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COMPLETE SPECIFICATION

Production of Ferric Chloride and Phosphorus Trichloride

We, THE PENNSYLVANIA SALT MANUFACTURING COMPANY, a Corporation organised under the Laws of the State of Pennsylvania, United States of America, of Three Penn Center Plaza, Philadelphia, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of ferric chloride and phosphorus trichloride and more particularly to the production of these materials through the chlorination of ferrophosphorus and, if desired, the production and separation of the chlorides of substantially all the economically important elements contained in ferrophosphorus.

The term "ferrophosphorus" is used in its broad sense. By ferrophosphorus is meant, a mixture of iron phosphides, such as Fe_3P , Fe_2P , FeP , FeP_2 , and possibly others. It might even be considered as a continuous series, or a solid solution, in which the iron and phosphorus are present in any proportion. Ferrophosphorus is generally obtained as a by product of the phosphate industry. Other elements besides the iron and phosphorus are present in the ferrophosphorus in substantially smaller amounts; those generally present in recoverable amounts are manganese, titanium, silicon, vanadium and chromium. For example, titanium and silicon are generally present in amounts of about 0.5 to 1.6% and 1.5 to 6% respectively. Commercially available ferrophosphorus is graded according to its phosphorus content, which may vary from 15 to 30%, and generally is present in amounts of about 22 to 26%, corresponding roughly to the formula Fe_2P . Any grade of ferrophosphorus is suitable in practicing the present invention, low grades with phosphorus contents of less than 20%, having been used with excellent success. This

low grade material has the advantage of being substantially less expensive since, prior to the present invention, no successful process had been devised whereby both the phosphorus and iron present could be economically recovered.

It has previously been known to chlorinate ferrophosphorus and by addition of fresh ferrophosphorus to the resulting product below red heat, to recover phosphorus trichloride. This is shown in Patent No. 312,685. This patent, however, discloses no process whereby the iron can be separated from the residue remaining after separation of phosphorus trichloride.

It has now been discovered that both the iron and the phosphorus in ferrophosphorus can be substantially, completely separated from the ferrophosphorus, each without contamination by the other, in the form of ferric chloride and phosphorus trichloride if the ferrophosphorus is first fully chlorinated with anhydrous chlorine, the resulting product then added to fresh ferrophosphorus at a temperature sufficiently high to volatilize off phosphorus trichloride but below the volatilization temperature of the fully chlorinated ferrophosphorus, and the residue then further chlorinated. During this last chlorination step ferric chloride is volatilized from the reaction mixture in substantially pure form. Without the removal of phosphorus trichloride and further chlorination of the residual material, the substantially pure ferric chloride cannot be obtained.

In order to obtain the phosphorus trichloride substantially free of any iron, in the reduction step wherein the chlorinated ferrophosphorus is reacted with fresh unchlorinated ferrophosphorus, it is necessary that the unchlorinated ferrophosphorus be present in amounts at least equal to and preferably greater than the molar equivalent of the chlorinated product. As a result there is always an appreciable amount of unreacted

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ferrophosphorus in the residue after the removal of the phosphorus trichloride formed in the reduction step.



wherein n is any amount greater than 0. The iron which is left behind in the residue is so bound up with this ferrophosphorus that it apparently cannot be separated therefrom by any mechanical means. This problem of separation, however, has been solved by the discovery that if the resulting residue is chlorinated at a temperature between 315° to 486° C. the iron readily separates from the chlorinated mass in the form of ferric chloride vapor. This can be easily collected by any conventional means.

If the ferrophosphorus is not present in at least molar equivalent amounts or slightly greater than the fully chlorinated ferrophosphorus, then even though phosphorus trichloride can be separated from the chlorinated ferrophosphorus as described in Patent No. 312,685, phosphorus trichloride cannot be obtained free from any iron contamination. The reason for this is probably that the free ferric chloride present combines with some of the phosphorus trichloride to form a complex, $\text{FeCl}_3 \cdot \text{PCl}_3$, which is volatile at the same temperatures as phosphorus trichloride and which distills over with the phosphorus trichloride.

When ferrophosphorus corresponding roughly to the formula Fe_2P is used, a weight ratio of at least 0.15 part ferrophosphorus per part chlorinated ferrophosphorus must be used in order to obtain pure phosphorus trichloride, as hereinafter discussed. Adjustment of the amount of ferrophosphorus used can be made, according to the phosphorus content of the ferrophosphorus. Thus, more ferrophosphorus is needed when the phosphorus content is low, and less is needed when the phosphorus content is high. For a phosphorus content of 30%, at least 0.14 part ferrophosphorus is needed per part chlorinated ferrophosphorus. Any amount of ferrophosphorus greater than that required for molar equivalency of ferrophosphorus to chlorinated ferrophosphorus, is not detrimental to the process, and in some cases is desirable, as will be shown.

In practicing the invention, the ferrophosphorus, preferably in lump form, is fully chlorinated with substantially anhydrous chlorine. The chlorination is carried out in a chlorine resistant vessel fitted with an outlet for removal of volatile products. The reaction is strongly exothermic and proceeds rapidly, supplying sufficient heat to maintain itself, after initiation, the reaction generally being started by initial heating to a temperature of about 200° C. The chlorination may be carried out at any suitable temperature, it generally being preferred to carry out the chlorination below about 486° C. if the chlorinated ferrophosphorus is to be main-

The reaction is believed to proceed as follows:—

tained as a liquid. The temperature may conveniently be controlled by varying the flow of chlorine into the reaction vessel. Completion of chlorination may be determined by testing the exit gases. If appreciable amounts of chlorine are present, the reaction is essentially complete. The chlorinated product consists essentially of a complex of ferric chloride and phosphorus pentachloride, composed of 2 mols ferric chloride per mol phosphorus pentachloride. In appearance it is dark brown non-viscous liquid at temperatures of approximately 100 to 486° C.

After the chlorination is completed, the chlorinated product is mixed with fresh ferrophosphorus, preferably finely-divided. On mixing the chlorinated product with fresh ferrophosphorus, an exothermic reaction takes place and phosphorus trichloride, formed during the reaction, is volatilized. The temperature of the reaction is maintained at 270 to just below 486° C. As the phosphorus trichloride vapors come off they are removed and collected by any convenient means. Due to the exothermic nature of the reaction, it is not necessary to apply heat.

After removal of the phosphorus trichloride, the residue, a porous solid, is chlorinated with substantially anhydrous chlorine. The chlorination of this residue is a slightly exothermic reaction, and can be completed without addition of heat; however, the heat generated by the reaction is insufficient to volatilize off the ferric chloride formed and it is therefore necessary to supply some heat to this step to raise the temperature of the reaction mass to 315 to just below 486° C., the temperature range in which the ferric chloride is volatilized off in a substantially pure state. Its vapors may be removed and collected by any convenient means.

The residue consists essentially of chlorinated ferrophosphorus and, if it is present in sufficient amounts, may then be admixed with fresh amounts of unchlorinated ferrophosphorus to repeat the step wherein the phosphorus trichloride is produced as described. If it is present in only small amounts, it may be combined with more chlorinated ferrophosphorus from another source, and then mixed with unchlorinated ferrophosphorus, to produce the phosphorus trichloride.

The invention is preferably practiced as either of what may be called a two-step process or a three-step process, the latter being preferred. In the two-step process the chlorinated ferrophosphorus is heated at a temperature of 270 to 486° C. with a substantial excess of unchlorinated ferrophos-

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phorus in the step where the phosphorus trichloride is obtained. The excess should preferably be present in sufficient amounts so that when the residue, after removal of the phosphorus trichloride is chlorinated at temperatures of 315 to 486° C., there will be sufficient chlorinated ferrophosphorus present after the removal of the ferric chloride to proceed immediately to the step wherein the chlorinated ferrophosphorus is reacted with unchlorinated ferrophosphorus to again form the phosphorus trichloride. It is apparent that in this manner, a cyclic two-step process can be established wherein both steps may be carried out in a single reaction vessel, and the only additional heat needed is in the volatilization of ferric chloride. The chlorinated ferrophosphorus needed in the first step is prepared in the second step simultaneously with the formation and removal of the ferric chloride. Ferrophosphorus and chlorine are the only raw materials, and ferric chloride and phosphorus trichloride are obtained alternately as products.

It was further discovered that the chlorination of the ferrophosphorus could be carried out much more rapidly if the fully chlorinated ferrophosphorus were removed from the chlorination chamber as formed. Though different methods may be employed for separating the chlorinated ferrophosphorus from the unreacted ferrophosphorus, either one of the following is preferred:—

In the first of these chlorination is carried out at a temperature above 486° C., the volatilization temperature of the chlorinated ferrophosphorus and preferably at about 800° C. As the chlorinated ferrophosphorus is formed it volatilizes and its vapors are removed from the chlorination chamber and condensed.

The alternate method is to support the ferrophosphorus in such a manner that the chlorinated ferrophosphorus, which is either liquid or gaseous at the reaction temperature, will flow by gravity or distil away from the reaction mass as formed. The most convenient way of doing this is to support the ferrophosphorus on a grate, and introduce the chlorine directly into the bed of ferrophosphorus. The temperature in such a case may be such that the chlorinated ferrophosphorus formed is either liquid or vapor. The chlorinated ferrophosphorus as formed either distils or drains down through the grate, thus effecting its separation from the unreacted ferrophosphorus.

Where the chlorinated ferrophosphorus is prepared separately, the invention is preferably practiced in what might be referred to as a three-step process, the additional step being the production of the chlorinated ferrophosphorus in a separate reactor, preferably by one of the more rapid methods outlined above.

In practicing the invention in accordance with this procedure, the chlorinated ferrophosphorus as formed is stored preferably in the liquid state, i.e., at a temperature of 100° to about 486° C. As the chlorinated ferrophosphorus is needed, it is introduced into a reaction vessel together with at least a molar equivalent amount of ferrophosphorus, and substantially the major portion of phosphorus trichloride formed in the ensuing reaction is removed by distillation.

The residue remaining after removal of the phosphorus trichloride is then chlorinated, and, by the application of a little heat, ferric chloride as heretofore stated is volatilized from the reaction mass in the temperature range of 315° to just below 486° C. in a substantially pure state. The residue from this step is then combined with additional chlorinated ferrophosphorus and unchlorinated ferrophosphorus which react as described, volatilizing off phosphorus trichloride.

In the preferred method of carrying out this three-step process, two reaction vessels are used simultaneously, in which the last two steps of the procedure are carried out alternately thus making possible a substantially continuous production of both the phosphorus trichloride and the ferric chloride.

The following examples, which are given for purposes of illustration only, further show the practice of the invention:—

EXAMPLE I.

About 400 parts by weight of chlorinated ferrophosphorus prepared from a ferrophosphorus containing about 23% phosphorus and 70% iron were charged into a reactor having a vapor exit connected to a water-cooled receiving vessel. 180 parts by weight of ferrophosphorus, ground to pass a 115 mesh screen, were added. An exothermic reaction began when the mixture was heated to 270° C., and at about 300 to 400° C., phosphorus trichloride began to distil over into the receiver. When no more phosphorus trichloride distilled over, the reaction vessel was connected to another receiving vessel. A stream of anhydrous chlorine gas was then introduced into the reactor as the reactor was heated to 315 to 375° C. Ferric chloride, formed during the reaction was distilled over, forming fine crystals in the receiver. A slight excess of chlorine was present during this step. When ferric chloride no longer distilled from the reactor, the vapor exit was again connected to the phosphorus trichloride receiving vessel and the residue in the reactor was mixed with 180 parts by weight of fresh finely-divided ferrophosphorus. The reactor was again heated to about 270° C. to initiate the reaction and the phosphorus trichloride again produced in the manner previously described. The two-step cyclic procedure was repeated several times, the phosphorus tri-

chloride and ferric chloride being removed alternately as described. The phosphorus trichloride was fractionally distilled, with silicon tetrachloride being separated at 56° C. and phosphorus trichloride at 76° C. The ferric chloride as produced was substantially pure, containing less than 2% impurities.

EXAMPLE II.

One-half inch lumps of ferrophosphorus were charged into a steel, water-jacketed reactor, equipped with a top closure, inlets for chlorine near the bottom and a porcelain grate at the bottom having 2-mm perforations. A few red-hot lumps of ferrophosphorus were dropped into the reactor and the flow of anhydrous chlorine gas was introduced through the inlets, to initiate the reaction. Water at about 35 to 98° C. was circulated through the water jacket to protect the steel reactor, since the reaction, which was exothermic, was maintained at bright red heat. The top was thereafter kept closed except for periodic additions of fresh ferrophosphorus. The reaction was kept at from red to white heat by adjusting the chlorine flow rate. The chlorinated ferrophosphorus formed in the reaction drained or distilled down through the grate and condensed in a receiving vessel under the grate. The reaction was kept going with an excess of ferrophosphorus always present, using approximately 1 part by weight of ferrophosphorus for each 3.8 parts by weight of chlorinated ferrophosphorus formed. Very little excess chlorine was needed. The product was stored in a closed container at 300—400° C.

About 5457 parts by weight of the chlorinated ferrophosphorus were charged into a brick-lined steel reactor and 845 parts by weight of 115-mesh ferrophosphorus were added to it. From this, 2246 parts by weight phosphorus trichloride were distilled at a temperature of 300 to 400° C. and collected in a water-cooled receiver. When the reaction had stopped, anhydrous chlorine was passed over the residue in the reactor, and heat was applied simultaneously. About 4948 parts by weight of ferric chloride were distilled at a temperature of 315 to 375° C. and collected in a separate receiver. The residue, consisting of chlorinated ferrophosphorus, was mixed with additional chlorinated ferrophosphorus and unchlorinated ferrophosphorus, and the cycle repeated. The ferric chloride contained less than 2% impurities. (The phosphorus trichloride was contaminated with silicon and titanium compounds and required fractional distillation).

The phosphorus trichloride, as produced in the practice of this invention, is usually contaminated with as much as 10% impurities. By fractional distillation, silicon tetrachloride may be separated in the low-boiling fraction, about 56° C., in substantially pure form.

Phosphorus trichloride can be distilled pure in the fraction boiling at a temperature of 76° C. The residue after distillation consists of compounds containing titanium tetrachloride and phosphorus oxychloride.

The present invention may be advantageously included in an integrated process wherein substantially all of the phosphorus, iron, silicon and titanium impurities which may be found in ferrophosphorus are recovered separate from each other.

In the integrated process only two relatively cheap raw materials are needed—ferrophosphorus and chlorine. The separation of the various elements present in the ferrophosphorus is effected by taking advantage of the physical properties of certain intermediate products and of the final products themselves. There is no waste in the process, the materials used in one part of the process being returned to the system at another point. This makes possible substantially complete recovery of all the valuable elements in ferrophosphorus. An additional advantage to the process of the present invention is that the exothermic nature of the reactions involved is fully utilized, very little additional heat being necessary. The advantage of this is apparent when it is considered that the reactions themselves all take place at temperatures higher than 100° C., and some take place at 300° C. or higher.

In practicing the present invention, ferrophosphorus is first fully chlorinated under conditions such that the chlorination product is substantially separated from the ferrophosphorus as it is formed. The chlorination product is stored, preferably in liquid form and periodically supplied to a reaction chamber, together with fresh ferrophosphorus, at a temperature suitable for the distillation of crude phosphorus trichloride. The residue after removal of phosphorus trichloride is chlorinated with excess chlorine at a temperature suitable for the distillation of pure ferric chloride.

In the chlorination of ferrophosphorus, which is preferably carried out at elevated temperatures, silicon tetrachloride, titanium tetrachloride and phosphorus oxychloride are formed and given off as vapors. The silicon tetrachloride vapor can be separated from the titanium tetrachloride and phosphorus oxychloride by contacting these vapors with a bed of ferrophosphorus as hereinafter described. Most of the vapors condense on the ferrophosphorus at the temperature employed, and silicon tetrachloride passes through in substantially pure state. The ferrophosphorus used in the bed, and thereby enriched with the more volatile chlorides, is conveniently used as a source of ferrophosphorus for the production of the phosphorus trichloride.

The crude phosphorus trichloride is purified by fractional distillation, with some

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additional silicon tetrachloride being recovered in the low boiling fraction, and phosphorus trichloride at higher temperature. The residue which contains substantially all of the titanium in the form of a complex of titanium tetrachloride and phosphorus oxychloride, formed in the reaction is treated with chlorine and phosphorus trichloride, which replaces and thereby releases the phosphorus oxychloride in the complex, at a temperature suitable for the distillation of pure phosphorus oxychloride. The residue after removal of the phosphorus oxychloride is then treated with ferric chloride, which replaces and releases the titanium tetrachloride, at a temperature suitable for the removal of titanium tetrachloride by distillation. This process is described and claimed in co-pending Application No. 20029/56, (Serial No. 805,154). The final residue, which consists essentially of a complex of ferric chloride and phosphorus pentachloride is combined with the chlorination product resulting from the chlorination of ferrophosphorus, and the cycle is repeated.

The integrated process can best be described by reference to the flow diagram shown in the accompanying drawing.

Referring to the drawing, the ferrophosphorus, preferably in lump form, from storage chamber 1 is fed into chlorinator 2 where it is reacted with substantially anhydrous chlorine to completely chlorinate all of the reactive material in the ferrophosphorus. The reaction is initiated at temperatures of about 200° C. but is preferably carried out at temperatures of about 500° C. to 1200° C. Temperatures above 1200 may be used, the ferrophosphorus melting at about 1300° C. The chlorination is preferably carried out on a grate, or in some other manner such that the chlorinated product as formed is passed from the chlorination chamber 2 to the storage vessel 3. The products of chlorination are primarily a ferric chloride-phosphorus pentachloride complex having the formula $(\text{FeCl}_3)_2\text{PCl}_5$ described above, and a small quantity of gaseous material consisting primarily of silicon tetrachloride and a titanium tetrachloride-phosphorus oxychloride complex mixture, such as that described in co-pending Application No. 20029/56 (Serial No. 805,154).

These gaseous materials are passed through a rotating bed 4, which contains a moving mass of finely-divided ferrophosphorus. The titanium tetrachloride-phosphorus oxychloride complex mixture is condensed on the ferrophosphorus in rotating bed 4, which is maintained at a temperature of 56° to 140° C., while the major portion of the silicon tetrachloride vapor passes on through and is condensed in condenser 5.

The hot ferric chloride-phosphorus pentachloride complex from storage vessel 3 is fed with ferrophosphorus from rotating bed 4 into reactor 6, where the complex and ferrophosphorus react at a temperature of 270° to 486° C. to release phosphorus trichloride, which is passed to condenser 7 and treated as hereinafter described. The ferrophosphorus and complex reactor 6 are in such proportions that the ferrophosphorus is present in at least the required molar amounts to release all of the phosphorus present in the form of phosphorus trichloride and preferably present in a slight excess as previously described.

After the reaction of the ferric chloride-phosphorus pentachloride complex with the ferrophosphorus has been completed, chlorine is admitted into the reactor 6 to chlorinate the residue. The chlorine is substantially anhydrous chlorine, and is preferably used in excess amounts, the chlorination being carried out at a temperature of 315° to 486° C. In this reaction it is necessary to add some heat to maintain the reactor at this temperature. The ferric chloride formed during this chlorination step is passed to sublimation chamber 8 where it is condensed and from which it can be removed and packaged. In this step, the small excess of ferrophosphorus used in the previous step is fully chlorinated to form the ferric chloride-phosphorus pentachloride complex and remains in reactor 6 after the ferric chloride is distilled. The complex remaining in reactor 6 is combined with fresh complex from storage chamber 3 and ferrophosphorus from rotating bed 4, and phosphorus trichloride is again produced as previously described.

(While the chlorination is proceeding in reactor 6, ferric chloride-phosphorus pentachloride complex from storage chamber 3 and ferrophosphorus from rotating bed 4 are charged into reactor 6' in the same manner in which they were originally charged into reactor 6. The charge of complex and ferrophosphorus is then reacted in reactor 6' as previously described for reactor 6, the phosphorus trichloride released being passed to condenser 7 as previously described. In this way reactors 6 and 6' are alternately used for reacting complex with ferrophosphorus or chlorinating the residue from said reaction so that the process is essentially continuous.)

The phosphorus trichloride and other vapors present therewith, which include any silicon tetrachloride not previously removed and substantially all of the titanium tetrachloride-phosphorus oxychloride complex, are condensed in condenser 7, and the condensate stored in storage vessel 9. The condensate is then passed from storage vessel 9 to a fractional distillation apparatus 10, wherein the phosphorus trichloride and silicon tetrachloride are separated from the titanium tetrachloride phosphorus oxychloride complex. The silicon tetrachloride separates in the low-boiling fraction at a temperature of 56° C. whereas the phosphorus trichloride is separa-

ted in the fraction boiling at 76° C. The residue consists of the titanium tetrachloride-phosphorus oxychloride complex.

5 The titanium tetrachloride-phosphorus oxychloride complex mixture is then passed into reactor 11 where it is reacted with phosphorus pentachloride which is obtained either by
10 first combining some of the phosphorus trichloride obtained from the fractional distillation column 10 with chlorine or by passing the phosphorus trichloride and chlorine directly into the reactor 11. This reaction is carried to completion at a temperature of
15 85° to 140° C., and the phosphorus oxychloride is then distilled off at a temperature of about 107 to 239° C. The residue which consists of a complex of titanium tetrachloride and phosphorus pentachloride is mixed with
20 ferric chloride obtained from sublimation chamber 8 and the ferric chloride and titanium tetrachloride-phosphorus pentachloride complex is then heated to 100° to 239° C.; and the titanium tetrachloride released is distilled off at a temperature of about 136 to 486° C.
25 The residue is a complex of ferric chloride and phosphorus pentachloride which is essentially the same as that stored in storage vessel 3 and is accordingly returned to this vessel.

30 If desired, a single reactor may be used in place of the two reactors 6 and 6¹; however, it is apparent that in such a case the process would not be continuous since it would be necessary to wait until either the reaction between the ferric chloride-phosphorus penta-
35 chloride complex and ferrophosphorus had been completed or the reaction wherein the residue was chlorinated to produce ferric chloride had been completed before the next step could be taken.

40 Though in the modification described, the phosphorus trichloride, silicon tetrachloride and titanium tetrachloride and phosphorus oxychloride are all condensed in the condenser 7 and then later separated by fractionation,
45 in the preferred process only a partial condensation at 7 would occur. At this point only the titanium tetrachloride and phosphorus oxychloride would be condensed and the condensate passed directly to the reactor
50 11. The gaseous phosphorus trichloride and silicon tetrachloride would then be passed to another partial condenser not shown wherein the phosphorus trichloride would be condensed, thus separating it from the silicon
55 tetrachloride.

60 When ferrophosphorus is charged into the chlorination chamber 2, it is preferably added in lump form; whereas, when the ferrophosphorus is charged into the rotating bed 4, it is better to have it finely-divided. This finely-divided material is also more suitable for the reaction in which phosphorus trichloride is produced, in reaction chamber 6 or 6¹. The degree of comminution of ferrophosphorus is
65 not critical.

It is apparent from the description of the above process that not only is a substantial saving achieved due to the utilization of the heat evolved in the exothermic reactions but that the process gives a self-sufficient system wherein the only raw materials used are the ferrophosphorus and the chlorine; also, by the process a substantially complete recovery and separation of all of the most important elements in the ferrophosphorus is obtained.

70 In the specification and in the claims the present invention is described as being carried out at atmospheric pressure. As with most chemical reactions, pressures greater or less than atmospheric pressure may be used. If pressures substantially below or above atmospheric pressure are employed it is apparent that the temperature limitations will vary somewhat as would be expected, the temperatures being slightly lower for reduced pressures and slightly higher for higher pressures. Any such variations are intended to be included in the present specification and claims.

WHAT WE CLAIM IS:—

90 1. A process of recovering at least phosphorus trichloride from fully chlorinated ferrophosphorus, which comprises reacting at least a molar equivalent amount of the unchlorinated ferrophosphorus with the chlorinated
95 ferrophosphorus at a temperature of 270 to 486° C. to form phosphorus trichloride vapor and a residue, and chlorinating the residue at a temperature of 315 to 486° C., thereby recovering ferric chloride as its vapor.

100 2. A process according to Claim 1, in which a substantial molar excess of unchlorinated ferrophosphorus is reacted with the chlorinated ferrophosphorus.

105 3. A process according to Claim 1 or 2, in which the chlorinated ferrophosphorus is obtained by chlorinating at a temperature below 486° C.

110 4. A process according to any one of Claims 1—3, in which the chlorinated ferrophosphorus has the empirical formula $(\text{FeCl}_2)_2 \cdot \text{PCl}_5$ and that at least 0.14 part by weight of the ferrophosphorus is reacted therewith.

115 5. A process according to any one of the preceding claims, in which the final residue containing substantial amounts of chlorinated ferrophosphorus which remains after the recovery of ferric chloride is heated further with fresh unchlorinated ferrophosphorus at a temperature of 270 to 486° C. to repeat said
120 process.

125 6. A process according to any one of the preceding claims, in which the fully chlorinated ferrophosphorus is obtained by the chlorination of ferrophosphorus with anhydrous chlorine.

7. A process according to Claim 6, in which the fully chlorinated product is removed as formed.

8. A process according to Claim 7, in which the ferrophosphorus is supported on a grate while chlorinated and the chlorinated product is separated from the ferrophosphorus as formed by passing said chlorinated product downwards through the grate.
9. A process according to Claim 7, in which the ferrophosphorus is chlorinated at a temperature in excess of 486° C. and the chlorinated product is removed from the ferrophosphorus as a vapor.
10. A process of recovering at least phosphorus trichloride from fully chlorinated ferrophosphorus substantially as herein described with reference to the examples.
11. An integrated process for recovering iron, phosphorus, silicon and titanium from ferrophosphorus containing silicon and titanium comprising completely chlorinating the ferrophosphorus to convert all of these elements into their chlorides which comprises treating the fully chlorinated ferrophosphorus according to the process of any one of the preceding claims thereby separating the phosphorus trichloride vapor and ferric chloride vapor, said phosphorus trichloride vapor containing admixed therewith silicon tetrachloride, titanium tetrachloride and phosphorus oxychloride, collecting and fractionating the phosphorus trichloride vapors into substantially pure phosphorus trichloride, silicon tetrachloride and a complex of titanium tetrachloride-phosphorus oxychloride, heating said titanium tetrachloride-phosphorus oxychloride complex with sufficient amounts of phosphorus pentachloride, formed by chlorinating said previously prepared phosphorus trichloride, at a temperature of 85° to 140° C. to release all of said phosphorus oxychloride and to form a complex of titanium tetrachloride and phosphorus pentachloride, removing said phosphorus oxychloride and heating said complex of titanium tetrachloride and phosphorus pentachloride with sufficient amounts of said ferric chloride at a temperature of 100° to 239° C. to release substantially all of the titanium tetrachloride and form a complex of iron chloride and phosphorus chloride, removing said complex of iron chloride and phosphorus chloride and adding it to fresh chlorinated ferrophosphorus and repeating the process.
12. A process according to Claim 11, in which silicon tetrachloride, titanium tetrachloride and phosphorus oxychloride in the form of their vapors from the chlorination of the ferrophosphorus are passed over a bed of ferrophosphorus maintained at a temperature of 56° to 140° C. to selectively absorb out titanium tetrachloride and phosphorus oxychloride in order to separate the silicon tetrachloride therefrom.
13. A method according to Claim 12, in which said bed of ferrophosphorus is rotated.
14. A process according to Claim 12 or 13, in which the bed is an agitated bed of finely divided ferrophosphorus.
15. A process according to Claim 11, in which the withdrawn vapors comprising titanium tetrachloride, phosphorus oxychloride, phosphorus trichloride and silicon tetrachloride are cooled at least to 56° C., to condense all the vapors and the resulting liquid mixture separated by fractional distillation, the silicon tetrachloride being removed in the low-boiling fraction at a temperature of about 56° C. and the phosphorus trichloride being separated in the fraction boiling at about 76° C. and the titanium tetrachloride and phosphorus oxychloride remaining in the residue in the form of a complex.
16. A process according to Claim 11, in which the withdrawn vapors comprising titanium tetrachloride, phosphorus oxychloride, phosphorus trichloride and silicon tetrachloride are cooled to a temperature of 140° C. to condense out the titanium tetrachloride and phosphorus oxychloride as a complex, including the steps of removing said complex and then further cooling the remaining vapors to a temperature of about 76° C. to condense out the phosphorus trichloride, removing said condensed phosphorus trichloride and then further cooling the remaining uncondensed gases to a temperature of about 56° C. to condense out the silicon tetrachloride.
17. A process according to any one of Claims 11—16, in which the ferrophosphorus is chlorinated at temperatures of 200° to 1200° C. and the complex formed by said chlorination is removed as formed.
18. A process according to any one of Claims 11—17, in which the fully chlorinated ferrophosphorus is stored in the liquid state at a temperature of 100° to 486° C., and the complex of iron chloride and phosphorus chloride is maintained at a temperature of 136° to 486° C. to drive off all of said titanium tetrachloride as a vapor after the previous heating at 100° to 239° C., said vapor being collected and condensed.
19. A process according to Claim 18, in which the fully chlorinated ferrophosphorus complex is stored as a liquid, in a container at a temperature of 100° to 486° C. and two reactors are used to carry out the reaction of said complex with ferrophosphorus and the chlorination of the residue of said reaction between said complex and ferrophosphorus after removal of the phosphorus trichloride formed, said reactors being operated simultaneously each alternately first being used to react complex from said container with ferrophosphorus and then being used to chlorinate the residue.
20. A process according to any of Claims 1 to 10, which includes isolating any silicon tetrachloride present along with the phosphorus

phorus trichloride vapor by separating the fraction of said vapor boiling at 56° C.

- 5 21. An integrated process substantially as herein described with reference to the accompanying drawing.

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