

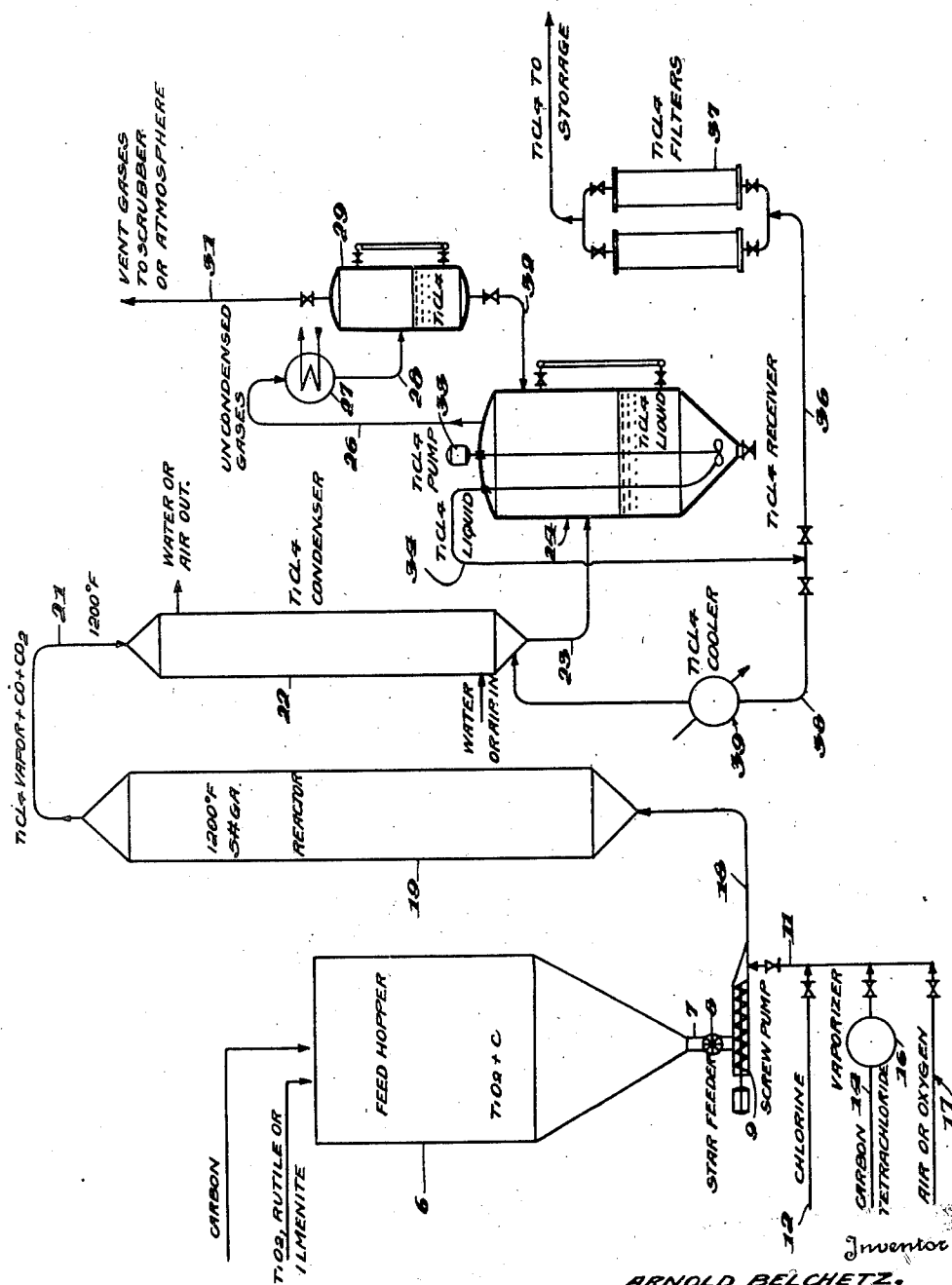
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PROCESS FOR PRODUCING TITANIUM TETRACHLORIDE

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PROCESS FOR PRODUCING TITANIUM
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1

This invention relates to the production of titanium tetrachloride from natural minerals, such as rutile or ilmenite, which may contain from 20% to 57% of titanium and from 3% to 50% iron. Rutile consists essentially of titanium dioxide (TiO_2), but is usually found to be associated with appreciable amounts of iron, sometimes as much as 10%, while ilmenite, which is ferric metatitanate and has the composition FeTiO_3 , contains about 37% iron in combination and usually contains additional iron, up to a total of approximately 50% Fe, in association, depending upon the nature of the ore in which the ilmenite is found.

Titanium tetrachloride has been produced heretofore from relatively expensive materials, i. e., pigment grade titanium dioxide, titanium carbide and titanium cyanonitride. Utilization of cheaper and more available titanium sources, such as rutile and ilmenite, has been proposed but, so far as I am aware, has never previously been successfully accomplished as a commercial operation. Rutile and ilmenite either contain or occur in association with so much iron, that conversion of the titanium oxide to the tetrachloride and recovery of the titanium tetrachloride in a pure form, free from ferric chloride which is also produced, are very difficult operations. As a result, it is the present commercial practice to produce titanium tetrachloride by feeding a prepared charge to a shaft furnace, the charge usually consisting of a mixture of pigment grade titanium dioxide and carbon, or pigment grade titanium oxide and titanium carbide or titanium cyanonitride with carbon. When titanium dioxide is reacted alone with chlorine and carbon to form titanium tetrachloride in a shaft furnace, it is necessary to suspend the chlorination operation and to reheat the bed periodically by blowing with air, in order to maintain the bed at the temperature necessary for efficient chlorination. This periodic reheating can be eliminated by including a certain proportion of titanium carbide or cyanonitride with the TiO_2 and carbon in the furnace charge, since both the carbide and cyanonitride chlorinate readily with a large evolution of heat.

Now if the charge to a shaft furnace be prepared so as to include a substantial quantity of rutile, all conditions otherwise remaining the same, it will be found that the great bulk of the rutile will pass through the furnace substantially without reaction, while the high grade titanium dioxide, carbide or cyanonitride will be converted completely to the tetrachloride. If rutile be

2

employed to replace completely the high grade titanium dioxide, carbide or cyanonitride in an operating shaft furnace, the formation of titanium tetrachloride virtually ceases as soon as the rutile charge has replaced a substantial portion of the previous charge in the furnace. The process of the present invention enables rutile and ilmenite to be utilized successfully in the continuous formation of titanium tetrachloride at temperatures between 1100°F . to 1900°F . and preferably between 1200°F . to about 1650°F . Since these materials are relatively cheap sources of titanium as compared with the grade of titanium dioxide heretofore employed or titanium carbide or titanium cyanonitride, the cost of producing titanium tetrachloride is reduced correspondingly.

All commercial production of titanium tetrachloride has heretofore included the use of a shaft furnace. Since the furnaces are charged several times a day, operating conditions vary widely and the conditions most favorable to formation and evolution of titanium tetrachloride exist only for a comparatively short time. While the formation of titanium tetrachloride from the usual source materials is theoretically exothermic, provision of an auxiliary source of heat has always been found necessary. External heating of a shaft furnace involves so many different problems that it has not proved practical in this operation. Internal heating can be accomplished by including excess carbon in the charge, which excess carbon is usually burned intermittently in the furnace by blowing with air, or by including a titanium feed material such as titanium cyanonitride and titanium carbide which can be readily chlorinated with evolution of considerable heat. The first practice, namely burning carbon to supply heat, is undesirable since it involves an interruption in the normal operation and the dismantling of part of the equipment when done intermittently, and because it introduces conditions unfavorable to formation and recovery of the tetrachloride when the air is introduced at the same time as the chlorine, while the latter requires comparatively expensive feed materials, the use of which is also difficult to control.

I have found that by carrying on the formation of titanium tetrachloride from rutile or ilmenite in what can be considered as a gas phase operation, the charge can be delivered to the reaction zone continuously, the reaction zone generally can be maintained without external heating and in a condition favorable at all times to

formation of titanium tetrachloride including a temperature in the range of 1100° F. to 1900° F. Thus, one is able to use simple equipment and avoid employment of a shaft furnace. In addition, the operation is made truly continuous and this with the successful utilization of the relatively low-grade, inexpensive materials, rutile and ilmenite, neither of which has been successfully handled heretofore. The invention is not of course limited to use with rutile and ilmenite, since obviously, if it is satisfactory with these, it is useful with the high grade titanium dioxide, the carbide or the cyanonitride.

The titanium source material should be dry and sufficiently comminuted to form a gaseous suspension in the reaction zone. Usually if the material is so fine that substantially all of it will pass a 40 mesh screen with about 95% passing a 200 mesh screen, the material will be satisfactory.

In practicing the present invention, the titanium source material and carbon are first reduced to a finely divided form, so that they can be handled successfully in gaseous suspension. Chlorine in the requisite quantity is made available for suspending the titanium source material and carbon in a reaction zone wherein the reduction-chlorination of the titanium dioxide occurs to form titanium tetrachloride. The suspension of the titanium source material and carbon in chlorine should be introduced into a reactor where suitable conditions are maintained for the production of titanium tetrachloride. The optimum temperature range is between about 1250° to 1650° F. but temperatures as high as 1800° to 1900° F. can be employed. At a temperature of about 1100° F., the reaction between chlorine and a mixture of titanium oxide and carbon proceeds slowly; the optimum is from 1200° F. to about 1650° F.

In practicing the invention one can, for example, form a mixture of finely divided rutile or ilmenite and carbon and feed this in suspension in a chlorine stream into the reactor at the required rate. One can also feed the titanium dioxide source material alone, passing this into the reactor in a stream of vaporized carbon tetrachloride sufficient in amount to supply the carbon and chlorine necessary to the reduction-chlorination. In place of carbon tetrachloride one can use other compounds containing carbon and chlorine such as perchlorethylene. However, the latter is relatively expensive and carbon tetrachloride is therefore to be preferred. Because of the adverse effect of the presence of hydrogen on the efficiency of the process, through loss of chlorine to HCl, it is generally not desirable to employ a chlorinated hydrocarbon containing hydrogen.

It is in general the broad object of the present invention to provide a novel process for production of titanium tetrachloride from low-grade titanium source materials such as rutile and ilmenite.

Another object of the present invention is to provide a continuous gas phase process for production of titanium tetrachloride.

The invention includes other features and objects of advantage, some of which, together with the foregoing, will appear hereinafter wherein certain methods of operation are set as illustrative of the practice of the invention.

The single figure of the drawing accompanying and becoming a part hereof is a diagrammatic showing of the apparatus and a flow sheet.

Referring to the drawing, a feed hopper 6 is provided for retaining the titanium dioxide source

material alone or in a suitable mixture with carbon. Material from the hopper 6 is delivered through its outlet 7 to a star feeder 8 which in turn discharges the mixture at a regulated rate into a screw pump generally indicated at 9. The solid material is discharged by the screw pump into a stream of gas from line 11 and a gaseous suspension formed in line 18. Depending upon the titanium source material and the conditions of operation desired, this stream includes either chlorine delivered from line 12 or carbon tetrachloride delivered from line 14 after being vaporized in vaporizer 16 or a mixture of these. Provision is also made for introducing air or oxygen through line 17.

The suspension formed at the discharge of the screw pump is passed through line 18 into the bottom of vertical reaction vessel 19. Titanium tetrachloride vapors and carbon oxides, i. e., carbon monoxide and carbon dioxide, and other reaction products are removed from the top of the reaction vessel through line 21 to a water or air-cooled condenser 22. The liquid formed in the condenser is taken off by line 23 and is delivered to a receiver 24 wherein the bulk of the titanium tetrachloride is collected. If iron or aluminum oxides are present in the titanium source material, the chlorides of these metals are formed in the reactor and condense to form solids which are maintained as a slurry in titanium tetrachloride in the receiver 24. Uncondensed gases are removed from receiver 24 through line 26 to a refrigerated condenser 27. Titanium tetrachloride liquid formed in condenser 27 is carried by line 28 to another receiver 29. Gases from this receiver are vented to a scrubber or to the atmosphere through line 31 while the condensed liquid is returned to receiver 24 through line 32.

Liquid titanium tetrachloride is removed from receiver 24 by pump 33 and is discharged into line 34. A portion of this liquid is passed through line 36 to filters 37 while another portion is recycled through line 38 and through subcooler 39 back to line 23 to mix with and cool the hot liquid and vapors issuing from condenser 22. The filter separates solid ferric and aluminum chloride present from the liquid titanium tetrachloride. If the slurry in receiver 24 becomes too thick, some of the filtered titanium tetrachloride can be returned to receiver 24, to form a pumpable slurry.

In one apparatus, the vessel 19 was 22.5 feet long with an internal diameter of 20 inches. It was well insulated against heat loss and was preheated to reaction temperature, by introduction of hot flue gas or by introduction of air and fuel and combustion of this mixture in the reactor. As a typical and representative operation, finely divided rutile containing 228 pounds of TiO₂ mixed with 68 pounds of powdered carbon were placed in hopper 6. 405 pounds of chlorine vapor were fed through lines 11 and 12 to pick up and form a gaseous suspension of the rutile and carbon, the mixture being injected into reactor 19 wherein the temperature in the reaction zone was maintained at 1380° F. and at slightly above atmospheric pressure. The aforementioned quantities were fed in at a constant and uniform rate over a period of one hour, producing 542 pounds of titanium tetrachloride as a reaction product. The solid ferric chloride formed a slurry in receiver 24, the titanium tetrachloride being separated from this in the filters 37. Under the feed rates and operating conditions mentioned, the superficial gas velocity in the reactor was 1.5

feet per second, with a theoretical gas residence time of approximately 15 seconds. With a gas velocity of 1.5 feet per second in the reactor, any unreacted solids form a dense bed containing approximately 15 pounds of solids per cubic foot of flowing gas in the reactor. The holding time of the solids in the reactor is very long, as the solids fed to the reactor are continually being consumed in the reaction to form gaseous products. Only a very small proportion of unreacted solids escaped from the top of the reactor with the gaseous reaction products.

In an operation conducted with carbon tetrachloride, reactor 19 was 15 feet high and 3 feet internal diameter. Rutile was discharged by the screw pump at a constant rate to feed 800 pounds per hour of titanium dioxide into a stream of 1540 pounds per hour of carbon tetrachloride vapor at 250° F. and slightly above atmospheric pressure. The gas velocity in the pipe conveying the mixture to the reactor was 30 feet per second, but in the reactor, the vapor velocity was reduced to one foot per second, based on the volume of reaction products leaving the reactor. The reactor was at a temperature of 1350° F. and at slightly above atmospheric pressure. The products, titanium tetrachloride and carbon dioxide with a small amount of carbon monoxide, passed into the condenser wherein they were cooled, issuing at a temperature of about 270° F. The cold (90° F.) stream of titanium tetrachloride liquid, injected at the outlet of the condenser, further lowered the temperature of the reaction products to about 104° F. 1880 pounds per hour of titanium tetrachloride were withdrawn from the main receiver and passed to the filter as the product of the operation.

The reactions of rutile and ilmenite with chlorine and carbon are sufficiently exothermic to maintain the reaction temperature between 1200° to 1650° F., when all the feed materials are introduced at atmosphere temperatures, provided precautions are taken to avoid excessive heat losses by radiation to the atmosphere. In the case where carbon tetrachloride is used as the source of carbon and chlorine, the carbon tetrachloride should be vaporized and superheated to 250° F. to sustain the reaction at 1200° F. When using a reactor of small diameter, in which case radiation heat losses are excessive even with good insulation, it is necessary to provide a secondary source of heat to maintain the reactor between 1200°-1650° F. This secondary source of heat can be provided by preheating one or more of the reactants or by heating the outside shell of the reactor by means of an electrical heating element wound around the reactor or fashioned in the wall of the reactor or by supplying hot flue gas to a shell around the walls of the reactor. Another method of supplying additional heat to the reactor is to feed an excess of carbon with the rutile or ilmenite and to introduce air or oxygen with the chlorine into the reactor. The combustion of carbon with oxygen will supply the additional heat required. However, the use of air or oxygen during reaction, increases the quantity of noncondensable gases and makes the efficient recovery of $TiCl_4$ more difficult. The use of air or oxygen is however desirable for heating the reactor when starting up.

This is a continuation in part of my application Serial No. 589,597, filed December 23, 1944, and which is now abandoned.

I claim:

1. A continuous process for the production of $TiCl_4$ comprising suspending finely divided particles of carbon and of a titanium oxide bearing material which contains from 20% to 57% titanium and from about 3% to 50% iron in a stream of chlorine, said particles being of such size that a majority thereof will pass a 200 mesh screen, introducing said suspension into a lower portion of a reaction zone at a rate sufficient (a) to maintain the solid reactants in suspension in said reaction zone and (b) to maintain the concentration and the residence time of the carbon, chlorine and material in said zone sufficient for the carbon, chlorine and material to react exothermically to form $TiCl_4$ as a gaseous reaction product in said zone and to supply the heat necessary to maintain said reaction zone at a temperature between about 1200° F. and 1900° F. without external heating thereof, removing gaseous reaction products from an upper portion of said reaction zone, and separating $TiCl_4$ from said removed gaseous reaction products.

2. A continuous process for the production of $TiCl_4$ comprising suspending finely divided particles of carbon and of a rutile in a stream of chlorine, said particles being of such size that a majority thereof will pass a 200 mesh screen, introducing said suspension into a lower portion of a reaction zone at a rate sufficient (a) to maintain the solid reactants in suspension in said reaction zone and (b) to maintain the concentration and the residence time of the carbon, chlorine and rutile in said zone sufficient for the carbon, chlorine and rutile to react exothermically to form $TiCl_4$ as a gaseous reaction product in said zone and to supply the heat necessary to maintain said reaction zone at a temperature between about 1200° F. and 1900° F. without external heating thereof, removing gaseous reaction products from an upper portion of said reaction zone, and separating $TiCl_4$ from said removed gaseous reaction products.

3. Continuous process for the production of $TiCl_4$ comprising suspending finely divided particles of carbon and of ilmenite in a stream of chlorine, said particles being of such size that a majority thereof will pass a 200 mesh screen, introducing said suspension into a lower portion of a reaction zone at a rate sufficient (a) to maintain the solid reactants in suspension in said reaction zone and (b) to maintain the concentration and the residence time of the carbon, chlorine and ilmenite in said zone sufficient for the carbon, chlorine and ilmenite to react exothermically to form $TiCl_4$ as a gaseous reaction product in said zone and to supply the heat necessary to maintain said reaction zone at a temperature between about 1200° F. and 1900° F. without external heating thereof, removing gaseous reaction products from an upper portion of said reaction zone, and separating $TiCl_4$ from said removed gaseous reaction products.

4. A continuous process for the production of $TiCl_4$ comprising suspending finely divided particles of carbon and of a titanium oxide bearing material which contains from 20% to 57% titanium and from about 3% to 50% iron in a stream of chlorine, said particles being of such size that a majority thereof will pass a 200 mesh screen, introducing the so-formed suspension into a reaction zone at a rate sufficient (a) to maintain the solid reactants in suspension in said reaction zone and (b) to maintain the concentra-

7

tion and the residence time of the carbon, chlorine and material in said zone sufficient for the chlorine, carbon and material to react exothermically to form $TiCl_4$ as a gaseous reaction product in said zone and to supply the heat necessary to maintain said reaction zone at a temperature between about 1200° F. and 1900° F. without external heating thereof, removing gaseous reaction products from said reaction zone, and separating $TiCl_4$ from said removed gaseous reaction products.

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8

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