United States Patent Office 2,694,617 Patented Nov. 16, 1954

2,694,617

PRODUCTION OF TITANIUM FLUORIDES

Samuel Z. Cardon, Euclid, and Eugene Wainer, Cleveland Heights, Ohio, assignors, by mesne assignments, to Horizons Titanium Corporation, Princeton, N. J., a corporation of New Jersey

No Drawing. Application June 10, 1952, Serial No. 292,743

6 Claims. (Cl. 23—88)

This invention relates to the production of alkali metal fluotitanates and, more particularly, to a novel method of producing alkali metal fluotitanates in substantially pure form from relatively impure titaniferous raw materials.

The increasing field of use of alkali metal fluotitanates, such as sodium fluotitanate, potassium fluotitanate and ammonium fluotitanate, has increased the demand for a method of producing these fluotitanates from relatively inexpensive, and hence relatively impure, titaniferous sources. A variety of methods has already been described and used heretofore for the production of alkali metal fluotitanates, but these prior art methods have either required the use of a relatively pure titaniferous starting material or the practice of one or more extraneous steps to insure the absence of iron in the final product. In pyrolytic processes, for example, many if not all of any impurities in the titaniferous starting material are carried over into the alkali metal fluotitanate produced therefrom, and in wet chemical methods the presence of ferric ions must be controlled in order to prevent precipitation of the iron in the form of an alkali metal ferric fluoride along with the desired alkali metal fluotitanate.

We have now discovered that by a combination of pyrolytic and aqueous phase chemical techniques the aforementioned alkali metal fluotitanates may be produced directly from all grades of titaniferous materials without contamination of the final product with significant amounts of any of the impurities indigenous to the titaniferous material. In the case of the most troublesome impurity, iron, it appears that our pyrolytic step in which the titanium oxide component of the titaniferous material is converted to an alkaline earth metal titanate, coupled with the subsequent digestion of the alkaline earth metal titanate with more dilute acid than has previously been used for the digestion of other titaniferous materials, results in segregation of the iron content of the initial titaniferous material in a form which makes it possible to avoid the presence of this iron in the final product.

Our novel method of producing alkali metal fluotitanates thus comprises heating a titanium dioxide-containing material in admixture with an oxidic alkaline earth metal compound to a temperature of at least about 1200° C. with the resulting formation of the corresponding alkaline earth metal titanate, incorporating said titanate in an acidic aqueous medium containing about 20 to 50% by weight of sulfuric or hydrochloric acid, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of an added source of fluoride ions and of alkali metal ions, effecting separation from the resulting aqueous phase of any insoluble phase while maintaining a temperature of at least 90° C., and crystallizing from said aqueous phase the resulting alkali metal fluotitanate. Digestion of the titanate in the acidic medium may either precede or accompany the aforementioned heating step carried out in the presence of fluoride and alkali metal ions.

The titaniferous materials which may be used in practicing our invention comprise virtually all naturally-occurring and beneficiated or artificially produced titanium dioxide-containing products. For example, titaniferous ore such as ilmenite containing 30–40% titanium dioxide and titaniferous beach sand containing 50–70% titanium dioxide may be used directly without beneficiation. In both of these titaniferous sources, the titanium is present predominantly in the form of a combination of titanium and iron oxides. However, titaniferous concentrates prepared from such naturally-occurring ilmenites may be used, including the titanium slag concentrate produced according to the United States Patent No. 2,476,453 to Peirce et al. and containing 65–75% titanium dioxide. Other suitable titaniferous materials for use in practicing the invention include the mineral brookite, in which the titanium dioxide content may be as high as 75%, native rutile comprising 92–98% titanium dioxide, and substantially chemically pure titanium dioxide of commercial or pigment grade in which the titanium dioxide content may be at least 96%. Inasmuch as the method of our invention makes possible the production from any of these titaniferous materials of an alkali metal fluotitanate substantially free of any of the impurities indigenous to the titaniferous raw material, the method of our invention has particular utility when used to produce alkali metal fluotitanates from ilmenite ore, the most abundant and least expensive of the many available titaniferous raw materials. Regardless of the source of the titaniferous material, all naturally-occurring and beneficiated titaniferous materials are characterized by the presence therein of titanium essentially in the form of titanium dioxide. Whether this titanium dioxide is present in its substantially free form or in combination with other metal oxides as it is in ilmenite and the various silicates, the titanium dioxide component of the starting material is readily available for combination with an oxidic alkaline earth metal compound with the resulting formation of the corresponding alkaline earth metal titanate.

The oxidic alkaline earth metal compounds which are useful in the practice of our invention, as distinguished from the alkali metal salts used in the copending application of Eugene Wainer, Serial No. 269,142, filed January 21, 1952, include such compounds of calcium, strontium and barium, the calcium compounds being generally more economically attractive. The useful oxidic compounds of these alkaline earth metals are those which, when subjected to the heating conditions used in the pyrolytic step of our method, will yield corresponding alkaline earth metal oxides. The compounds which answer this requirement include, in addition to the oxides themselves, the carbonates, sulfates and nitrates. Of these useful compounds, the nitrates are relatively expensive whereas the carbonates, which occur naturally, are preferred because of their economy. However, although the sulfates in general are more expensive than the carbonates, the alkaline earth metal sulfates may be precipitated in a later stage of our method and can therefore be recycled with relatively little loss, and because of this recycling possibility the sulfates are substantially as attractive commercially as the carbonates. Regardless of the specific composition of such alkaline earth metal compounds, we have found them all to be suitably reactive with the titanium dioxide component of the titaniferous material so as to form an alkaline earth metal titanate under our pyrolytic reaction conditions.

The relative amounts of titaniferous material and oxidic alkaline earth metal compound which are converted to an alkaline earth metal titanate in the practice of our invention may advantageously be those amounts stoichiometrically required for producing the titanate from the titanium dioxide and alkaline earth metal oxide components of the charge to the pyrolytic operation. Thus, if the titaniferous material is substantially free of an indigenous alkaline earth component, then substantially stoichiometric quantities of the titaniferous material and oxidic alkaline earth metal compound should be used. However, if a significant quantity of alkaline earth metal compound is present in the titaniferous material, as in the case of ilmenite ore or in the aforementioned titanium slag concentrate, the amount of extraneous oxidic alkaline earth metal compound required for conversion of the titanium dioxide to titanate should be determined with a credit for the amount of such alkaline earth metal compound present in the titaniferous material. Furthermore, the affinity of silica in the titaniferous raw material for the added alkaline earth metal com-

pound must also be considered, and in general we have found it advantageous to use about 10% molar excess of the alkaline earth metal compound when the silica content of the titaniferous raw material exceeds about 5%.

The rapidity of conversion of the titaniferous starting material to the alkaline earth metal titanate is facilitated by a fine degree of subdivision of the reactants. Thus, we have found it advantageous to crush or grind the charge components to minus 35 mesh (Tyler Standard). In general, we prefer to prepare the charge with a particle size of minus 200 mesh, and charges of minus 325 mesh have been found to be still more amenable to pyrolytic reaction within a reasonable period of time. Although somewhat longer treatment periods are required when the charge particles are coarser than minus 325 mesh, we have found in all instances that the desired titanate was produced within a reasonable period of time, generally a matter of a few hours at the most, when using a treatment temperature of at least 1200° C.

The pyrolytic conditions which we have found to be useful comprise heating the titaniferous material and the oxidic alkaline earth metal compound to a temperature of at least 1200° C. Unless as described hereinafter it is desired to effect partial smelting of the titaniferous material in the course of this pyrolytic treatment, the nature of the ambient atmosphere is unimportant. At temperatures of 1200° C. and higher, conversion of the reactants to an alkaline earth metal titanate is effected in a reasonable period of time. For example, charges of all types of titaniferous material have been found to be adequately converted to the desired alkaline earth metal titanate in a period of about one hour at temperatures of the order of 1350° C., whereas at about 1200° C. a heating period of about two hours is required for adequate conversion of the titanium dioxide component of the charge to the titanate. On the other hand, if the pyrolytic treatment is carried out at a temperature sufficient to effect fusion of the reactants, and particularly in the added presence of an extraneous reducing agent as described further herein, a reaction period of a fraction of an hour is sufficient. The duration of the pyrolvic treatment thus depends upon the degree of subdivision of the charge components, the nature of the titaniferous material and the results to be accomplished by the pyrolytic treatment.

The product of the pyrolytic treatment will contain substantially all metal components of the charge when the aforementioned heating conditions prevail. Thus, a sintered calcined product will contain substantially all of the iron and silica components of the titaniferous starting material. If it is desired to remove during the pyrolytic treatment a major portion of the iron oxide and silica components of the titaniferous material, rather than to do so during the aqueous phase of our method, such separation may be effected by carrying out the pyrolytic treatment of the titaniferous material and oxidic alkaline earth compound at somewhat higher temperatures and in the further presence of a solid carbonaceous reducing material in amount sufficient to reduce at least a maior portion of the iron oxide and silica components of the titaniferous material. The latter pyrolytic smelting conditions, advantageously carried out by fusion of such a charge in an electric arc furnace, will produce a fluid slag consisting predominantly of an alkaline earth metal titanate and a metallic product composed predominantly of ferrosilicon. Subsequent separation of the slag from the metallic product, such for example as by magnetic separation of the metallic product, will yield the desired alkaline earth metal titanate largely free of iron and silicon. In addition to the fact that fusion of the titaniferous charge under the aforesaid reducing conditions removes a substantial portion of the unwanted iron and silicon components of the charge, this treatment is particularly amenable to the use, as the requisite oxidic alkaline earth metal compound. of an alkaline earth metal sulfate such as that obtained as a precipitate in the subsequent aqueous phase of our method.

The aqueous phase of our method comprises digestion of the alkaline earth metal titanate produced by the aforementioned pyrolytic treatment, whether merely sintering or smelting in character, followed by conversion of this digestion product to an alkali metal fluotitanate in an aqueous phase. A characteristic feature of the digestion operation is the use of more dilute acid than is conventionally used for the digestion of titaniferous material in prior art processes for the aqueous phase production of alkali metal fluotitanates. The use of such relatively dilute acid, in conjunction with the previous pyrolytic treatment of the titaniferous material as described hereinbefore, results in dissolution of the titanate while leaving substantially undissolved both the iron oxide and silica components which may have been carried over with the product of the pyrolytic treatment. The comparative insolubility of the iron component, in particular, may be caused by the pyrolytic treatment converting the iron oxide to a difficultly soluble crystalline form or to a refractory ferrite, or the lack of solubility may be a result of the relatively low acid concentrations used in practicing the digestion step of our method, or a combination of these causes may be involved. Regardless of the aforesaid possible explanations, the fact remains that the iron component, like the silica, remains in a relatively insoluble form in the practice of our invention. By separating any such undissolved iron and silicon components, the resulting solubilized titanium component can be subsequently converted to the desired alkali fluotitanate without contamination of the latter with the former.

Digestion of the alkaline earth metal titanates obtained by the pyrolytic treatment described hereinbefore can be effected with either sulfuric or hydrochloric acid. The use of sulfuric acid is advantageous, however, because it results in the ultimate precipitation of the alkaline earth metal component of the titanate in the form of the sulfate which, as pointed out hereinbefore, may be recycled for use as the oxidic alkaline earth metal compound in the preceding pyrolytic step. Regardless of the specific acid used, acid concentrations ranging from about 20 to 50% by weight are preferred in practicing our invention, and within this range we have found that digestion of the alkaline earth metal titanate can be effected within a reasonable period of time.

Digestion of the alkaline earth metal titanate may be effected either prior to or concurrently with the conversion of the digestion product to the desired alkali metal fluotitanate. The choice of these two alternatives is generally determined by the amount of the iron oxide and silica components of the titaniferous material carried over into the titanate product to be digested. For example, when the total of iron oxide and silica exceeds about 10% by weight of the titanium dioxide content of the alkaline earth metal titante produced by the pyrolytic treatment, we have found it advantageous to effect digestion of the titanate prior to conversion of the digestion product to the fluotitanate in order to facilitate the intermediate separation of the resulting large amount of insoluble iron and silicon components. When the digestion of the titanate is carried out prior to conversion of the digestion product to the fluotitanate, digestion temperatures of about 50°–75° C. will promote substantially complete digestion in a period of one to two hours, the actual digestion period required for this purpose varying inversely with the acid concentration within the aforementioned acid range. However, digestion temperatures upward of 90° C., and advantageously at about the boiling point of the mixture of titanate and acid, will effectuate substantially complete digestion of the titanate in less than one hour. At the conclusion of such an independent digestion operation, the residue, which is composed largely of iron hydroxide and silica and also of an alkaline earth metal sulfate if sulfuric acid is used for digesting, is separated from the aqueous phase. The resulting clarified aqueous phase is then subjected to conversion of its titanium component to the desired alkali metal fluotitanate.

Conversion of the acid-solubilized titanium component of the alkaline earth metal titanate to the alkali fluotitanate requires merely the addition to the titanium-containing aqueous phase of a substantially stoichiometric amount of fluoride ions and alkali metal ions to form the desired alkali metal fluotitanate. At least a portion of this necessary fluorine component can be supplied in the form of relatively inexpensive fluorspar (CaF_2). The fluorspar will react with the dissolved titanium component, which is either a titanium chloride or a titanium sulfate depending upon the acid used for digestion, to form titanium tetrafluoride. A sufficient excess of fluorine ions is further required to satisfy the stoichiometric demands of the desire dalkali metal fluotitanate containing six fluorine atoms. Within the prevailing optimum pH range

of about 4 to 6 in the aqueous phase at the conversion stage of our method, an excess of fluorspar will be ionized in the presence of an added alkali metal compound so as to form the alkali metal fluotitanate. However, the additional fluorine required to convert the titanium tetrafluoride to the fluotitanate may alternatively be supplied by adding a substantially stoichiometric amount of an ionizable fluorine compound such as hydrofluoric acid, sodium fluoride, potassium fluoride, ammonium fluoride, ammonium bifluoride, or the like. When this latter alternative source of ionizable fluorine is used, it is advantageous to add it to the reaction mixture in the form of a compound of the alkali metal whose fluotitanate it is desired to produce.

The alkali metal component of the desired alkali metal fluotitanate may comprise either sodium, potassium or the ammonium radical, each of these components being included herein and in the claims by the expression "alkali metal." These materials may be of commercial origin or, if used in the form of chlorides and fluorides, they may be derived from spent fused salt baths used for the electrolytic production of titanium metal. As previously explained, it is advantageous to supply the alkali metal component in the form of the fluoride used as a source of fluoride ions for the conversion reaction. However, when the fluorine requirements of the conversion reaction are satisfied by a source such as fluorspar or hydrofluoric acid, the alkali metal may be introduced in the form of substantially any soluble salt thereof such as the sulfate, chloride, nitrate, or the like. In any event, the alkali metal compound should be added to the conversion reaction mass in amount at least stoichiometrically equivalent to the alkali metal fluotitanate to be formed. We have found it advantageous, in order to accelerate crystallization of the alkali metal fluotitanate, to have present at the conversion stage a small excess, of the order of 1 to 3% by weight, of alkali metal ions or of fluoride ions, or both. In general, particularly satisfactory results are obtained by incorporating in the aqueous phase prior to crystallization of the alkali metal fluotitanate about 1 to 3% by weight of potassium chloride, this amount of potassium being calculated as that in excess of any potassium which may be combined with the titanium to form potassium fluotitanate.

Conversion of the acid digestion product to the desired fluotitanate is effected readily with the aforementioned reagent by heating the reaction mixture to a temperature of at least 90° C. In general, we prefer to use reaction temperatures of at least 95° C. and find it advantageous to closely approach the boiling temperature of the reaction mixture during the conversion period. When digestion of the product of the pyrolytic treatment is carried out simultaneously with this conversion of the digestion product to the fluotitanate, such reaction temperatures of at least 90° C. promote rapid digestion as well as conversion of the digestion product to the fluotitanate. Regardless of whether digestion of the product of the pyrolytic treatment with acid takes place simultaneously with or precedes conversion of the digestion product to the fluotitanate, completion of the conversion is insured by maintaining the conversion reaction mixture at the aforesaid elevated temperature for a period of at least one to two hours.

At the conclusion of the conversion stage of our method, substantially all of the titanium component of the alkaline earth metal titanate will be in solution in the form of the desired alkali metal fluotitanate and can be readily crystallized therefrom by cooling. Hence, the amount of aqueous medium used for the digestion and conversion steps should be such that the ultimate content of dissolved alkali metal fluotitanate in the aqueous phase prior to crystallization is at least 5 parts of the fluotitanate per 100 parts of solution. Within the range of about 5 to 10 parts of the alkali metal fluotitanate per 100 parts of solution, the fluotitanate will not crystallize from the solution while its temperature is maintained above about 90° C. Accordingly, any insoluble substances present at the conclusion of the conversion step should be separated from the aqueous phase by filtration or the like while maintaining the aqueous phase at a temperature of at least 90° C. and within the concentration range of 5 to 10% of dissolved alkali metal fluotitanate. For example, when digestion of the alkaline earth metal titanate and conversion of this digestion product to the desired alkali metal fluotitanate are carried out simultaneously as described hereinbefore, the elevated reaction temperature should be maintained while carrying out separation of the insolubles in order to prevent premature crystallization of the alkaline earth metal fluotitanate.

Crystallization of the alkaline earth metal fluotitanate from its mother liquor takes place upon cooling to ambient temperature. After separation of the first crop of fluotitanate crystals, a second crop may be readily obtained by further concentration of the fluotitanate in the separated mother liquor to 10 to 15%. Crystallization of the second crop by cooling the concentrated mother liquor from the first crystallization step will yield an alkali metal fluotitanate which is still substantially free of undesirable impurities carried over from the titaniferous starting material, and the combined products of the first and second crystallization steps will be found to be a high yield of high purity alkali metal fluotitanate.

The following specific examples will serve to illustrate the practice of our invention, although it must be understood that our method is not in any way restricted to these specific illustrations:

Example I

Calcium titanate was prepared by sintering an equimolecular mixture of calcium carbonate and pigment grade titanium dioxide at about 1300° C. for one hour in air. The resulting sinter was ground to minus 325 mesh, and 140 grams of this calcium titanate were dispersed in 300 cc. of water. While stirring the resulting slurry, 350 grams of 98% sulfuric acid were added as rapidly as possible. Within a few seconds a strongly exothermic reaction took place with the evolution of considerable quantities of steam, and stirring was continued until the mass had cooled to about 90° C. To the cooled reaction mass, 160 grams of minus 325 mesh fluospar (CaF_2) and 15 grams of potassium chloride were added and the resulting mixture was diluted with hot water to a total volume of 2000 cc. The mixture was then digested at 90° to 100° C. for 2 hours and was subsequently filtered hot, the precipitate being washed with hot water. No solids separated from the filtrate on cooling. A 25% solution of potassium fluoride containing 125 grams of this salt was added with stirring and a precipitate formed immediately. The precipitate, comprising potassium fluotitanate, was filtered off and washed. The filtrate was then evaporated to a total volume of 1000 cc. and was allowed to cool to room temperature in order to obtain a second crop of crystals of potassium fluotitanate. The two crops of crystals were combined and dried for an hour at 120° C. The dried product weighed 235 grams and contained 19.6% Ti, an analytical value close to the theoretical content for potassium fluotitanate (K_2TiF_6).

Example II

To 140 grams of calcium titanate, made as described in Example I and dispersed in 300 cc. of water, 350 grams of 98% sulfuric acid were added rapidly with stirring. After the resulting exothermic reaction had taken place, 160 grams of calcium fluoride and 15 grams of potassium chloride were added. The mixture was then diluted to 2000 cc. and was digested by boiling for 2 hours. At the conclusion of this digestion, 125 grams of potassium fluoride were added and the heating was continued for an additional 20 minutes, after which the solution was filtered hot and the precipitate (composed largely of calcium sulfate) was washed with hot water. The combined filtrate and wash water were allowed to cool to room temperature with slow stirring, and coarsely crystalline potassium fluotitanate crystallized from the solution. After filtering off this batch of crystals, the filtrate was concentrated by evaporation to a volume of 1000 cc. and upon cooling to ambient temperature a second crop of crystals was obtained. The two batches were combined, and after drying at 120° C. the combined batches totaled 232 grams of high purity potassium fluotitanate.

Example III

The same procedure was followed as that described in Example I, the only departure being the substitution of 90 grams of sodium fluoride for the 125 grams of potassium fluoride used in Example I. In addition, after the sodium fluoride was added to the clear filtrate for

precipitation of the sodium fluotitanate, the solution was evaporated to a volume of approximately 500 cc. before it was permitted to cool to effect crystallization of the fluotitanate in a single large batch. The crystals were dewatered by filtration, were washed two times with small amounts of cold water, were then pressed dry, and were completely dried by heating at 120° C. The dried product weighed 205 grams and consisted of substantially pure sodium fluotitanate (Na_2TiF_6).

Example IV

Calcium titanate and sulfuric acid of the type and amounts referred to in Example I were reacted as described in that example. After dilution to 2000 cc., the digestion product of the calcium titanate and sulfuric acid was further digested in the presence of 175 grams of sodium fluoride and 15 grams of potassium chloride for a period of 2 hours close to the boiling point of the mixture. The calcium sulfate precipitate was separated from the hot filtrate, and 125 grams of potassium fluoride in the form of a 25% aqueous solution were added to the hot filtrate. Potassium fluotitanate crystallized when the resulting solution was allowed to cool. The mother liquor separated from the first batch of crystals was then evaporated to 1500 cc. to obtain a second crop, and the combined yield of the two crops of potassium fluotitanate, after drying at 120° C., weighed 230 grams.

Example V

A mixture of 155 grams of ilmenite ore in finely divided form and 110 grams of precipitated calcium carbonate was calcined at 1300° C. for one hour with the resulting formation of a hard sinter. The sinter was ground to minus 325 mesh and was decomposed by digesting it with a 50% solution of sulfuric acid containing 375 grams of H_2SO_4. A strongly exothermic reaction took place and a heavy brown sludge developed. After digesting for one hour within the range of 50° to 75° C. in the thick paste-like form obtained from the initial reaction, 1000 cc. of warm water were added and the digestion was continued for several minutes more. The insoluble constituents, consisting chiefly of calcium sulfate and iron hydroxide, were separated from the water-soluble constituents by filtration followed by washing with hot water. Potassium fluotitanate was then prepared as described in Example II with a yield of 225 grams of the dried product.

Example VI

A charge of 140 grams of minus 325 mesh calcium titanate, obtained as described in Example I, was added rapidly with stirring to an acid bath composed of 500 cc. of hydrochloric acid containing 0.45 gram of HCl per cc. Within a few seconds a strongly exothermic reaction took place and a clear solution was obtained. To the solution, heated to about 90° C., there was rapidly added with stirring a similarly heated solution composed of 175 grams of sodium fluoride and 125 grams of potassium fluoride dissolved in 1500 cc. of water. A slight opalescence or precipitate was noticeable and consequently the hot solution was clarified by filtration to remove these insoluble siliceous and aluminous materials carried over from the raw titaniferous material. The filtrate was allowed to cool to room temperature, whereupon profuse crystallization took place. After filtering, washing the separated crystals with a 1% potassium fluoride solution and drying them, a yield of 220 grams of potassium fluotitanate was obtained. Inasmuch as potassium fluotitanate is more insoluble than the corresponding sodium compound, the aforementioned addition of sodium fluoride merely provided a source of fluorine and did not otherwise enter into the precipitated product.

Example VII

A hydrochloric acid solution of calcium titanate, derived from 140 grams of calcium titanate, was prepared as described in Example VI. To this solution, 240 grams of fluorspar and 15 grams of potassium chloride were added, and the resulting mixture was diluted to 2000 cc. and digested for 2 hours at about 95° C. The digestion mass was filtered to remove an opalescent precipitate of siliceous and aluminous impurities derived from the raw titaniferous material, and the precipitate was washed with hot water to recover the entrained aqueous phase. To the clear filtrate, 175 grams of potassium sulfate and 290 grams of sodium sulfate were added and digestion was continued at about 95° C. until these salts were completely dissolved, after which the liquor was allowed to cool to room temperature. A yield of 225 grams of potassium fluotitanate was obtained after filtration, washing and drying of the crystallized product.

Example VIII

Additions of 240 grams of fluorspar, 15 grams of potassium chloride, 175 grams of potassium sulfate and 290 grams of sodium sulfate were made to a titanate-acid mixture prepared as described in Example VI by incorporating 140 grams of calcium titanate in 500 cc. of hydrochloric acid containing 0.45 gram of HCl per cc. After diluting the resulting mixture to 2000 cc., it was digested at about 95° C. until all of the salts were completely dissolved. The solution was filtered while at about 90° C., and the filtrate was allowed to cool with the resulting crystallization of potassium fluotitanate. The yield of this product after drying at 120° C. was 225 grams.

It will be seen, accordingly, that the method of our invention is characterized by the ability to produce alkali metal fluotitanates of high purity from all grades of titaniferous raw materials. The product thus obtained by the practice of our invention may be used in any capacity heretofore developed for the alkali metal fluotitanates, and in many instances it will be found that the high degree of purity, particularly in the substantial absence of iron, imparts greater value and utility to such products.

We claim:

1. The method of producing an alkali metal fluotitanate which comprises heating a titanium dioxide-containing material in admixture with an oxidic alkaline earth metal compound to a temperature of at least about 1200° C. with the resulting formation of the corresponding alkaline earth metal titanate, incorporating said titanate in an acidic aqueous medium containing about 20 to 50% by weight of an acid of the group consisting of sulfuric and hydrochloric acids, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of an added source of fluoride ions and of alkali metal ions, effecting separation from the resulting aqueous phase of any insoluble phase while maintaining the aqueous phase at a temperature of at least 90° C., and crystallizing from said aqueous phase the resulting alkali metal fluotitanate.

2. The method of producing an alkali metal fluotitanate which comprises heating a titanium dioxide-containing material in admixture with an oxidic alkaline earth metal compound to a temperature of at least about 1200° C. with the resulting formation of the corresponding alkaline earth metal titanate, incorporating said titanate in an acidic aqueous medium containing about 20 to 50% by weight of an acid of the group consisting of sulfuric and hydrochloric acids, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of an added source of fluoride ions and of alkali metal ions in amount sufficient to combine with substantially all of the titanium component of the titanate to form the corresponding alkali metal fluotitanate, effecting separation from the resulting aqueous phase of any insoluble phase while maintaining the aqueous phase at a temperature of at least 90° C., and crystallizing from said aqueous phase the resulting alkali metal fluotitanate.

3. The method of producing an alkali metal fluotitanate which comprises heating a titanium dioxide-containing material in admixture with an oxidic alkaline earth metal compound to a temperature of at least about 1200° C. with the resulting formation of the corresponding alkaline earth metal titanate, incorporating said titanate in an acidic aqueous medium containing about 20 to 50% by weight of an acid of the group consisting of sulfuric and hydrochloric acids, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of an added source of fluoride ions and of alkali metal ions in amount sufficient to form an aqueous phase containing at least 5% by weight of the corresponding alkali metal fluotitanate, effecting separation from the resulting aqueous phase of any insoluble phase while maintaining a temperature of at least 90° C. and a maximum concentration of about 10% by weight of the alkali metal fluotitanate in the aqueous phase, and crystallizing from said aqueous phase the resulting alkali metal fluotitanate.

4. The method of producing an alkali metal fluotitan-

ate which comprises heating a titanium dioxide-containing material in admixture with an oxidic alkaline earth metal compound to a temperature of at least about 1200° C. with the resulting formation of the corresponding alkaline earth metal titanate, incorporating said titanate in an acidic aqueous medium containing about 20 to 50% by weight of an acid of the group consisting of sulfuric and hydrochloric acids, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of an added source of fluoride ions and of alkali metal ions in amount sufficient to form an aqueous phase containing at least 5% by weight of the corresponding alkali metal fluotitanate, effecting separation from the resulting aqueous phase of any insoluble phase while maintaining a temperature of at least 90° C. and a maximum concentration of about 10% by weight of the alkali metal fluotitanate in the aqueous phase, crystallizing from said aqueous phase the resulting alkali metal fluotitanate, concentrating by evaporation the mother liquor from said crystallization to about 15% by weight of the alkali metal fluotitanate, and subsequently cooling the concentrated mother liquor to crystallize a second batch of the alkali metal fluotitanate.

5. The method of producing an alkali metal fluotitanate which comprises heating a titanium dioxide-containing material in admixture with an oxidic alkaline earth metal compound to a temperature of at least about 1200° C. with the resulting formation of the corresponding alkaline earth metal titanate, digesting said titanate in an acidic aqueous medium containing about 20 to 50% by weight of an acid of the group consisting of sulfuric and hydrochloric acids at a temperature of at least 50° C., subsequently adding to the resulting mass a source of fluoride ions and of alkali metal ions and heating the mass to a

temperature of at least 90° C., effecting separation from the resulting aqueous phase of any insoluble phase while maintaining the aqueous phase at a temperature of at least 90° C., and crystallizing from said aqueous phase the resulting alkali metal fluotitanate.

6. The method of producing an alkali metal fluotitanate which comprises smelting an iron oxide- and silica-containing titaniferous material with a solid carbonaceous reducing material in the further presence of an oxidic alkaline earth metal compound with the resulting formation of the corresponding alkaline earth metal titanate and an iron- and silicon-containing product, separating the titanate from the metallic product, incorporating the titanate in an acidic aqueous medium containing about 20 to 50% by weight of an acid of the group consisting of sulfuric and hydrochloric acids, subsequently heating the resulting mass to a temperature of at least 90° C. in the further presence of an added source of fluoride ions and of alkali metal ions, effecting separation from the resulting aqueous phase of any insoluble phase while maintaining a temperature of at least 90° C., and crystallizing from said aqueous phase the resulting alkali metal fluotitanate.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,911,396	Saklatwalla et al.	May 30, 1933

OTHER REFERENCES

"Titanium," by Jelks Barksdale, pages 303, 308, 341 (1949 ed.), The Ronald Press Co., N. Y.