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## PRODUCTION OF POTASSIUM TITANIUM FLUORIDE

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This invention relates to the production of potassium titanium fluoride and contemplates a novel process for the production of potassium titanium fluoride of high purity from titanium ore and calcium fluoride as principal starting materials.

The rapidly expanding use of potassium titanium fluoride as an addition agent to baths of molten aluminum, in which the added titanium serves as a grain refining agent for the aluminum, has created a demand for large quantities of potassium titanium fluoride. Potassium titanium fluoride ($K_2TiF_6$), known also as potassium fluotitanate, has been produced heretofore by treating titanium dioxide with hydrofluoric acid in the presence of potassium chloride. This process, however, requires relatively expensive starting materials which have presented an effective barrier to large scale production.

The present invention contemplates the production of potassium titanium fluoride by a method which uses as its principal starting materials naturally occurring and relatively inexpensive titanium ore and calcium fluoride. The method of the invention comprises reacting calcium fluoride with an aqueous solution of a titanium sulfate product obtained by sulfuric acid digestion of a titanium ore, treating the resulting solution of titanium fluoride with an ionizable fluorine compound in the presence of potassium chloride, and separating from the resulting solution crystals of potassium titanium fluoride.

The titanium sulfate product is obtained by conventional digestion with concentrated sulfuric acid at an elevated temperature and generally comprises a plastic mass containing most if not all of the titanium of the ore in the form of titanium sulfate. The titanium sulfate product is advantageously slurried with sufficient water to form an aqueous solution of the titanium sulfate, and in this form the titanium sulfate is reacted with calcium fluoride to produce titanium fluoride. The resulting titanium fluoride in aqueous solution, and preferably in the absence of ferric ions, is then converted to potassium titanium fluoride by an ionizable fluorine compound in the presence of potassium chloride. The potassium titanium fluoride is preferably maintained in solution as it is formed and is subsequently separated from the reaction mixture by crystallization.

The method of the invention is adapted to being carried out with such a limited quantity of water that the final solution of potassium titanium fluoride is of sufficient concentration to

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permit commercially effective recovery of the titanium compound by simple crystallization. In the now preferred embodiment of the invention, the total amount of water used in the entire method is limited to that quantity which will yield a final potassium titanium fluoride solution from which the titanium compound may be readily crystallized.

The method of the invention is adapted to the treatment of any titanium ore, or titanium concentrate obtained from such ore, susceptible to digestion with sulfuric acid. The method is particularly adapted to the production of potassium titanium fluoride from ilmenite, either in the naturally occurring condition of this ore or in concentrated form. Particularly effective results have been obtained by the treatment of an ilmenite concentrate containing about 54% titanium dioxide. When ilmenite is used as the source of titanium, the sulfuric acid digestion product will contain ferrous and ferric sulfates in addition to the titanium sulfate. Digestion of the titanium ore may be effected readily by contact with an excess of concentrated sulfuric acid. A mixture of the ore and acid is heated according to conventional practice to initiate the reaction. Once the reaction has started, its exothermicity promotes substantially complete conversion of the titanium dioxide to titanium sulfate.

The calcium fluoride reacted with the titanium sulfate product in the method of the invention may advantageously comprise fluorospar, although other calcium fluoride products may be used. Regardless of its source, the calcium fluoride is advantageously ground to a fine state of subdivision, preferably such that 90% passes through a 200 mesh screen, in order to facilitate the reaction.

The reaction between calcium fluoride and the titanium sulfate in the product resulting from digestion of the titanium ore with sulfuric acid takes place readily at an elevated temperature. For this purpose, I have found that a reaction temperature of at least about 100° C. is particularly effective. Such a temperature may be obtained readily by introducing live steam into the reaction mixture. In a practical embodiment of this step of the method, live steam is introduced into the reaction mixture to heat it to and maintain it at or near is boiling point (about 104° C.) throughout the entire reaction period.

The period required for effective reaction between the calcium fluoride and titanium sulfate depends, in addition to the reaction temperature,

upon the effectiveness of the distribution of calcium fluoride throughout the reaction mixture and the concentration of the titanium sulfate solution. Distribution is enhanced by finely subdividing the calcium fluoride, by mechanically agitating the reaction mixture throughout the reaction period, and by controlling the consistency of the reaction mixture. The consistency of the titanium sulfate product resulting from the digestion of ilmenite with sulfuric acid resembles that of wet plaster. Accordingly, the titanium sulfate product is slurried with an additional quantity of water in order to bring all of the titanium sulfate into solution and to promote effective contact between the titanium sulfate and added calcium fluoride. The amount of water used in making up such a slurry should be limited to that amount sufficient to form a fluid slurry containing a high concentration of dissolved titanium sulfate. The speed of reaction between the titanium sulfate and calcium fluoride depends largely upon the concentration of titanium sulfate, high concentrations promoting faster and more complete reaction in shorter periods of time. At the end of the reaction period, the reaction mixture comprises a solution containing titanium fluoride, in the form of titanic fluoride, together with other water-soluble products of the sulfuric acid digestion of the titanium ore, and nisoluble material comprising calcium sulfate and insolubles present in the starting materials.

The titanium fluoride solution will contain ferrous sulfate and ferric sulfate when the titanium ore used as a starting material contains an appreciable amount of iron, as in the case of ilmenite. The ferrous and ferric sulfates are both soluble under conditions prevailing during the reaction between the titanium sulfate product and the calcium fluoride and would normally be carried along in solution with the titanium fluoride up to that stage of my novel method in which the titanium fluoride is converted to potassium titanium fluoride. Ferric ions present in this stage of the method would react with the ionizable fluorine compound and potassium chloride used to convert the titanium fluoride to potassium titanium fluoride and would precipitate an insoluble potassium ferric fluoride ($K_3FeF_6$). Inasmuch as the precipitation of this product represents a loss of both fluorine and potassium which would otherwise be available for combination with the titanium fluoride to produce the desired potassium titanium fluoride, it is desirable to remove the ferric ions prior to this stage of the method. Accordingly, in the preferred embodiment of the invention ferric sulfate is reduced to ferrous sulfate prior to the conversion of titanium fluoride to potassium titanium fluoride.

The reduction of ferric sulfate to ferrous sulfate may be effected in the conventional manner by the addition of scrap iron to the acidic solution containing the ferric sulfate. Thus, scrap iron, such as scrap iron powder, may be added to the slurry of the titanium sulfate product before reaction with the calcium fluoride, or the scrap iron may be added to the titanium fluoride-containing solution obtained by the reaction between the titanium sulfate product and the calcium fluoride. This reduction of ferric ions to ferrous ions is accompanied by the evolution of a substantial quantity of hydrogen which causes foaming. Inasmuch as it is desirable to maintain a relatively concentrated solution of titanium sulfate in the slurry which is reacted with calcium fluoride, the addition of scrap iron to this slurry presents a problem in controlling the foaming product by the liberated hydrogen. On the other hand, after reaction has been effected between the titanium sulfate product and the calcium fluoride, the reaction mixture may be further diluted without detriment to the method of the invention, and the evolution of hydrogen in such a diluted mixture causes less serious foaming. What foaming does tend to occur can be effectively reduced by adding a trace of a vegetable oil such as cottonseed oil or the like. Accordingly, it is my preferred practice to add the iron to the titanium fluoride-containing solution under more dilute conditions than those which would prevail prior to the conversion of the titanium sulfate to titanium fluoride.

The amount of iron which is employed to reduce the ferric ions to ferrous ions, either before or after conversion of the titanium sulfate to titanium fluoride, should be such as to effect only the desired reduction of ferric ions. An appreciable excess of added iron over and above that required to effect reduction of ferric ions will also reduce the titanic fluoride to titanous fluoride. Inasmuch as it is a particular object of the invention to introduce as much fluorine as possible into the titanium by means of a relatively inexpensive source of fluorine (calcium fluoride), reduction of titanic fluoride to titanous fluoride should be avoided. Accordingly, the scrap iron powder should be added in small increments with a test after each addition for the presence of residual ferric ions. When the titanium fluoride solution is substantially free from ferric ions, the solution, separated from insolubles by filtration, becomes a suitable environment for the conversion of the titanium fluoride to potassium titanium fluoride.

The conversion of titanium fluoride to potassium titanium fluoride should be effected in an aqueous medium maintained at a temperature of about 60° C. to avoid premature crystallization of the final product. Premature crystallization of the potassium titanium fluoride occasioned by maintenance of an unduly low temperature produces a slimy mass of fine crystals of the desired product in a form which is difficult to wash free from entrained mother liquor. Temperatures materially below 60° C. are generally inadequate to maintain a relatively high concentration of potassium titanium fluoride in solution. Temperatures above about 50° C. may be used although such temperatures appear to offer no advantage and represent a waste of heat.

The conversion of titanium fluoride to potassium titanium fluoride is effected by the addition to the hot titanium fluoride-containing solution of an ionizable fluorine compound and potassium chloride. The two compounds may be added to the titanium fluoride solution in any order. Suitable ionizable fluorine compounds include hydrofluoric acid, sodium fluoride, potassium fluoride, ammonium bifluoride, ($NH_4HF_2$), etc. Ammonium bifluoride is a dry material easy to handle in commercial operation and may be used with particular advantage. The amount of ionizable fluorine compound added to the titanium fluoride solution should be at least stoichiometrically equivalent to the titanium fluoride content of the solution, and an excess of the ionizable fluorine compound is preferred. The potassium chloride is advantageously added in

the form of the dry salt. Its presence affords both the source of potassium for the formation of potassium titanium fluoride and a controlled solubility effect which markedly facilitates the crystallization of potassium titanium fluoride from the solution thereof. Accordingly, the potassium chloride should be present in amount sufficient to provide the stoichiometric quantity of potassium required to convert the titanium fluoride content of the solution to potassium titanium fluoride and should be present in a sufficient excess to provide the desired solubility control over the potassium titanium fluoride. The amount of potassium chloride required to effect conversion and to facilitate crystallization of potassium titanium fluoride can be determined readily from the concentration of titanium fluoride in the solution thereof.

Crystallization of the potassium titanium fluoride from the resulting hot solution thereof may be effected by conventional procedure for the attainment of relatively large crystals. For example, the hot solution may be allowed to cool slowly to the ambient temperature or may be artificially cooled to a still lower temperature. The large crystals of potassium titanium fluoride thus produced may be readily separated from the mother liquor by conventional filtration or centrifuging. More complete removal of the mother liquor may be effected by washing the filtered or centrifuged crystals with a cold saturated solution of potassium chloride. The resulting crystals are then dried, advantageously in an oven adapted to produce anhydrous crystals of potassium titanium fluoride. The product is completely stable under such drying conditions and, if desired, may even be fused at a dull red heat without noticeable decomposition.

The complete method of the invention thus comprises digesting a titanium ore, advantageously such an ore as ilmenite, with sulfuric acid in order to effect substantially complete conversion of the titanium dioxide of the ore to titanium sulfate. The resulting titanium sulfate-containing product is preferably slurried with added water, is then agitated with an addition of a stoichiometric excess of finely divided calcium fluoride and is heated to a temperature of about 100° C. with continued agitation and for a sufficient period of time to effect conversion of the titanium sulfate to titanium fluoride. The reaction product, comprising a solution of titanium fluoride containing dissolved ferrous sulfate and ferric sulfate, as well as insoluble calcium sulfate produced in the course of the reaction and insolubles present in the titanium ore, is then diluted with a further quantity of water to facilitate the step of reducing ferric ions to ferrous ions. This reduction is effected by adding increments of scrap iron, advantageously in the form of foundry iron dust, with an appropriate test of the solution between additions of iron for the presence of ferric ions. After a sufficient quantity of metallic iron has been added to reduce ferric ions to ferrous ions, without reduction of the titanic fluoride to titanous fluoride, the mixture is filtered to remove insolubles. The filter cake is washed with water to recover entrained titanium fluoride solution, the wash water being combined with the filtrate. The combined filtrate and wash water are heated to about 60° C. and the titanium fluoride content of the resulting solution, which further contains dissolved ferrous sulfate, is converted to potassium titantium fluoride by the addition of a stoichiometric excess of



an ioniziable fluorine compound and a substantial excess of potassium chloride. After complete dissolution of the added fluorine compound and potassium chloride, the solution is cooled slowly to at least ambient temperature, and the crystallized potassium titanium fluoride is separated from the mother liquor. Entrained mother liquor, containing dissolved ferrous sulfate, may be substantially completely removed by washing the separated crystals with a cold saturated solution of potassium chloride. The washed crystals are then dried and comprise potassium titanium fluoride of high purity.

The following description of a commercial scale operation in accordance with the invention illustrates a physical embodiment thereof. It must be understood, however, that the method of the invention is not limited to the specific conditions recited in this example. A charge of 800 pounds of concentrated ilmenite and 1800 pounds of 66° Bé. sulfuric acid was worked up into a slurry in a lead lined tank. The concentrated ilmenite analyzed about 54% $TiO_2$ and about 46% FeO and was ground to such an extent that 90% passed through a 200 mesh screen. The amount of sulfuric acid used was substantially in excess of the 1,560 pounds theoretically required to digest the ore. Steam was blown into the slurry, while continuing mechanical agitation, until the mixture attained a temperature of about 160° C. by virtue of the heating effect of the steam and the exothermic heat of dilution of the concentrated sulfuric acid. The introduction of steam and mechanical agitation were then discontinued, and the reaction between the ore and sulfuric acid generated such additional heat as to raise the temperature of the mass to about 200–210° C. within a few minutes. After the reaction was completed and the reaction mass was allowed to cool, the mass assumed a consistency resembling that of moist plaster.

The viscous reaction mass, comprising titanium sulfate, ferric and ferrous sulfates and excess sulfuric acid, was then slurried with sufficient water to make up a total volume of about 300 gallons. The titanium sulfate-containing slurry was agitated mechanically while steam was blown thereinto until the slurry approached its boiling point of 104° C. A charge of 875 pounds of fluorospar, ground to such fineness that 90% of it passed through a 200 mesh screen, was then thoroughly mixed with the slurry while maintaining its elevated temperature of about 104° C. by continuous introduction of steam. The charge of fluorospar was appreciably in excess of the 842 pounds theoretically required to convert all of the titanium sulfate to titanium tetrafluoride. Heating and agitation were continued for about 1 hour in order to insure thorough reaction. At the end of this period, the reaction mixture comprised a solution of titanium tetrafluoride containing dissolved ferrous sulfate and ferric sulfate in admixture with insoluble calcium sulfate produced during the course of the reaction.

The ferric sulfate present in the hot titanium tetrafluoride-containing mixture was then reduced to ferrous sulfate by diluting the mixture with enough warm water to make a total liquid volume of about 500 gallons and by adding foundry iron powder first in 10 pound lots to minimize foaming and later in smaller 5 pounds and 2 pounds lots as the reduction of ferric ions neared completion. Foaming was suppressed by adding a trace of cottonseed oil to the mixture. After each addition of iron powder a small sample of

the reaction solution was tested with potassium thiocyanate-impregnated paper, the red coloration produced by ferric ions serving as an indicator. Successive lots of iron powder were added until a test sample of the reaction solution failed to produce a red coloration with the indicator paper. The total amount of iron added was approximately 100 pounds. The still-hot titanium fluoride solution free from ferric ions was then separated from the insolubles in a filter press. The filter cake was washed with water until the combined filtrate and wash water made up a total liquid volume of about 800 to 1,000 gallons, this amount of wash water being sufficient to effectively wash the filter cake without unduly diluting the aqueous medium from which the final product was to be crystallized.

The combined filtrate and wash water, containing titanium tetrafluoride and ferrous sulfate in solution, was heated by blowing in steam until a temperature of about 60° C. was attained. This temperature was maintained while about 1,000 pounds of potassium chloride and about 400 pounds of ammonium bifluoride were separately added. Both of the added salts dissolved readily in the hot solution. A small sample of the solution was removed for testing for complete conversion of the titanium fluoride to potassium titanium fluoride. The sample was cooled to room temperature, crystals of potassium titanium fluoride were filtered off, and a small amount of ammonium bifluoride was added to the filtrate. The formation of additional crystals of potassium titanium fluoride would indicate the need for more ammonium bifluoride in the hot solution from which the sample was taken.

The final hot solution of potassium titanium fluoride further containing dissolved ferrous sulfate, excess potassium chloride and excess ammonium bifluoride, was allowed to cool slowly to room temperature while being stirred gently. As the solution cooled, relatively large crystals of potassium titanium fluoride were formed. A portion of the mother liquor was separated from the crystals by decantation and the remaining mass of crystals and mother liquor were separated from one another in a filter-bottom tank. The crystals were washed with a cold saturated solution of potassium chloride to remove entrained mother liquor, and the washed crystals were then dried in a conventional drying oven at a temperature of about 100° C. The washed and dried crystals of substantially anhydrous potassium titanium fluoride ($K_2TiF_6$) were of high purity and contained less than 0.1% iron.

It will be seen, therefore, that the method of the present invention provides means for producing potassium titanium fluoride of excellent quality directly from titanium ore. The method also makes it possible to introduce the major portion of the fluorine content of the potassium titanium fluoride by means of a relatively inexpensive raw material in the form of naturally occurring calcium fluoride. The solid potassium titanium fluoride is obtained by selective crystallization from a solution thereof with the result that the final product is characterized by a high degree of purity in spite of the presence of extraneous compounds introduced or produced in the course of its preparation.

I claim:

1. The method of producing potassium titanium fluoride which comprises digesting a titanium ore with sulfuric acid to form a titanium sulfate-containing product, treating said product with calcium fluoride in an aqueous medium to form titanium fluoride, separating the resulting titanium fluoride solution from the insolubles, treating the resulting solution of titanium fluoride with an ionizable fluorine compound in the presence of potassium chloride, and separating from the resulting solution crystals of potassium titanium fluoride.

2. The method according to claim 1 in which the titanium sulfate-containing product is treated with calcium fluoride at a temperature of at least about 100° C.

3. The method according to claim 1 in which the titanium sulfate-containing product treated with calcium fluoride contains excess sulfuric acid.

4. The method according to claim 1 in which the titanium sulfate-containing product is slurried with water to facilitate its treatment with calcium fluoride.

5. The method according to claim 1 in which the titanium ore comprises ilmenite.

6. The method according to claim 1 in which an iron-containing titanium ore is digested with sulfuric acid, and ferric sulfate produced by said digestion is reduced to ferrous sulfate prior to conversion of the titanium fluoride to potassium titanium fluoride.

7. The method according to claim 1 in which the titanium fluoride solution is heated to a temperature of about 60° C. before being treated with said ionizable fluorine compound.

8. The method according to claim 1 in which the ionizable fluorine compound comprises ammonium bifluoride.

9. The method according to claim 1 in which the titanium fluoride solution is treated with an ionizable fluorine compound in the presence of an excess of potassium chloride.

10. The method of producing potassium titanium fluoride which comprises digesting a titanium ore with sulfuric acid to form a titanium sulfate-containing product, treating said product in an aqueous medium with calcium fluoride at a temperature of at least about 100° C. to form a titanium fluoride-containing solution, separating the resulting titanium fluoride solution from the insolubles, treating the titanium fluoride solution at a temperature of about 60° C. with an ionizable fluorine compound in the presence of an excess of potassium chloride, and separating from the resulting solution crystals of potassium titanium fluoride.

11. The method according to claim 10 in which an iron-containing titanium ore is digested with sulfuric acid, and ferric sulfate produced by said digestion is reduced to ferrous sulfate prior to conversion of the titanium fluoride to potassium titanium fluoride.

12. The method of producing potassium titanium fluoride which comprises treating an iron-containing titanium ore with sulfuric acid to form a reaction product containing a mixture of titanium sulfate, ferric sulfate and ferrous sulfate, treating an aqueous solution of said mixture of sulfates with calcium fluoride at an elevated temperature sufficient to effect reaction between the titanium sulfate and calcium fluoride and thereby form titanium fluoride in solution, reducing the ferric sulfate to ferrous sulfate, separating from the reaction mixture an aqueous solution containing said titanium fluoride and ferrous sulfate substantially free from ferric ions, adding to the titanium fluoride solution an ionizable fluorine compound and potassium chloride

in amount sufficient to convert the titanium fluoride to potassium titanium fluoride, and separating therefrom crystals of potassium titanium fluoride.

13. The method of producing potassium titanium fluoride which comprises treating a titanium ore with sulfuric acid to form a titanium sulfate product, reacting said titanium sulfate with calcium fluoride in an aqueous medium, separating from the reaction mixture an aqueous solution of titanium fluoride substantially free from ferric ions, adding to said solution an ionizable fluorine compound and potassium chloride, and separating therefrom crystals of potassium titanium fluoride.

14. The method of producing potassium titanium fluoride which comprises reacting calcium fluoride with an aqueous solution of a titanium sulfate product obtained by sulfuric acid digestion of a titanium ore, separating the resulting titanium fluoride solution from the insolubles, treating the resulting solution of titanium fluoride with an ionizable fluorine compound in the presence of potassium chloride, and separating from the resulting solution crystals of potassium titanium fluoride.

15. The method of producing potassium titanium fluoride which comprises reacting a water-soluble titanium compound with an excess of calcium fluoride in an aqueous medium, separating from the reaction mixture the resulting aqueous solution of titanium fluoride compound,



adding to said solution an ionizable fluorine compound and potassium chloride, and separating therefrom crystals of potassium titanium fluoride.

16. The method of producing potassium titanium fluoride which comprises forming an aqueous solution of titanium tetrafluoride by reacting a water-soluble titanium compound with calcium fluoride in an aqueous medium, separating the resulting titanium tetrafluoride solution from the insolubles, reacting said solution of titanium tetrafluoride with an ionizable fluorine compound in the presence of potassium chloride with the formation of an aqueous solution of potassium titanium fluoride, and crystallizing the potassium titanium fluoride from said solution thereof.

HENRY C. KAWECKI.


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## Certificate of Correction

July 5, 1949

Patent No. 2,475,287

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It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 30, for "nisoluble" read *insoluble*; column 4, line 55, for "50° C." read *60° C.*; column 6, lines 71 and 72, for the word "pounds" read *pound*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of December, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
*Assistant Commissioner of Patents.*