 50% of the total weight thereof as aluminum trichloride. This titanium powder is then transferred to the heater 90 which is at a temperature on the order of 300° C. At this point the titanium powder, contaminated with aluminum trichloride, is heated under a subatmospheric pressure so that the aluminum trichloride is rapidly sublimed from the titanium powder. From the heater 90 the titanium powder is fed into the feed hopper of an arc-melting chamber 92 where it is melted in an arc 94 to form a titanium ingot. One preferred type of arc-melting chamber is that described in the copending application of Findlay, Serial No. 235,535, filed July 6, 1951, now U. S. Patent 2,709,842. Other melting techniques, such as that shown in U. S. Patent 2,564,337 may equally be used.

The aluminum trichloride which has been utilized for washing the sodium chloride out of the titanium powder is passed through a heater 96 which is maintained at a sufficiently high temperature and low pressure so that the sodium aluminum tetrachloride therein is liquid and the aluminum trichloride is vaporized therefrom. This aluminum trichloride is then recirculated to the aluminum trichloride storage tank 86. The sodium aluminum tetrachloride residue from the heater 96 may be taken to a second heater (not shown) where the temperature is raised above the decomposition temperature (about 800° C.) of the sodium aluminum tetrachloride to drive substantially all of the aluminum trichloride therefrom. The sodium chloride resulting from this last heating step may be discarded or fed to the sodium chloride electrolysis cell.

The general over-all arrangement of elements of Fig. 2 also includes the previously mentioned electrolysis cell 100 in which the by-product sodium chloride is electrolyzed to sodium and chlorine. The resultant sodium is taken from the electrolysis cell 100 through a filter 102, where impurities such as oxides are removed, and is returned to the sodium storage tank 72. The chlorine generated in electrolysis cell 100 is introduced into a titanium tetrachloride plant 104 where titanium tetra-

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chloride is manufactured by well-known techniques, such as by the chlorination of titanium dioxide in the presence of carbon. The resultant titanium tetrachloride is purified and introduced into the titanium tetrachloride storage tank 70.

For quenching the by-product sodium chloride vapors in the reaction chamber, sodium chloride may be pumped from the electrolysis cell 100, by means of a pump 106, up to the line 36 which introduces this molten sodium chloride into the reaction chamber as described more fully in connection with the discussion of Fig. 1. If desired, a low-melting eutectic salt may be used for this quench.

A condenser 108 is preferably included for condensing excess sodium vapors passing through the pressure relief valve 28 and also coming out of the reaction vessel 10 through the pipe 56. In order to prevent the formation of lower chlorides during the reduction of the titanium tetrachloride, it is preferred that an excess of sodium over that stoichiometrically required be utilized. A vacuum pump 110 may be provided for initially removing substantially all of the air from the reaction vessel 10, from sodium condenser 108, and from the associated piping. It should be readily apparent that oxygen and nitrogen must be kept out of the reaction chamber, otherwise the product titanium will be sufficiently contaminated by oxygen and nitrogen so as to make the product commercially useless.

Referring now to Fig. 3 there is shown an additional modification of the process illustrated in Fig. 2. In the Fig. 3 process a preliminary wash step is utilized wherein the contaminating sodium chloride is dissolved in a complex salt which has a relatively low melting point. This complex salt is preferably sodium aluminum tetrachloride which is formed when sodium chloride and aluminum trichloride are mixed together. The use of this salt has the advantage that it is relatively inert, both to sodium chloride and to aluminum trichloride, and may be conveniently recycled so as to provide a minimum of loss of the relatively expensive aluminum trichloride. In Fig. 3 where like numbers refer to like elements in the other figures, it can be seen that a preliminary wash tank 120 is inserted in the line leading from the gross filter 32 to the aluminum trichloride wash tank 84. In this wash tank 120 the titanium powder, contaminated with sodium chloride, is washed by a large excess of sodium aluminum tetrachloride (at about 600° C.) introduced into tank 120 from storage tank 122. This wash step is also preferably a countercurrent washing and the sodium chloride content in the wash solution is reduced to a very low percentage. The powder is also preferably added to the wash salt to prevent freezing of the sodium chloride. After essentially all of the sodium chloride has been washed from the titanium powder, the bulk of the sodium aluminum tetrachloride is removed from the titanium powder by filtering in a second filter 124. The titanium powder, which is now contaminated with only sodium aluminum tetrachloride, is then introduced into the wash tank 84 where it is washed with aluminum trichloride as fully described in connection with the operation of Fig. 2.

The sodium chloride-sodium aluminum tetrachloride resulting from the washing of the initially contaminated titanium powder is introduced into a filter 126 where the liquid is cooled to a temperature well below the freezing point of the dissolved sodium chloride. The sodium aluminum tetrachloride is thus separated from the sodium chloride solid particles and is recycled to the storage tank 122. The sodium chloride from filter 126 is preferably discarded.

The remaining steps illustrated in Fig. 3 are essentially identical to those illustrated in Fig. 2, with the exception that the sodium aluminum tetrachloride recovered from the heater 96 may be recycled to the sodium aluminum tetrachloride storage tank 122.

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Referring now to Fig. 4 there is shown one schematic form of apparatus for accomplishing the various steps illustrated in Fig. 3 a number of these steps being performed in a single apparatus rather than in different pieces of equipment as illustrated in Fig. 3. In Fig. 4, where like numbers refer to like elements in the other figures, the filter 32 is illustrated as comprising a double-walled filter chamber 130 having a removable top 132. Positioned within this chamber 130 is a reinforced fine metal filter 134 which is arranged to collect all of the titanium powder introduced into the filter chamber 130 from the reactor. This filter 134 is preferably a micro-metallic, sintered, stainless steel filter. The filtering efficiency of the filter 134 may be improved by use of a filter aid such as titanium wool or titanium granules. The filter chamber 130 is provided with a vacuum-tight valve 136 at the top thereof, and another vacuum-tight valve 138 at the bottom thereof. These valves 136 and 138 are so arranged as to provide a vacuum-tight chamber therebetween which can be removed from the system so that the titanium powder contained in the chamber 130 may be dumped in to the feed hopper of arc melting chamber 92. In normal operation of the filter chamber 130, the valve 138 is usually open and the flow of liquid through the chamber 130 is controlled by a three-way valve 140. As can be seen, in one position of this valve 140, the filter chamber 130 may be emptied directly into the sodium chloride electrolysis cell 100. In another position of the valve 140, the liquid contents of the chamber 130 may be dumped into a second double-walled chamber 142 in which sodium chloride may be crystallized out of a solution of sodium chloride in sodium aluminum tetrachloride. This second filter chamber 142 contains therein a filter element 144 for filtering out crystallized sodium chloride. A valve 146 is provided at the bottom of filter chamber 142, this valve permitting the sodium aluminum chloride in chamber 142 to be transferred to the sodium aluminum tetrachloride storage chamber 122.

In another position of the valve 140 at the bottom of the main filter chamber 130, the liquid contents from chamber 130 may be directed into a heater chamber 148 (corresponding to heater 96 of Figs. 2 and 3) in which aluminum chloride may be evaporated from a mixture of aluminum chloride and sodium aluminum tetrachloride.

A number of valves are provided, in addition to those previously mentioned, for controlling the flow of liquid into the chamber 130, and for providing escape of vapors therefrom. A first valve 141 is provided for controlling the introduction of sodium aluminum tetrachloride from chamber 122 into the main filter chamber 130. A second valve 143 provides for passage of aluminum trichloride vapors from main filter chamber 130 to the aluminum trichloride storage chamber 86, while a third valve 145 provides for introduction of liquid aluminum trichloride into the main filter chamber 130 from the aluminum trichloride supply 86. Additionally, a valve 149 provides for removal of sodium aluminum tetrachloride from the heater 148, this sodium aluminum tetrachloride being pumped by pump 150 back to the storage tank 122. A valve 151 permits passage of gaseous aluminum trichloride from heater 148 to the aluminum trichloride storage chamber 86.

From the above description of Fig. 4 it should be apparent that the main filter chamber 130 corresponds to the filter 32 of Figs. 1, 2 and 3, and also serves the functions of the wash tank 120, the filter 124, the wash tank 84, the filter 88, and the heater 90 of Fig. 3. In a similar manner the filter chamber 142 corresponds to the filter 126 of Fig. 3, and the heating chamber 148 corresponds to the heater 96 of Figs. 2 and 3.

In a preferred operation of the Fig. 4 device, when utilized with a "torch" reactor of the type illustrated in Fig. 1, fine titanium powder, suspended in molten sodium

chloride, enters the main filter chamber 130 at a temperature on the order of 850° C. During the introduction of this molten sodium chloride, the valve 30 is open, as is the valve 136. The valve 138 may also be opened and the valve 140 may be arranged to discharge the liquid sodium chloride directly into the electrolysis cell 100 or into a suitable holding tank. As soon as the desired quantity of titanium fines have accumulated on the filter 134, the valve 130 may be closed. When the bulk of the sodium chloride is drained from the fines suspended on the filter element 134, the valve 140 may be turned to the "Off" position. At this point approximately 50% of the total weight of the titanium fines may be sodium chloride, the actual percentage of weight depending upon the size of the titanium particles. The valve 141 from the sodium aluminum tetrachloride tank is then opened to permit introduction of sodium aluminum tetrachloride at a temperature on the order of 600° C. During the addition of the sodium aluminum tetrachloride, the temperature of the sodium chloride in the titanium powder remains at a considerably higher temperature, due to the heat stored therein, until sufficient sodium aluminum tetrachloride has been added to lower the melting point of the resultant solution. The main filter tank 130 is filled with sodium aluminum tetrachloride which dissolves the sodium chloride from the titanium powder suspended therein.

The valve 140 is then turned so that tank 130 is drained into the cooling and filtering chamber 142 where the sodium chloride solution is crystallized out at a temperature on the order of 200° C., this sodium chloride being retained by filter 144 and the sodium aluminum tetrachloride passing through the filter 144. This washing of the titanium fines in the tank 130 may be repeated several times so that essentially all of the sodium chloride has been removed therefrom. Valve 141 is then closed, as is valve 140. The temperature in the main filtering tank 130 is then lowered to about 200° C. by circulating a suitable cooling liquid in the double wall of the tank 130, and the valve 145 is opened to permit the tank 130 to be filled with aluminum trichloride. At this time the pressure in the tank 130 may be raised to several atmospheres by introducing an inert gas such as argon through the gas inlet 154. The valve 140 is turned to a position so that the aluminum chloride and the dissolved sodium aluminum tetrachloride may be discharged into the heater chamber 148, this chamber being at a relatively low temperature on the order of 200° C., and being at superatmospheric pressure. This washing with aluminum trichloride is repeated several times until essentially all of the sodium aluminum tetrachloride has been washed out of the titanium powder held by the filter screen 134. Valve 140 is then moved to the closed position, valve 145 is closed, the pressure in chamber 130 is reduced to below atmospheric pressure, and the valve 143 leading to the aluminum trichloride storage tank is opened. The temperature of the double-walled chamber 130 is then raised to about 300° C. to volatilize all of the aluminum trichloride from the titanium powder, this aluminum trichloride condensing in the aluminum trichloride storage tank 86. Valve 143 may then be closed and chamber 130 may be allowed to cool. Vacuum-tight valve 136 is then closed, as is vacuum-tight valve 138. Argon is then introduced into chamber 130 so that it is approximately at atmospheric pressure. The chamber 130 is then disconnected from the associated piping at the top and bottom thereof and may be transported to the feed hopper of the vacuum-melting chamber 92. By inverting the filter chamber 130 over the feed hopper of the arc-melting chamber, and suitably operating the vacuum-tight valve associated therewith, the titanium powder contained in the chamber 130 may be dumped into this hopper, the titanium powder being protected at all times from contact with the atmosphere.

The sodium chloride remaining in the chamber 142,

after removal of the sodium aluminum tetrachloride therefrom, may be discarded, if desired, or it may be further purified by heating to a relatively high temperature to drive off any contained aluminum trichloride. The aluminum trichloride in the chamber 148 is recovered from the sodium aluminum tetrachloride by heating the chamber walls to a temperature on the order of about 300° C., the chamber 148 being at subatmospheric pressure during this heating and the valve 151 leading to the aluminum trichloride storage chamber being open. After substantially all of the aluminum trichloride has been driven out of the chamber 148, the sodium aluminum tetrachloride may be pumped therefrom, by the pump 150, back to the sodium aluminum tetrachloride storage chamber 122.

In the above discussion of the invention the vaporization and condensation of the aluminum trichloride has been primarily described as being done at subatmospheric pressures. This, of course, implies fairly drastic temperature changes in the aluminum trichloride condensing and holding chamber 86, since aluminum trichloride sublimes from the solid state. Aluminum trichloride cannot exist as a fluid at pressures below atmosphere. Thus when chamber 86 is acting as a condenser at low pressures it must be chilled to below about 100° C. When it is acting as a source of liquid aluminum trichloride, it must be heated to a temperature on the order of 200° C. and be maintained under a pressure of several atmospheres. In order to simplify the heating and cooling requirements for storage chamber 86, it may be continually maintained hot (200° C.) and at a superatmospheric pressure. In this case the aluminum trichloride may be condensed therein if the aluminum trichloride vapors are brought into chamber 86 at a superatmospheric pressure. A more convenient arrangement, however, is to provide a separate condenser for condensing subatmospheric aluminum trichloride vapors to the solid state. When this separate condenser is full, the temperature and pressure therein can be raised to liquefy the aluminum trichloride therein so that it can be run into the aluminum trichloride storage chamber 86.

In still another embodiment of the invention the titanium powder is produced in an electrolytic cell which is operated at a sufficiently high voltage so that an alkali metal halide is electrolyzed in the presence of titanium tetrachloride to reduce the titanium to at least a lower valence state. In one preferred operation thereof the electrolysis cell includes a crucible which is relatively inert to titanium tetrachloride and the alkali metal chlorides, one preferred crucible having a lining of molybdenum. The electrolyte preferably comprises, by weight, 40.4% lithium chloride, 53.2% potassium chloride, and 6.4% sodium chloride. In such a cell the anode is preferably carbon and is surrounded by a sleeve to remove chlorine from the anode region so as to prevent reaction between the chlorine and the bath in the neighborhood of the cathode. The cathode may be formed of titanium and the anode-cathode spacing can be about six inches. With such a cell an atmospheric pressure of titanium tetrachloride vapor is maintained over the electrolyte bath and the cell is operated under the following conditions:

Voltage—10 volts

Current density at the cathode—5 to 15 amps./in.²

Temperature—about 428° C. to 566° C.

Under the above conditions the cell showed considerable evidence of evolution of alkali metal at the cathode with reaction between this alkali metal and the titanium tetrachloride atmosphere above the electrolyte bath. The form of the resultant titanium metal, which collected as a powder at the bottom of the bath, indicates that the reduction is primarily by the alkali metal rather than by electrolysis of titanium tetrachloride or a lower chloride of titanium.

The resultant titanium powder is then removed from

the electrolysis cell as a suspension in the alkali metal halide electrolyte. This suspension is filtered and the residual contaminating electrolyte is then washed out of the titanium powder as illustrated in Figs. 2 or 3.

In the preceding discussion of the invention, reference has been made primarily to the removal of sodium chloride from titanium powder or sponge. The principles of the invention are equally applicable to the removal of other alkali metal halides or alkali earth metal halides or mixtures thereof from titanium and like metals. When an aluminum trichloride wash is used as the sole treatment, the procedure is in accordance with Fig. 2. Where a preliminary wash is employed, the preliminary wash salt is preferably the complex aluminum salt which is the eutectic mixture of the aluminum trichloride and the alkali metal halide to be dissolved. This complex salt, therefore, preferably includes that salt which is predominant in the contaminating salt. For example, if the contaminating salt contains a high percentage of potassium chloride, the complex aluminum wash salt may comprise potassium aluminum tetrachloride. Equally, the corresponding aluminum complex salts formed with the chlorides of lithium, calcium, magnesium, and barium may be employed when the contaminating salt predominates in such other alkali metal or alkali earth metal chloride. Where the complex salt does not dissolve all of the contaminating salts, a second preliminary wash may be employed or the undissolved contaminating salt may be removed during the aluminum trichloride wash step.

While the preferred aluminum trihalide has been described as aluminum trichloride, aluminum tribromide may equally be used. Although aluminum tribromide is more expensive than aluminum trichloride, it has the advantage that it can be maintained as a liquid at atmospheric pressures. When referring to aluminum trichloride in the specification and claims, it is intended that this expression include the dimer (Al_2Cl_6) as well as the monomer (AlCl_3).

It should be apparent from the above discussion that the filtering steps referred to above may include the use of centrifugal filtration as well as gravity or pressure filtration. Equally, decantation can be employed, although it is not as effective for separating gross amounts of liquid from the titanium powder.

In the preceding discussion of the various embodiments of the invention, various heating and cooling steps have been shown. Such heating and cooling is preferably accomplished by the use of a liquid heat-exchange medium, but other heating or cooling may be readily utilized.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of purifying a readily oxidized metal powder suspended in a molten salt from the group consisting of the alkali metal halides and the alkaline earth metal halides, said metal powder being selected from the group consisting of titanium and zirconium, said process comprising the steps of mechanically separating said metal powder from the bulk of said molten salt, washing the resultant concentrated suspension of metal powder in a bath comprising a substantial amount of a molten aluminum trichloride, separating the bulk of said dilute solution of said wash salt from said metal powder, heating the resultant metal powder to drive off residual aluminum trichloride, and consolidating the thus purified metal powder prior to exposure to air.

2. The process of purifying titanium powder suspended in a contaminating molten salt, said molten salt compris-

ing at least one salt from the group consisting of the alkali metal halides and the alkaline earth metal halides, said process comprising the steps of mechanically separating said titanium powder from the bulk of said molten salt, washing the resultant concentrated suspension of titanium in a bath comprising a substantial amount of a molten aluminum trihalide selected from the group consisting of aluminum trichloride and aluminum tribromide, separating the bulk of said dilute solution of said contaminating salt from said titanium powder, heating the resultant titanium powder to drive off residual aluminum trihalide, and consolidating the thus purified titanium powder.

3. The process of purifying titanium powder contaminated with a relatively large percentage by weight of a contaminating salt, said contaminating salt comprising at least one salt from the group consisting of the alkali metal chlorides and the alkaline earth metal chlorides, said process comprising the steps of washing said titanium powder with a large excess of an aluminum trihalide selected from the group consisting of aluminum trichloride and aluminum tribromide, separating the bulk of said dilute solution of said contaminating salt from said titanium powder, and heating the resultant titanium powder to drive off residual aluminum trihalide.

4. The process of claim 3 wherein said aluminum trihalide is used in sufficiently large quantities so as to reduce the percentage of said contaminating salt to less than about 5% by weight of said titanium powder.

5. The process of claim 3 wherein said purified titanium and aluminum trihalide are maintained at a pressure less than atmospheric pressure during said heating.

6. The process of claim 3 wherein said aluminum trihalide bath is maintained at a pressure greater than atmospheric pressure.

7. The process of producing titanium which comprises electrolyzing a titanium compound in a fluid salt bath to form titanium powder, removing from said salt bath said titanium powder contaminated with said salt, said salt bath comprising at least one salt from the group consisting of the alkali metal halides and the alkaline earth metal halides, mechanically separating said titanium powder from the bulk of said salt, washing the resultant concentrated suspension of titanium in a bath comprising a substantial amount of a molten aluminum trihalide from the group consisting of aluminum trichloride and aluminum tribromide, mechanically separating said dilute solution of said salt from said titanium powder, heating the resultant titanium powder to drive off residual aluminum trihalide, and consolidating the thus purified titanium powder to a nonpyrophoric form prior to exposure to air.

8. The process of claim 3 wherein said aluminum trihalide washes said titanium powder in countercurrent so as to reduce the concentration of said contaminating salt in the final purified titanium powder to less than about 5%.

9. The process of claim 2 wherein said contaminating salt comprises a complex aluminum salt which has been introduced into said powder to displace another salt comprising at least one salt from the group consisting of the alkali metal halides and the alkaline earth metal halides.

10. The process of claim 2 wherein said contaminating salt comprises sodium aluminum tetrachloride which has been introduced into said powder to displace another salt comprising at least one salt from the group consisting of the alkali metal chlorides and the alkaline earth metal chlorides and said aluminum trihalide comprises aluminum trichloride.

11. The process of claim 2 wherein said contaminating salt comprises sodium aluminum tetrachloride which has been introduced into said powder to displace sodium chloride from said powder.

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