

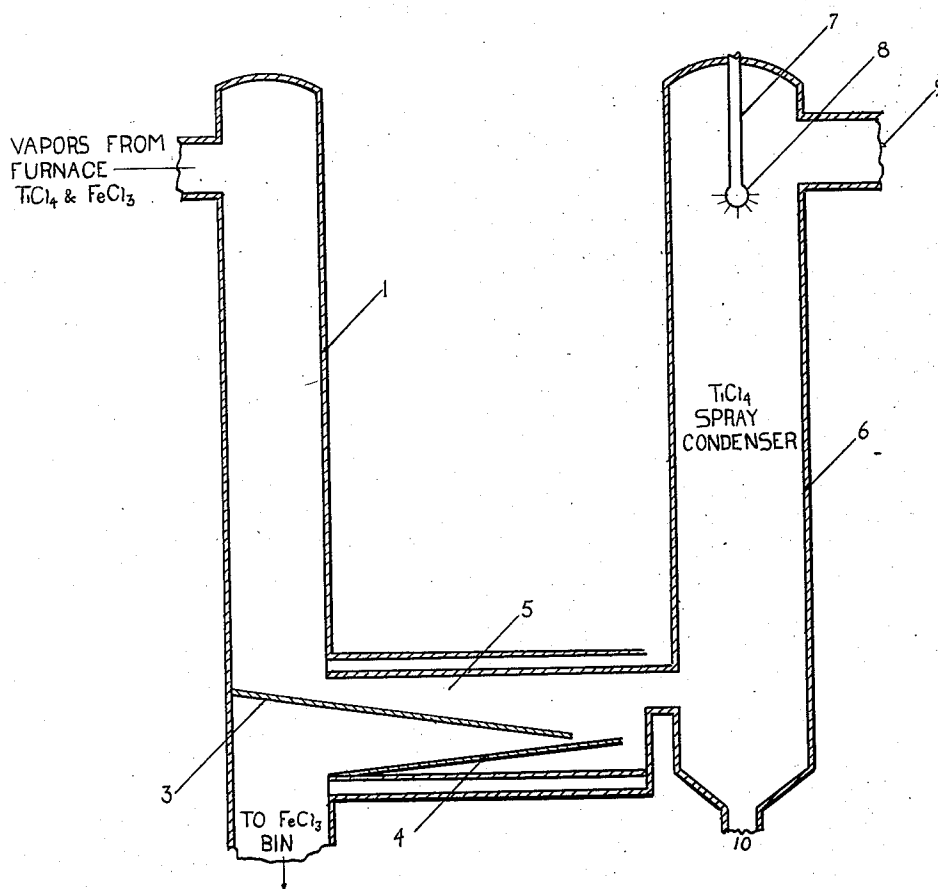
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CHLORINATION OF TITANIUM BEARING MATERIALS

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CHLORINATION OF TITANIUM BEARING MATERIALS

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This invention relates to a method of chlorinating titanium bearing materials containing a substantial quantity of iron, generally in excess of 10 percent, and is particularly adapted to the chlorination of ores such as ilmenite. In the chlorination of such ores it is known to conduct the treatment in the presence of sufficient reducing agent and at temperature sufficiently high to form and volatilize a mixture of iron and titanium chlorides. However, this process has never achieved success due to the fact that the apparatus rapidly becomes plugged with condensed iron chloride. Attempts to fractionally condense the iron chloride and thus to separate the iron from the titanium tetrachloride vapor have not been satisfactory due to the fact that it is practically impossible to achieve an accurate separation of the iron chloride by ordinary methods.

In accordance with my invention, I have discovered a method of avoiding plugging of the condenser system. I have found that if the mixed vapors of iron and titanium chlorides are cooled to condense iron chloride, the cooled vapor mixture contains a large amount of iron chloride suspended therein in the form of very fine particles. This iron chloride collects in the various conduits within the condenser system thus plugging the apparatus. I have also found that by washing the gaseous mixture containing solid iron chloride and more or less uncondensed titanium tetrachloride with liquid titanium tetrachloride, substantially complete removal of iron chloride from the vapor may be secured. This washing may be conducted during cooling of the vapors whereby a portion of the titanium tetrachloride is condensed, or subsequent to such cooling.

The vapor mixture may be produced by any convenient method. I have found it desirable to utilize the process described in a copending application of Irving E. Muskat, Serial No. 282,198, filed June 30, 1939. In accordance with this process ilmenite ore or other titanium-iron bearing material is mixed with 15 to 35 percent of carbon and is chlorinated at a temperature above 600° C., preferably at 850 to 1250° C. Other chlorination methods may be used if desired.

The vapors containing iron chloride and titanium tetrachloride may be cooled to a convenient temperature below the temperature at which ferric chloride vaporizes. In the event that it is desired to avoid condensation of titanium tetrachloride with the iron chloride the vapor temperature should be held above the dew

point of titanium tetrachloride, for example, above 75° C. However, in many cases it is found advantageous to condense a quantity, generally not less than about 20 to 30 percent, of the titanium tetrachloride with the iron chloride and in such a case the vapor temperature will be maintained at or below the vaporization point of titanium tetrachloride.

I have found that when a mixture of iron and titanium chlorides is cooled a large portion or substantially all of the iron chloride solidifies. However, much of the solidified iron chloride remains suspended in the vapor mixture and as a consequence is carried over into other parts of the condenser system. By washing the gaseous mixture with liquid titanium tetrachloride, however, the major portion of the suspended iron chloride is removed and the residual vapor may be conducted to another portion of the condenser and cooled to condense titanium tetrachloride without fear of plugging the apparatus. The washing may be effected by spraying the gases with titanium tetrachloride.

The iron chloride thus precipitated is collected with a substantial quantity of condensed liquid titanium tetrachloride. The tetrachloride may be distilled off by heating at a temperature above the boiling point thereof and below the vaporization point of the iron chloride, and may be recovered by suitable means. The uncondensed vapors which remain after condensation and removal of the iron chloride may be cooled to condense titanium tetrachloride vapor thus permitting the production of the tetrachloride in a relatively high state of purity.

In accordance with one modification of my invention the titanium tetrachloride which is collected and/or condensed with the iron chloride may be separated from the iron chloride by distillation in inert gas. I have found that the washed gases from which the iron chloride initially was removed to be particularly suitable as an inert gas for this purpose. Thus, in a preferred modification the condensed and precipitated iron chloride containing more or less liquid titanium tetrachloride is heated in a stream of the washed vapor mixture from which iron chloride initially has been removed. By heating at a suitable temperature the titanium tetrachloride may be volatilized without volatilizing iron chloride.

The accompanying drawing diagrammatically illustrates a convenient apparatus for conducting the process in accordance with my invention. In accordance with the modification herein illus-

trated, vaporized iron and titanium chlorides are discharged from the chlorination furnace into ferric chloride condenser 1, where iron chloride and a substantial quantity of titanium tetrachloride are condensed by reduction of the temperature to a suitably low value for example, 75° C., or below. The condensed mixture settles to the sloping floor 3, where it is transported by scrapers or other conveying means (not shown) into jacketed chamber 5. During passage of the condensed chlorides through chamber 5, they are contacted with the uncondensed vapors leaving condenser 1, whereby all or a major portion of the titanium tetrachloride is revaporized. Eventually, the ferric chloride is discharged into chute 4, and is conveyed to a ferric chloride bin (not shown).

The vapors containing the titanium tetrachloride and a quantity of unprecipitated ferric chloride which is generally in the form of fine solid particles are then conveyed to a suitable condenser or chamber 6, which is provided with a sprayhead 10, to which liquid titanium tetrachloride is supplied through conduit 7. The incoming vapors are thus bathed with liquid titanium tetrachloride whereby a portion of the titanium tetrachloride therein may be condensed and the residual iron chloride is separated from the vapors. The liquid titanium tetrachloride containing the iron chloride is removed through outlet 10, filtered and a portion thereof returned to the sprayhead. Uncondensed gases are withdrawn through conduit 9 and subjected to further condensing operations for recovery of the remainder of the titanium tetrachloride in a very pure state.

The following example is illustrative:

Using a furnace having an internal diameter of 15 inches which was preheated to a temperature of 1000° C., briquettes prepared from a mixture containing 100 parts ore, 23 parts C and 14 parts molasses, were introduced at a rate of 120 pounds per hour and chlorine at 2.0 to 2.5 pounds per minute. The temperature was maintained at 850-1000° C. throughout the experiment. The vapors were withdrawn from the furnace and cooled to 40° C. whereupon 90 percent of the ferric chloride and a portion of the titanium tetrachloride were simultaneously condensed. The gaseous mixture containing condensed iron chlorides suspended therein was passed through a spray of liquid titanium tetrachloride until all of the solid iron chloride was precipitated. The washed uncondensed vapor was withdrawn and cooled to 0° C. to recover titanium tetrachloride. The process was carried on continuously for many hours by introducing briquettes at a rate of 210 pounds per hour, chlorine at a rate of 2.0 to 2.5 pounds per minute. The condensed and precipitated iron chloride containing liquid titanium tetrachloride was transferred to another portion of the condenser system and was heated to 140° C. in a stream of the washed uncondensed gas, which was obtained after removal of the iron chloride, until all of the titanium tetrachloride was vaporized. The titanium tetrachloride in the vapors was then recovered by cooling to 0° C. No plugging occurred during the entire operation. In addition the step of washing the vapors resulted in a more complete condensation of ferric chloride. Thus the liquid titanium tetrachloride used not only precipitated the condensed and suspended iron chloride, but also produced a more efficient condensation of the iron chloride vapors.

The process is found to be applicable to the treatment of various titanium bearing materials including ferrotitanium, ilmenite, titanomagnetite or the residue derived from the chlorination of iron titanium ores for the preliminary removal of titanium as described in a copending application of Irving E. Muskat and Robert H. Taylor, Serial No. 206,219, filed April 30, 1938, or other materials which contain in excess of 20 percent of titanium.

While titanium tetrachloride is found to be particularly effective as a means of removing suspended iron chloride from vapor mixtures, other liquid metallic halides such as silicon or stannic tetrachloride or titanium tetrabromide or titanium tetrafluoride also may be used for this purpose. Similarly, certain organic halides such as carbon tetrachloride are found to be effective where the halide is sufficiently stable and is liquid at the temperature of operation.

Although the present invention has been described with reference to specific details of certain embodiments 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.

I claim:

1. A method of removing iron chloride from a vaporized mixture of iron chloride and titanium tetrachloride which comprises condensing iron chloride in the mixture and washing the vapor mixture containing at least a portion of the iron chloride with liquid titanium tetrachloride to precipitate suspended solid iron chloride.

2. A method of conducting the chlorination of an iron titanium bearing material while minimizing plugging within the system which comprises chlorinating the material at a temperature above the vaporization point of iron chloride and titanium tetrachloride to produce a vapor mixture of said chlorides, cooling the mixture to condense iron chloride and washing the vapor mixture containing at least a portion of the iron chloride with liquid titanium tetrachloride to remove suspended iron chloride.

3. A method of removing iron chloride from a vaporized mixture of iron chloride and titanium tetrachloride which comprises condensing iron chloride in the mixture, washing the vapor mixture containing at least a portion of the condensed iron chloride with liquid titanium tetrachloride to precipitate suspended solid iron chloride and subsequently separating condensed titanium tetrachloride from the condensed and precipitated iron chloride by distilling the same in the presence of the washed uncondensed vapors.

4. A method of removing iron chloride from a vaporized mixture of iron chloride and titanium halide which comprises condensing iron chloride in the mixture and washing the vapor mixture containing at least a portion of the iron chloride with liquid titanium tetrahalide to precipitate suspended solid iron chloride.

5. A method of removing iron chloride from a vaporized mixture of iron chloride and titanium tetrachloride which comprises condensing iron chloride in the mixture and washing the vapor mixture containing at least a portion of the iron chloride with liquid metallic halide to precipitate suspended solid iron chloride.

6. A method of removing iron chloride from a vaporized mixture of iron chloride and titanium tetrachloride which comprises condensing iron chloride in the mixture and washing the vapor

mixture containing at least a portion of the iron chloride with liquid metallic halide of the group consisting of silicon tetrachloride, stannic chloride, and titanium tetrachloride.

7. A method of removing iron chloride from a vaporized mixture of iron chloride and titanium tetrachloride which comprises condensing iron chloride in the mixture and washing the vapor mixture containing at least a portion of the iron chloride with liquid halide to precipitate suspended solid iron chloride.

8. A method of removing suspended solid iron chloride from a vaporized titanium tetrachloride which comprises washing the vapor with liquid titanium tetrachloride to remove the suspended solid iron chloride and removing the washed vaporized titanium tetrachloride.

9. A method of removing iron chloride from a

vaporized mixture of iron chloride and titanium tetrachloride which comprises condensing iron chloride in the mixture together with a portion of the tetrachloride and washing the vapor mixture containing a portion of the iron chloride with liquid titanium tetrachloride to precipitate suspended solid iron chloride, and recovering the washed titanium tetrachloride vapor.

10. A method of removing iron halide from a vaporized mixture of iron chloride and titanium halide which comprises condensing iron chloride in the mixture together with a portion of the titanium halide and washing the vapor mixture containing a portion of the iron chloride with liquid titanium tetrahalide to precipitate suspended solid iron chloride and recovering the washed titanium halide vapor.

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