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A. W. EVANS ET AL

2,855,273

METHOD OF PREPARING TITANIUM TETRACHLORIDE

Filed May 20, 1955

2 Sheets-Sheet 1

FIG. 2

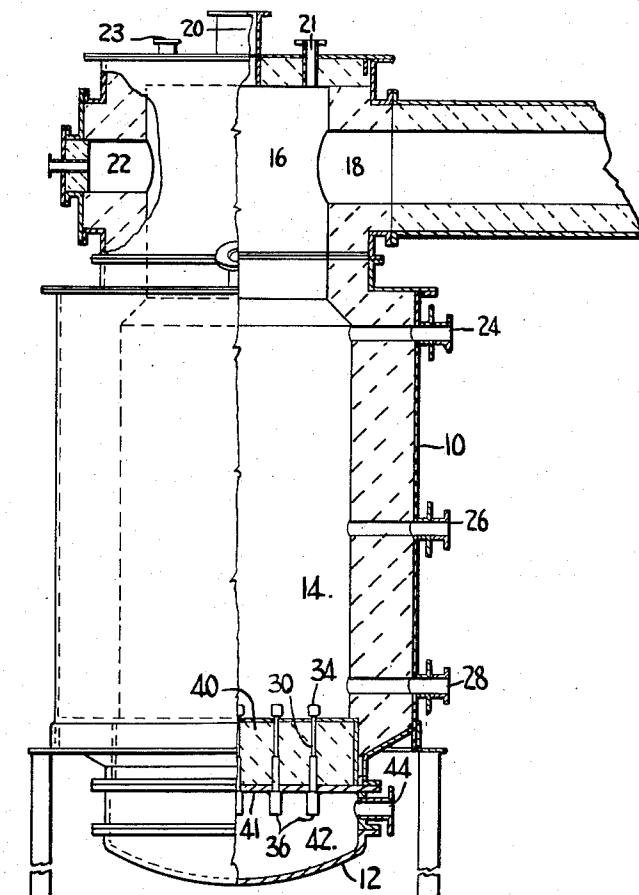
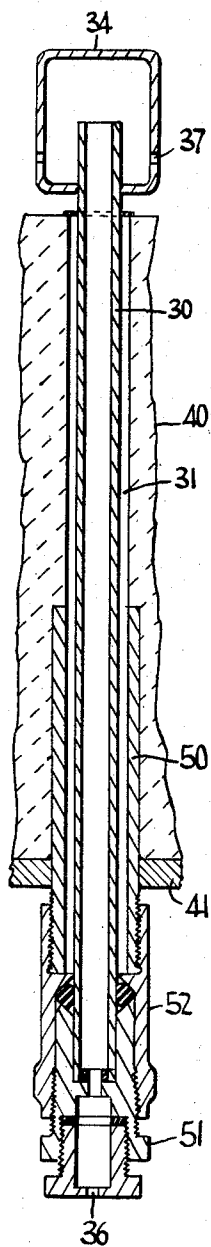


FIG. 1

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FIG. 3

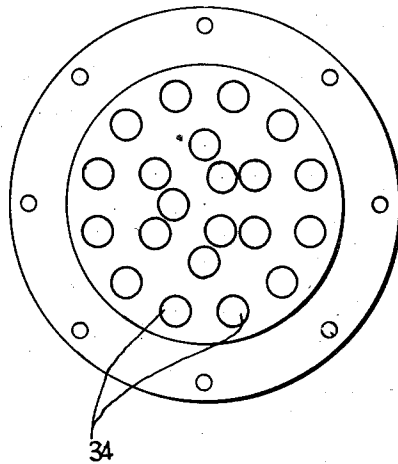
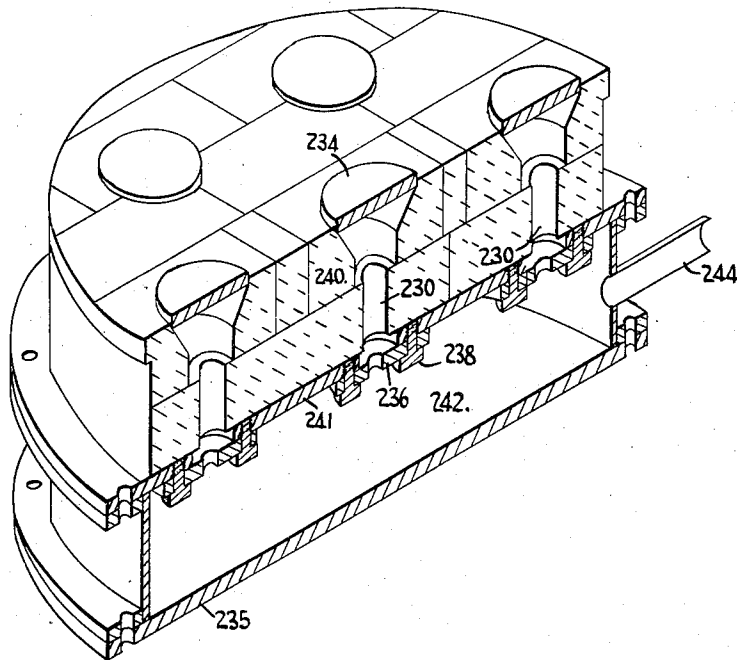


FIG. 4



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2,855,273

METHOD OF PREPARING TITANIUM TETRACHLORIDE

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Application May 20, 1955, Serial No. 509,964

15 Claims. (Cl. 23—87)

This invention relates to a novel method of chlorinating metal bearing materials, notably titanium-bearing materials, and is particularly directed to the chlorination of titanium bearing materials which contain in excess of about 90 percent TiO_2 , such as rutile. Prior to the present invention, it has been known that titanium and like metal bearing materials may be chlorinated in the presence of carbon or equivalent carbonaceous reducing agent in a shaft furnace and at an elevated temperature, by introducing titanium or like metal bearing ore, carbon, and chlorine at a rate sufficient to maintain a temperature within the reaction zone at which the reaction can proceed without introduction of external heat. In the practice of such processes, titanium tetrachloride can and has been successfully produced on a substantial scale.

One of the difficulties which has been encountered in the practice of a process of this character has been the poor utilization of chlorine. That is, as a consequence of the reaction, metal chlorides are formed and volatilized. These metal chlorides escape from the chlorination furnace and are subsequently condensed. At the same time, carbon monoxide and/or carbon dioxide are formed. These gases normally are allowed to escape from the system. In addition, it has been found that a very substantial amount of chlorine normally is present in the exit gases. As a matter of fact, chlorine utilization at times has been so poor that as little as 50 to 75 percent of the chlorine introduced into the reaction zone has been converted to metallic chlorides, the balance simply escaping with the exit gases.

It has also been observed that a number of other difficulties have been encountered. For example, in the chlorination of certain metal bearing materials, difficulty is encountered due to the fact that the reaction bed undergoing chlorination tends to clinker or agglomerate to an objectionable degree. This clinkering and/or agglomeration is particularly noticeable when certain materials are subjected to chlorination, notably materials containing magnesium oxide.

Moreover, serious loss of unreacted titanium bearing material from the reaction furnace may occur due to entrainment in the vapours of metal chloride recovered from the furnace. This is particularly true when a fluidized or dynamic bed of a titanium oxide bearing material is subjected to chlorination.

When a gas is passed through a bed of solid material, several types of conditions can be established depending upon the velocity of the gas. Where the gas velocity is low, the bed of solids remains static and the gas simply passes through the pores of the bed. As the gas velocity is increased, some or all of the particles become suspended in the upwardly flowing gas stream and are thus in more or less constant movement. This results in expansion of the bed and the bed consequently expands in height. Beds which are expanded by such flow of gas from the height which they exhibit in static state may be termed "dynamic beds."

With further increase in the velocity of gases, all of the

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particles become suspended and expansion of the bed increases with increasing velocity, thereby increasing the average distance between the suspended particles. At the higher velocities, the bed is highly turbulent and has many of the characteristics of a boiling liquid.

In the production of a fluidized or dynamic bed, it will be understood that there is a minimum velocity of upwardly flowing gas at which such bed can be fluidized. This velocity depends upon a number of things, including particle size, density of fluidizing gas, and density of solid particle. Wilhelm and Kwauk, Chemical Engineering Progress, volume 44, page 201 (1948), states that the minimum fluidizing velocity may be approximately determined according to the following equation:

$$Re = \frac{abc}{e} \text{ and } \frac{a^3cg}{2e^2}(d-c) = k$$

where

Re = the Reynolds number

a = diameter of the particle being fluidized

b = minimum fluidizing velocity

c = density of the fluidizing gas

d = density of the solid particle being fluidized

e = viscosity of the gas effecting fluidization

g = acceleration due to gravity

k = a constant

At 900° C., chlorine has a density of 0.00074 gram per cc. and a viscosity of 0.00049 poise. The density of a solid particle of rutile is 4.2 grams per cc.

In a typical case where the diameter of the particle is 130 microns or 0.013 centimeter and g is 981 centimeters per second, the constant k may be computed as follows:

$$k_{\Delta p} = \frac{(0.013)^2 \times 0.00074 \times 981}{(0.00049)^2 \times 2} (4.2 - 0.00074) = 10.5$$

From the graph on page 215 of the Wilhelm and Kwauk article, the Reynolds number is 3×10^{-2} and thus the minimum fluidizing velocity for this particle at 900° C. is about 2 centimeters per second. This corresponds to a mass velocity of about 12 pounds of chlorine per hour per square foot of reactor cross-section. It is also possible to determine the approximate minimum fluidizing velocity for a particular bed by laboratory experiment.

According to the present invention it has been found that chlorination of titanium and like metal oxide bearing ores may be effected readily, and utilization of 98 percent or more of the chlorine introduced achieved, by conducting the chlorination while suspending a titanium oxide bearing material having a particle size of 75 to 500 microns in a fluidized bed comprising elemental chlorine, and introducing the elemental chlorine into the bed at a rate at least three times, but not in excess of about 20 times, the minimum velocity required to fluidize the titanium oxide or other metal oxide bearing material in the bed. Thus, it has been found that where the chlorine is introduced at a rate less than three times the minimum fluidizing velocity of the bed, only 90 percent or less of the chlorine introduced is converted to metallic chloride. In contrast, when the rate of chlorine introduction exceeds about three times the minimum fluidizing velocity, but not in excess of about 20 times the minimum fluidizing velocity, chlorine utilization is so high that only minor amounts, usually less than one percent, of elemental chlorine escape in the exit gases, and 98 to 99 percent or more of the chlorine is used in the production of metallic chlorides. This materially reduces the cost and improves the efficiency of the chlorination.

In the practice of this process it is important to effect the chlorination of titanium oxide or like metal oxide bearing materials which have a particle size in the range of about 75 to 500 microns, preferably having an average

particle size of about 75 to 200 microns, as supplied to the chlorination zone. The exact rate of flow of chlorine into the bed for optimum operation depends to an appreciable degree upon the temperature of the reaction zone. For example, where the average particle size of titanium bearing material supplied to the reactor is approximately 130 microns and the temperature is 900° C., optimum efficiency of chlorination is achieved when the rate of chlorine introduction is approximately 100 pounds per hour per square foot of cross-section of reaction zone. On the other hand, where the temperature is allowed to fall to 800° C., optimum chlorination is effected at approximately 60 pounds of chlorine per hour per square foot of reaction zone.

It will be understood that the minimum velocity of chlorine which is required to be introduced in order to effect fluidization of particles having an average particle size in the range of 75 to 200 microns is in the range of about 12 pounds per hour per square foot of cross-sectional area of bed. Thus, the rate of chlorine introduction into the fluidizing bed should exceed about 36 pounds per hour per square foot but rarely should be in excess of about 200 to 250 pounds per hour per square foot.

In order to achieve maximum utilization of chlorine in the chlorine or like chlorinating gas in a fluidized bed, it is necessary to perform the fluidization of the bed under conditions such that uniform chlorination takes place throughout the bed, and consequent escape of chlorine gas due to non-uniformity of the bed is avoided. This is not a difficult procedure where the cross-sectional diameter of the bed is relatively small, for example, 12 inches or less. On the other hand, where the diameter of the bed becomes large, serious escape of chlorine or other chlorinating gas can occur because of such nonuniformity. At the same time, the large scale production of titanium tetrachloride requires the use of reactors of substantial cross-sectional diameter, usually exceeding 3 feet and frequently being as much as 10 feet or more. Avoidance of local irregularity in the density of the bed in such cases becomes exceedingly difficult.

According to the present invention it has been found that the irregularity in the density of the bed may be minimized and chlorine utilization may be improved in beds of such substantial diameter by introducing the chlorine from a header or other common source into the lower portion of the fluidized bed through a distributor extending across the reaction zone, which may comprise a porous bed or a distributor having a plurality of orifices or channels, in which substantial pressure drop takes place as the chlorine passes therethrough. This pressure drop is in excess of 2 pounds per square inch, generally in the range of 3 to 6 pounds per square inch. The chlorinating gas supplied to such orifices is at a super-atmospheric pressure in excess of that of the surrounding atmosphere by the sum of the pressure drop across the bed and the pressure drop across the distributor channels or orifices. Thus, the gas is so supplied at a gauge pressure of at least about 3 pounds per square inch. The gas also may be supplied to the orifices or other distributor at higher pressures, rarely above 100 pounds per square inch gauge.

Especially good results may be achieved by proper correlation of the pressure drop across the orifices or like distributor with the pressure drop across the bed, according to this invention. Thus, it will be understood that the pressure drop of the chlorinating gas across the bed will depend to a large degree upon the density and the depth of the bed. When the character of the material undergoing chlorination is substantially uniform, a convenient manner of controlling the pressure drop across the bed is to control its depth. According to a preferred embodiment of this invention, it has been found that maximum utilization of chlorine is achieved when the

depth of the bed is correlated with the pressure drop across the orifices so that the ratio of the pressure drop across the orifices and/or channels to the pressure drop across the bed is not less than one-half, but rarely should be in excess of about 50 to 1. Preferably the pressure drop across the orifices should exceed the pressure drop across the bed. This may be conveniently accomplished at a pressure drop across the orifices or channels of at least about 2 to 3 p. s. i., when the particles have an average particle range of 75 to 200 microns, by controlling the bed depth within the approximate range of about 4 inches to about 12 feet in depth, the specific depth at any time depending upon the magnitude of the pressure drop across the orifices and/or channels at such time.

This invention, involving establishment of a substantial pressure drop across a plurality of orifices introducing the chlorine into a fluidized bed of material undergoing chlorination, as described above, is especially applicable to the above described embodiment in which titanium oxide bearing ore of particle size ranging from 75 to 200 microns is subjected to chlorination in elemental chlorine flowing at a rate of 3 to 20 times minimum fluidizing velocity. However, such invention may be applied to chlorination of titanium or other metal bearing materials of different particle size and also to the use of other chlorinating gases, such as phosgene, carbon tetrachloride or the like.

It will be understood that the practice of any of the above processes is conducted in a shaft or like furnace which is not externally heated. Thus, in effecting the reaction, the heat evolved in the reaction maintains the temperature of the reaction zone sufficiently high to support the reaction. It will be understood, therefore, that the reaction bed must contain a substantial amount of heat in order to compensate for heat loss due to introduction of reactants as well as heat loss by virtue of radiation, convection, and the like. This is particularly true where the oxide ore is introduced at a temperature below the reaction temperature. Introduction of the ore and carbon at such lower temperature is desirable since otherwise it becomes difficult to avoid the possibility of prereaction of the carbon in the ore with air outside the reaction zone and consequent establishment of a carbon concentration in the bed which is so low that sufficient chlorination does not take place.

According to a further embodiment of the present invention, it has been found desirable and advantageous to establish and maintain a fluidized or dynamic bed containing a substantial amount of zircon. This zircon which is maintained in the bed retains a major portion of sensible heat in the bed and serves to dilute the incoming titanium oxide bearing material and transfer heat thereto. As a consequence, it is possible to effect the desired reaction conveniently and without preheating the ore to a temperature equal to or above the temperature of the reaction bed. Furthermore, when the ore contains certain components which tend to cause sintering or agglomeration of the bed particles as, for example, magnesium oxide or the like, the presence of the zircon in the bed may minimize this difficulty.

Where the ore itself contains an appreciable amount of zircon, an especially convenient method of establishing the zircon in concentration in the bed involves operation at temperature conditions such that zircon is not chlorinated. Thus, it has been found that by maintaining the temperature of the bed high enough to chlorinate the titanium components (usually above 700° C. but below about 950° C.), it is possible to build up and establish a substantial concentration of zircon in the bed since chlorination of the zirconium components of the ore undergoing introduction is substantially minimized.

In the practice of the operations herein contemplated, it is desired to make use of a bed containing about 7 to 45 percent by weight of ZrO_2 . However, the composition of the bed should not be allowed to fall below about 15

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percent by weight of titanium dioxide at all events. The actual composition of the bed will depend to a large degree upon the concentration of titanium dioxide in the oxide bearing material fed to the bed. However, a good useful range of titanium dioxide content is from about 20 percent to about 90 percent TiO_2 by weight. Silica in concentration ranging from about 3 to 25 percent by weight of the bed usually will be present either as such or in association with the ZrO_2 . Moreover, other components, such as coke, may be present in the bed if desired or at an inevitable consequence of the composition of the material undergoing chlorination. The particle size of the zircon in the bed may range from 75 to 500 microns or may be smaller.

To effect the chlorination herein contemplated, novel apparatus has been provided. The nature of the apparatus and the inventive embodiments thereof may be more fully understood by reference to the ensuing disclosure taken with the accompanying drawings, in which:

Fig. 1 is a diagrammatic elevational view partially in section of a furnace suitable for the practice of embodiments of the present invention;

Fig. 2 is an enlarged sectional view of one of the chlorine conduits illustrated in Fig. 1, the specific structure of which is described in copending United States application Serial No. 565,251, filed February 13, 1956, by William Henry Coates and John Hayden;

Fig. 3 is a plan view of the distributor illustrated in Fig. 1; and

Fig. 4 is a perspective view of an alternative embodiment.

Accomplishment of some or all of the inventive features mentioned above constitutes some of the principal objects of this invention, others of which will become more apparent from the ensuing disclosure. It will be understood that the above embodiments may be utilized individually if desired. In applicants' practice of the invention, applicants have found it desirable to make use of all of these embodiments and thereby to effect production of metallic chlorides, such as titanium tetrachloride, with maximum efficiency and economy.

As shown in the drawing, the furnace in which the reactions herein contemplated may be conducted conveniently may be a shaft furnace 10 having a shaft or reactor section 14, a top section 16, and a bottom or chlorine distributor section 12. The reactor section 14 comprises a shaft lined with refractory brick capable of withstanding the attack of chlorine at the temperature of operation. The internal diameter of such shaft may be of any convenient size and, in commercial operation, normally exceeds about 3 feet. Several outlets 24, 26, and 28 extend through the reactor wall and provide means for withdrawing samples of the bed or the chloride vapors or for introduction of coolants, such as titanium tetrachloride, into the bed.

Disposed in the top section 16 is a vapor outlet duct 18 for removal of vapors resulting from the chlorination of the metal bearing material and an inlet 22 for introduction of ore-carbon mixtures into the reaction section. Several top inlets 20, 21, and 23 are provided in the head of the furnace for easy access into the furnace from the top.

The chlorine distributor section 12 is removably attached to the bottom of the reactor section 14 and is designed to provide a uniform supply of chlorinating gas to the bed within the reactor. This section consists of a refractory base 40 which serves as the bottom or floor of the reactor and which rests upon metal plate 41 which in turn is bolted to the bottom of the shaft.

A plurality of spaced gas conduits 30 extend through the plate 41 and the base 40, providing communication between the chlorinating gas header 42 and the interior of the shaft furnace. These conduits are uniformly disposed throughout the base (see Fig. 3) at a convenient

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spacing, for example, 3 to 15 inches, preferably less than 12 inches, between centers.

Each conduit is provided at its lower end with an orifice 36 which is carefully machined, usually of metal, to provide a substantial pressure drop across the orifice. To achieve substantially uniform flow through each orifice, each should be designed to provide substantially the same pressure drop. At the upper end of each conduit is a head 34 which is closed at the top in order to prevent fall of ore into the conduit and which provides ports 37 in the sides thereof to permit flow of the chlorinating gas into the reaction zone in the shaft furnace.

Fig. 2 illustrates a convenient means for mounting the orifices, the specific structure of which is claimed in the aforesaid application of Coates and Hayden. As shown therein, there is provided a metal sleeve 50 which is brazed to the plate 41 to provide a gas tight seal. This sleeve extends upwardly a short distance into the refractory base 40. On each such sleeve is a nipple 52 in which a refractory conduit 30 is mounted. This conduit extends through the opening 31 in the refractory 40 and terminates in a hollow head 34 above the top surface of refractory 40. These heads are provided with a plurality of ports 37. In the lower end of nipple 52 there is disposed another nipple 51 into which a plug having an orifice 36 is removably mounted. The various joints are gas tight and thus the header 42 is isolated from the reaction zone except through conduits 30 which in turn are non-porous and therefore essentially gas tight.

In the operation of the process, the furnace is brought up to temperature in any convenient way as, for example, by introducing a bed of coke or other carbonaceous material, usually having a particle size of 200 to 250 microns or smaller, into the reactor through inlet 22. The coke is ignited and air or oxygen is blown through the conduits 30 to support combustion and to fluidize the coke. After the temperature of the furnace has raised to the desired level, usually above 500°C . and preferably 700°C . to 900°C . and rarely over about 1200°C . to 1400°C ., it is ready for commencement of the chlorination process.

The ore or like material subjected to chlorination is mainly of the order of size 75 to 500 microns, with an average of 100 to 150 microns, and is mixed with powdered carbon, coke, anthracite or equivalent carbonaceous material with an average size of approximately 200 to 250 microns or below, but often having a wide scatter. The percentage of carbon to be added may vary according to other conditions such, for example, as the oxygen content of the chlorine gases fed in, but is usually from 10 to 50 percent by weight of the total ore. Normally, the ore-carbon mixture is blended before feeding to the furnace although separate feeds for each constituent may be used.

To initiate the reaction, a quantity of the ore-carbon mixture is introduced into the furnace in amount sufficient to establish a bed about 1 to 6 feet in height. Chlorine is introduced into the reservoir 42, with or without air or oxygen, and flows through conduits 30 at a rate sufficient to establish a fluidized or dynamic bed.

As explained above, the velocity of the gases to maintain the bed in the required fluid state will vary with the size of the particles. For example, with a mean weight particle size of 130 microns, the velocity necessary to fluidize the particles at 800°C . may range from 2 to 100 centimeters per second. However, for maximum utilization of chlorine as described above, the velocity of the gases preferably should be about 6 to 40 centimeters per second.

The chlorine thus introduced chlorinates metal components of the bed, forming and vaporizing titanium tetrachloride and iron chloride. These chlorides are carried away from the bed and are conducted to a condensation system through duct 18. As a consequence of the chlorination, heat is evolved, thus maintaining the temperature of the bed at reaction temperature.

The reaction can be carried out continuously by feeding further chlorine, ore, and carbon continuously or intermittently to the bed and withdrawing the vapors from the bed. The temperature of the bed may be maintained at a convenient level by controlling the rate of chlorination. When the temperature is low, the rate of chlorine introduced is increased and vice versa. Ore is introduced at a rate sufficient to maintain a bed at least one foot deep, measured when the bed is static, i. e. with chlorine flow off.

The carbon is introduced at a rate sufficient to maintain a substantial concentration of carbon in the reaction bed. For chlorination of rutile, the preferred concentration is approximately 20 percent by weight, based upon the weight of the ore. With other ores, the optimum concentration may be determined by laboratory experiments, as is understood in the art.

As explained above, it is advantageous to conduct chlorination of titanium bearing material in a bed which contains a substantial amount of zircon. By maintaining the temperature of the reaction bed below about 950° C. and by supplying as the ore undergoing chlorination a titanium bearing ore which contains a small amount of zircon, for example, 0.25 to 0.75 percent by weight of zirconium oxide, it is possible to gradually build up a bed which contains in excess of 10 percent by weight of zirconium oxide. If the temperature of the reaction mixture is maintained below 950° C. and the reaction using such an ore is carried out over a long period of time, the titanium dioxide content of the bed falls below 15 to 20 percent by weight. In such a case, chlorination becomes inefficient and thereupon it becomes important to remove a portion of the zircon.

Removal of the zircon may be conducted by a number of methods. For example, the zircon may be removed by withdrawal of a portion of the bed through outlet 23 and adding titanium oxide bearing material to replenish the bed.

According to a further embodiment, it is also possible to reduce the amount of zirconium in the bed by allowing the temperature to rise from time to time above 950° C., for example, 950 to 1150° C. or above (rarely above 1500° C.). As a consequence of such chlorination, the zirconium components chlorinate and can be reduced to any desired degree. On the other hand, such a high temperature may tend to cause chlorination of the fire brick or other lining of the furnace. Hence, it frequently is desirable to effect chlorination of the zirconium components for only a relatively small portion of the entire reaction period, allowing the zirconium to build up to a maximum, not in excess of about 45 percent zirconium oxide by weight, and thereupon reducing the zirconium oxide content by raising the temperature or by other removal means until it has fallen to the desired level.

To ensure accurate and uniform feed of chlorine through the orifices, it is preferable to make use of machined orifices which produce a predetermined pressure drop (or loss in static head), as a consequence of flow therethrough. This is important, as has already been explained, in order to promote uniformity of distribution of chlorine flow over the entire cross-sectional area of the reaction zone. Thus, it becomes important to avoid substantial change in the orifices as the process proceeds from day to day or week to week.

According to this invention, such change may be minimized by maintaining the temperature of the orifices below the temperature at which substantial attack of the metal of the orifice by the chlorinating gas can take place. Thus, if the orifice is of iron, the temperature thereof should be maintained below about 250° C., preferably below 200° C. If the orifice is of nickel, the temperature thereof may be somewhat higher, preferably below 600° C. This may be accomplished if the thickness of base plate 40 is sufficiently great and its heat in-

ulating properties sufficiently high. In such a case, the chlorinating gas supplied to header 42 is supplied at a temperature well below 150° C., usually in the range of 25 to 100° C. or below, and the temperature of the orifices thus remains below 150° C.

The pressure of the chlorinating gas in reservoir 42 normally is superatmospheric. The magnitude of this pressure must be sufficiently high at least to equal the sum of pressure drop across the orifices, the pressure drop across the bed, and the pressure drop due to frictional losses in the conduits. Frequently, the pressure in this header will be as low as 6 to 8 pounds per square inch gauge when the reaction is initiated and may rise to 20 to 25 pounds per square inch gauge or higher in later stages of the reaction.

The overall differential pressure between the interior of the header 42 and the top of the dynamic bed undergoing chlorination also depends upon the depth of the bed. To achieve best efficiency, the depth of the bed is kept low enough so that the pressure drop across the bed itself is not more than about twice the drop across the orifice. Where the drop across the orifice is about 2 to 5 pounds per square inch, the depth of the fluidized bed usually has been kept at about 1 to 6 feet.

After the chlorination proceeds for a long time, plugging of the ports in the heads may proceed to such a degree as to make further operation difficult. In such case the entire distributor 12 may be removed and replaced with a new one. Thereafter, further ore and carbon may be introduced into the furnace and the chlorination process restarted.

Fig. 4 illustrates a further embodiment of a chlorine distributor which may be used in lieu of the one described above. This distributor comprises a plate 241 fastened to a shell 235, thus providing a gas tight reservoir 242. Refractory base 240 is mounted on plate 241 and is provided with conduits 230 extending therethrough which are closed in their upper ends by porous discs 234 which permit free passage of chlorine therethrough. The lower ends of these conduits 230 are closed by orifice plates 236 fastened to plate 241 by studs 238. Reservoir 242 has a supply inlet 244 for supply of chlorinating gas thereto.

Numerous distributing means may be provided in lieu of those discussed, as will be understood in the art.

The following examples are illustrative:

EXAMPLE I

The chlorination of the titanium bearing material was conducted in a shaft furnace consisting of an outer steel shell lined with chlorine-resisting brickwork and having an internal diameter of 2 feet 6 inches. Near the base of the shaft furnace was a perforated plate, the perforations of which were fitted with orifices of restricted diameter and superimposed by ceramic gas-permeable barriers. The pressure drop across each of these orifices was 6 pounds per square inch. This plate comprises a refractory body, for example, jointed brickwork superimposed onto a steel base plate, the brickwork or a suitable cast refractory and base plate being formed with registering apertures each of which had an upper conical section at the top of which was inserted a disc of porous ceramic material, e. g. silica sand, cemented or lightly sintered. Beneath the base plate, apertured discs were attached to it and defined entrance orifices to the passages leading to the porous ceramic discs. These discs permitted the up-rising gases to enter the furnace but prevented dust or other solid material from passing down through the plate. Below the plate was a port through which chlorine gas was admitted. At the top of the shaft was provided a star valve through which a mixture of the titanium bearing material and carbon was admitted. Also on one side of the furnace near the top was provided a port from which the gases leaving the fluid bed were conveyed to the condensing system.

To commence the process, the chlorinator was filled with mineral rutile to a depth of 3½ feet and then fluidized by the admission of air and direct gas firing applied internally to raise the temperature to 900° C. Carbon was then added to produce a bed containing 20 percent of carbon by weight.

Thereafter, chlorine was fed into the hot mass at a uniform rate of 400 pounds per hour to maintain a fluidized bed with a fluid gas velocity of about 18 centimeters per second at the operating temperature. The bed was maintained by feeding continuously through the star valve a mixture of mineral rutile and coke having the following analysis:

Table I

	Rutile	Coke
	Percent	Percent
TiO ₂	97.40	96.50
C.....	0.40	1.40
SiO ₂	1.10	0.90
Fe ₂ O ₃	0.60	1.00
ZrO ₂	0.50	
V ₂ O ₅		
	100.00	99.80
Particle sizes.....	130 M.	20-100 mesh (British Standard Mesh Size).

the mixture being periodically controlled to maintain the carbon-ore mixture at 20 percent by weight of carbon in the bed. The temperature throughout was maintained at between 850 and 950° C. The gases leaving the furnace were cooled externally and titanium tetrachloride recovered therefrom.

The following table indicates the distribution of certain components other than TiO₂ and carbon in the mineral-carbon mixture within the fluid bed:

Table II

Running Time, Days	Weight of components in bed in Kilograms		
	ZrO ₂	SiO ₂	Other
0.....	4	5	13
4.7.....	73	42	79
6.7.....	116	41	35
10.0.....	171	102	22
15.7.....	155	94	41

During the first few days of operation there was an increase in the amount of certain components, mainly oxides of zirconium and silicon, in the bed. After further continuous operation, a state was reached in which the amount of such components present rose and fell mainly due to lower or higher temperatures of operation within the range given above, but there was no build up of impurity level above this approximately steady state. When these conditions were attained, it can be regarded that the ore feed was being completely chlorinated and the operation continued to the end of the 16 days' run without any necessity to purge the bed.

EXAMPLE II

The furnace used in this experiment had an internal diameter of 18 inches. The chlorine was introduced at the bottom to the distribution device of the type illustrated in Figs. 1 and 2 in which there were provided 21 gas ports each provided with orifices ¼ inch in diameter. The pressure drop across the gas distributor was approximately 6 pounds per square inch. The ore used was natural rutile having approximately the composition set forth in Example I.

Chlorination was initiated according to the method described in Example I, the amount of ore and carbon being introduced at a rate sufficient to establish a carbon

concentration of approximately 20 percent by weight, based upon the weight of the ore bed, and to introduce into the reactor enough ore such that the average height of the bed, when measured in static condition, normally was maintained at about 3.5 feet throughout the period of reaction. This operation was continued over a period of many days. The typical operation conditions were as follows:

Chlorine rate of introduction.....	180 pounds per hour.
Introduction of oxygen.....	25 liters per minute.
Pressure drop across the gas distributor.....	6 pounds per square inch.
Pressure drop across the bed.....	3 pounds per square inch.
Average composition of the bed.....	50% rutile, 30% zircon, 20% carbon.
Temperature of the bed.....	900° C.

During the period of operation, approximately 2.35 tons of titanium tetrachloride was produced per day. The chlorine utilization exceeded 99 percent.

Addition of ore was controlled so as to maintain the bed height in the range of 1.7 to 6.6 feet in depth, the depth being measured with the gas off, that is, as a static bed. Once a shift, introduction of chlorine was discontinued for a few minutes in order to measure the static bed and to estimate the composition of the bed in terms of rutile and coke.

The ore which was fed had the following average particle size:

	Percent by weight
44 to 76 microns.....	0.2
76 to 104 microns.....	3.9
104 to 124 microns.....	54.5
124 to 152 microns.....	30.2
152 to 188 microns.....	11.0
Greater than 188 microns.....	0.2

EXAMPLE III

The process of Example II was performed while conducting the chlorination at a temperature of 900° C. while introducing chlorine at a rate of 180 pounds per hour. At the end of each 8-hour period, chlorine flow was temporarily discontinued and the bed was sampled and the depth thereof measured while static.

The following table sets forth the composition of the bed at various intervals:

Table III

	Weight in bed, Kilograms			
	TiO ₂	ZrO ₂	SiO ₂	Remainder
After 1st day.....	39.8	27.3	15.7	28.2
After 14th day.....	49.6	42.9	15.5	13.0
After 18th day.....	43.6	63.4	37.0	8.3

Thereafter, the bed temperature was raised to 950° C. whereupon the zirconium oxide concentration fell substantially. At the end of the 25th day, the bed had the following composition:

	Kilograms
TiO ₂	157
ZrO ₂	57.8
SiO ₂	35.0
Remainder.....	15.2

i. e., more zircon was being chlorinated at the higher temperature than was being added in the feed material.

EXAMPLE IV

The process of Example II is performed while maintaining the pressure above the level of the bed of rutile undergoing chlorination above about 0.5 pound per

square inch. As a consequence, formation of oxychlorides and other contaminants (oxides and the like) was substantially prevented.

EXAMPLE V

A shaft furnace 18 inches in internal diameter and 11 feet high was fitted with a perforated base having a gas chamber below and ports fitting into the gas chamber for admitting chlorine or air separately. The top of the furnace was sealed with an inlet port for feeding the mineral and coke constituents, with provision for the temporary insertion of a gas burner described below for heating up the apparatus. A further port was provided for the admission of coolant titanium tetrachloride. The furnace was further fitted with an exit port at the side near the sealing cap for discharge of the gases from the chlorination zone to the initial cooling apparatus where the gases were cooled by the admission of ferric chloride to a temperature of 300° C. The perforations in the perforated plate, totalling 20, were each fitted with a detachable orifice on the under side of the plate and with a gas-permeable disc on the upper side. The orifices each had a diameter of 1.2 millimeters and the perforated discs were constructed of sintered ceramic material, each having a permeability to air at room temperature and pressure of eight liters per minute for a pressure drop of one inch of water.

The gases produced by the chlorination were led to a first cooling tower where ferric chloride was admitted as cooling agent. The gases leaving the latter tower were conveyed to a second tower where they were cooled by an atomized spray of titanium tetrachloride to 130° C. which precipitated the ferric chloride constituent of the gases into a comparatively coarse condition suitable for removal by settling at the base of the tower. The cooled gases were then led to a conventional indirect condenser where they were reduced to a temperature below 0° C. in order to remove in liquid form the titanium tetrachloride constituent. In the operation of this apparatus, the procedure was as follows:

Above the perforated plate of the chlorinator was introduced a bed 3 feet high consisting of 80 percent by weight of mineral rutile having a particle size 80 to 200 microns and 20 percent by weight of coke having a particle size 50 to 500 microns. This bed was fluidized by the passage of air through the perforated plate described above at the rate of 200 pounds per hour and was heated by means of a suitably constructed gas burner inserted through the top of the furnace, the flame playing onto the top of the fluidized mass. In this way the temperature was raised to 950° C. The gas jet was then removed and the air supply cut off. Chlorine was immediately admitted into the chamber below the perforated plate in order to fluidize the bed at the rate of 180 pounds per hour. At the same time, ilmenite ore of size 100 to 250 microns and coke of size as above were fed to the bed in such quantities that the height of the bed was maintained at 3 feet and the coke content of the bed was maintained at 20 percent by weight. These quantities averaged about 110 pounds ilmenite and 20 pounds coke per hour. The ore used was Quilon ilmenite containing 59.6 percent TiO_2 , 24.9 percent Fe, and a total of 1.2 percent by weight of alkali and alkaline earth oxides. Through the other port in the sealing cap at the top of the furnace, liquid titanium tetrachloride was added to the bed at the rate of 30 pounds per hour to control the temperature not to exceed 970° C. The gases left the chlorination furnace at a temperature of 900° C. and contained less than one percent of free chlorine. They were led to the first cooling tower to be cooled therein by addition of finely divided ferric chloride added at the rate of 300 pounds per hour. This addition, together with the heat losses taking place in the apparatus, sufficed to produce a gas from the cooler having a temperature of 300° C. The gases were subsequently cooled to a temperature of 130°

C. in the second tower by the injection of an atomized spray of titanium tetrachloride and the ferric chloride produced settled in a succeeding dust separator. The gases were subsequently passed through a series of tube condensers where they were cooled to below -10° C. to condense the titanium tetrachloride constituent.

The process as above described was carried on for 12 hours. During substantially the entire period of the run, the iron oxide content of the bed remained below 10 percent by weight.

The above examples have been described with reference to a shaft furnace of the type illustrated in the drawings wherein chlorinating gas is supplied to the reaction zone through a plurality of machined orifices in communication with a plurality of channels in a refractory base. While this is an excellent way for introduction of such chlorine, it is also possible to supply the chlorinating gas through other channels. Thus, a porous bed of large refractory granules or coke granules may be laid on a perforated plate having orifices therein disposed in the bottom or lower portion of the shaft furnace and chlorine or like gas allowed to flow through the channels in the porous bed. In such a case, the depth and density of the bed and the sizes of the orifices should be sufficient to establish a pressure drop in the gas flowing through the refractory bed of at least 2 to 3 pounds per square inch.

Although the various embodiments of the invention have been described with reference to specific details of certain features thereof, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

This application is a continuation in part of applications Serial No. 469,062, filed November 15, 1954, and Serial No. 449,002, filed August 10, 1954, now abandoned.

What is claimed:

1. A method of preparing titanium tetrachloride which comprises establishing a dynamic bed in a reaction zone, said bed comprising titanium oxide bearing material having a particle size largely in the range of 75 to 500 microns and at least about 15 percent by weight of carbon, said bed being fluidized by a fluidizing stream comprising elemental chlorine, supplying the chlorine to said bed at a rate of 40 to 250 pounds per hour per square foot of reaction zone cross-section from a reservoir of chlorine through a plurality of orifices, maintaining a pressure drop across said orifices of at least 2 pounds per square inch, maintaining the temperature of said bed above 700° C. whereby titanium tetrachloride is formed and volatilized, adding further titanium bearing material and carbon to said bed, and maintaining the depth of said bed sufficiently low to maintain the ratio of the pressure drop across the bed to the pressure drop across the orifices not in excess of two to one.

2. A method of chlorinating a titanium oxide bearing material which comprises establishing a dynamic bed of particles of said material in a fluidizing gas comprising elemental chlorine, supplying said gas to said bed from a reservoir of said gas through a plurality of orifices, maintaining a pressure drop across said orifices in excess of 2 pounds per square inch, maintaining the temperature of the bed sufficiently high to cause chlorination of titanium in the bed, adding further titanium oxide bearing material and carbonaceous material to said bed, maintaining the depth of said bed low enough to maintain the ratio of the pressure drop across the bed to the pressure drop across the orifices not in excess of two to one, and maintaining the TiO_2 content of the bed above 20 percent by weight.

3. A method of chlorinating a titanium oxide bearing material which comprises establishing a dynamic bed of particles of said material in a fluidizing and chlorinating gas, supplying said gas to said bed from a reservoir

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of said gas through a plurality of orifices below the bed, maintaining a pressure drop across each of said orifices substantially the same and in excess of 2 pounds per square inch, maintaining the temperature of said bed sufficiently high to cause chlorination of titanium in the bed, adding further titanium oxide bearing material and carbonaceous material to said bed, maintaining the depth of said bed low enough to maintain the ratio of the pressure drop across the bed to the pressure drop across the orifices not in excess of two to one, the depth of said bed being at least one foot, and maintaining the TiO_2 content of the bed above 20 percent by weight.

4. A method of chlorinating a metal oxide bearing material which comprises establishing a fluidized bed of particles of said material in a fluidizing and chlorinating gas, supplying said gas to said bed from a reservoir of said gas through a plurality of channels below the bed, maintaining a pressure drop across each of said channels substantially the same and in excess of 2 pounds per square inch, adding further metal oxide bearing material and carbonaceous material to said bed, and maintaining the depth of said bed sufficiently low to maintain the ratio of the pressure drop across the bed to the pressure drop across the channels not in excess of two to one.

5. A method of preparing titanium tetrachloride which comprises establishing a dynamic bed of TiO_2 bearing material having a particle size of 75 to 500 microns and finely divided carbonaceous material in a fluidizing gas comprising elemental chlorine, maintaining the temperature of the bed at not less than about 700°C . whereby said titanium oxide bearing material is chlorinated and titanium tetrachloride is formed and volatilized, and introducing elemental chlorine as a fluidizing gas into the lower portion of the bed through a plurality of orifices at a rate of at least three but not more than about 20 times the minimum velocity required to fluidize the titanium oxide bearing material in the bed and maintaining the depth of said bed low enough so that the ratio of the pressure drop across the bed to the pressure drop across the orifices does not exceed 2 to 1.

6. A method of preparing titanium tetrachloride which comprises establishing a dynamic bed in a reaction zone, said bed comprising titanium oxide bearing material having a particle size largely in the range of 75 to 500 microns and at least about 15 percent by weight of carbon, said bed being fluidized by a fluidizing stream comprising elemental chlorine, supplying the chlorine to said bed at a rate of 40 to 250 pounds per hour per square foot of reaction zone cross-section from a reservoir of chlorine through a plurality of orifices, maintaining a pressure drop across said orifices of at least 2 pounds per square inch, maintaining the temperature of said bed above 700°C . whereby titanium tetrachloride is formed and volatilized, adding further titanium bearing material and carbon to said bed, maintaining the depth of said bed sufficiently low to maintain the ratio of the pressure drop across the bed to the pressure drop across the orifices not in excess of two to one, and maintaining the temperature of chlorine introduced into said reservoir low enough to maintain the temperature of said orifices below 600°C .

7. A method of chlorinating a metal bearing material which comprises establishing a dynamic bed of particles of said metal bearing material in an upwardly rising stream of a chlorinating gas, maintaining the temperature within the bed above 700°C . whereby to form metal chlorides, supplying said chlorinating gas to the bed through a plurality of orifices below the bed from a common source of chlorine, maintaining a pressure drop across said orifices in excess of 2 pounds per square inch, maintaining the depth of said bed low enough to maintain a ratio of the pressure drop across the bed to the pressure drop across the orifices of not in excess of two to one, maintaining the temperature of chlorine introduced into

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said reservoir low enough to maintain the temperature of said orifices below 600°C .

8. A method of chlorinating a metal bearing material which comprises establishing a dynamic bed of particles of said metal bearing material in an upwardly rising stream of a chlorinating gas, maintaining the temperature within the bed above 700°C . whereby to form metal chlorides, supplying said chlorinating gas to the bed through a plurality of orifices below the bed from a common source of chlorine, maintaining the pressure drop across said orifices in excess of 2 pounds per square inch, maintaining the depth of said bed low enough to maintain a ratio of the pressure drop across the bed to the pressure drop across the orifices of not in excess of two to one, and maintaining the temperature of chlorine introduced into said reservoir low enough to maintain the temperature of said orifices below 250°C .

9. A method of chlorinating a metal bearing material which comprises establishing a dynamic bed of particles of said material in an upwardly rising stream of chlorine introduced into the bed, supplying the chlorine to the bed through a plurality of conduits below the bed leading from a common source of chlorine, and maintaining the depth of the bed low enough to maintain a ratio of the pressure drop across the bed to the pressure drop across the conduits of not more than two to one.

10. The process of claim 9 wherein the rate of flow of chlorine through the bed is held low enough so that the vapors of chlorination contain less than one percent chlorine and the metal is titanium.

11. A method of chlorinating a metal bearing material which comprises establishing a bed of particles of said material, introducing an upwardly rising stream of chlorine into the bed, supplying the chlorine to the bed through a plurality of orifices below the bed leading from a common source of chlorine, maintaining the temperature of the bed above 700°C . whereby to cause production of titanium tetrachloride, maintaining the depth of the bed low enough so that the ratio of the pressure drop across the bed to the pressure drop across the orifices is not more than 2 to 1, and maintaining the temperature of the chlorine supplied to said chlorine source low enough to hold the temperature of the orifices below 600°C .

12. The process of claim 11 wherein the temperature of the chlorine supplied to the common source is below 100°C .

13. The process of claim 11 wherein the metal bearing material is a titanium oxide bearing material, the TiO_2 content of the bed is maintained above 20 percent by weight, the rate of flow of chlorine is held low enough so that the vapors of chlorination contain less than one percent chlorine, and the temperature of the chlorine supplied to the common source is below 100°C .

14. The process of claim 9 wherein the metal bearing material is a titanium oxide bearing material.

15. The process of claim 11 wherein the metal bearing material is a titanium oxide bearing material.

References Cited in the file of this patent

UNITED STATES PATENTS

2,486,912	Belchetz	Nov. 1, 1949
2,608,474	Gilliam	Aug. 26, 1952
2,654,659	Friedman	Oct. 6, 1953
2,701,179	McKinney	Feb. 1, 1955
2,701,180	Krchma	Feb. 1, 1955
2,760,917	Ward	Aug. 28, 1956

OTHER REFERENCES

- "Fluidization in Chemical Reactions," by John C. Kalbach, pages 105-108 in Chem. Eng., January 1947.
 "Flow in Fluidized Reaction Systems," by Gordon Kiddo, Chem. Eng., May 1949, pages 112-114.