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PRODUCTION OF ALKALI METAL FLUOTITANATES AND FLUOZIRCONATES

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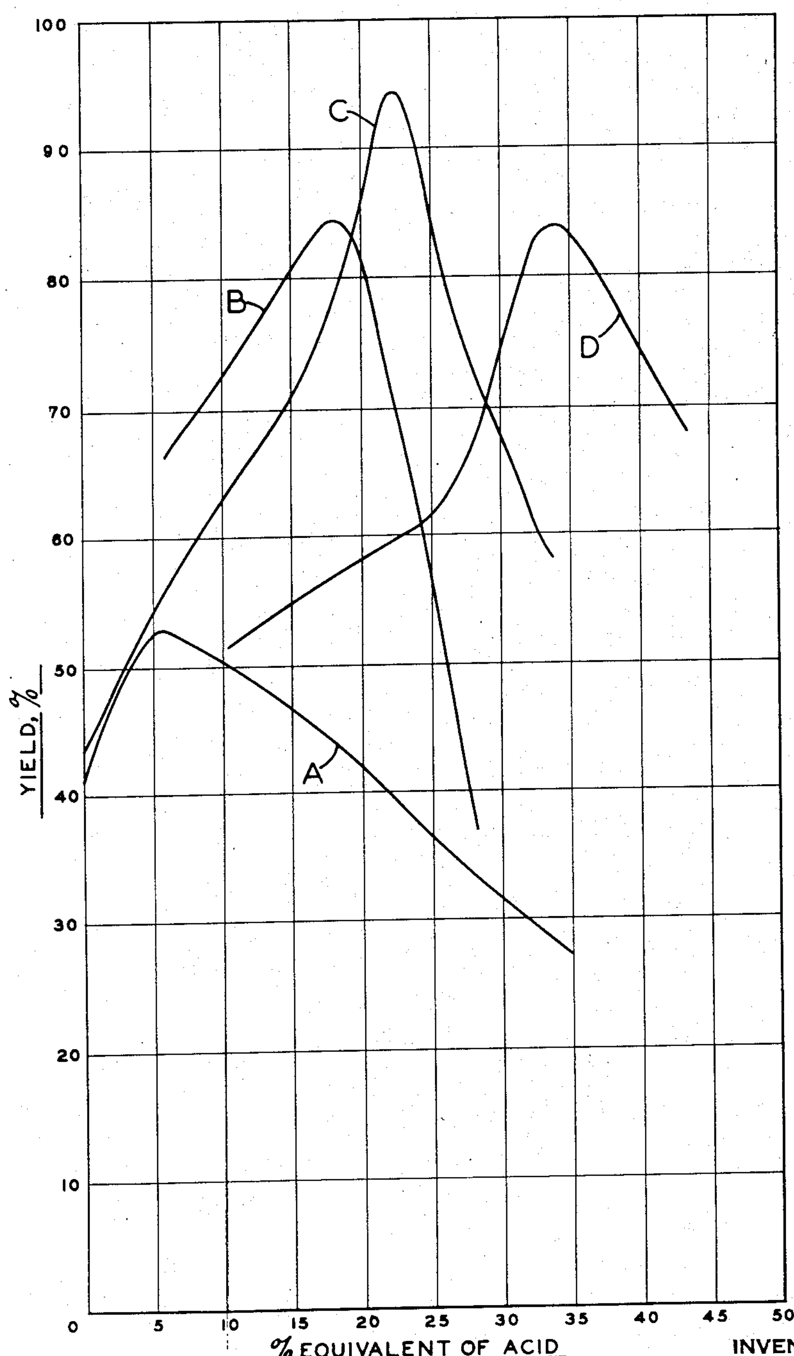

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PRODUCTION OF ALKALI METAL FLUOTITANATES AND FLUOZIRCONATES

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This invention relates to the production of alkali metal fluotitanates and fluozirconates and contemplates an improved process for the production of these compounds in a state of high purity from naturally occurring titaniferous and zirconiferous material.

Alkali metal fluotitanates and fluozirconates, and particularly the sodium and potassium compounds, are presently being used as addition agents for baths of molten metals wherein the titanium or zirconium content of the added salt is displaced by a portion of the molten metal with the result that titanium or zirconium is directly introduced into the molten metal. The effectiveness of such fluotitanates and fluozirconates for this purpose, and for other equally effective but wholly unrelated uses, has imposed particular emphasis upon the efficacy of procedures for the production of these compounds.

It is well-known that alkali metal fluotitanates and fluozirconates can be obtained by heating together a mixture of an oxidic compound of titanium or zirconium with an alkali metal fluosilicate. In the United States patent to Koerner No. 1,467,275, such a procedure is described wherein a mixture of a zirconium oxide, such as the silicate ore, is fused with an alkali metal fluosilicate. Fusion of such a mixture takes place at a temperature of about 1100° C. In my United States Patent No. 2,418,074, there is described an improvement in this procedure pursuant to which increased yields of recoverable alkali metal fluotitanate or fluozirconate are obtained by carrying out the heating of the mixture of titanium or zirconium oxide and alkali metal fluosilicate at a non-fusing temperature of about 600° to 800° C. for a considerable period of time. However, the requirement of a substantial holding period in the process of my aforementioned patent dictates a discontinuous or batch operation if uniformly high yields are to be obtained, whereas the higher temperature operation represented by the Koerner patent, wherein fusion of the mixture is obtained, lends itself readily to a continuous process. In spite of the potential advantages of a continuous process by the fusion method of the Koerner patent, the low yields of extracted fluotitanate or fluozirconate of the order of 40% in the case of water extraction and nearly 55% with acid extraction have discouraged the adoption of the fusion method.

I have now discovered that the yields of alkali metal fluotitanates and fluozirconates by the aforementioned fusion method can be raised to

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the level of the aforementioned lower temperature batch operation by incorporating in the mixture of the oxidic titanium or zirconium material and the alkali metal fluosilicate an oxidic compound of the same alkali metal. Although the addition of the oxidic alkali metal compound increases the yield of hot water-extracted fluotitanate or fluozirconate from the fusion product, an exceptionally high yield of the desired product is obtained when the fusion product is extracted with acid.

Accordingly, the method of producing an alkali metal fluotitanate or fluozirconate pursuant to the present invention comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxidic compound of the metal of the group consisting of titanium and zirconium, and an oxidic compound of an alkali metal, heating the mixture to effect fusion thereof, cooling the resulting product to effect its solidification, comminuting the solid product, and leaching the comminuted fusion product with an acidic aqueous medium. The alkali metal fluotitanate or fluozirconate thus obtained in solution is subsequently recovered by any suitable means such, for example, as crystallization.

The oxidic titanium and zirconium compounds which can be used in the practice of the improved method of my invention may be the oxides themselves or other oxidic compounds such as the silicate. These oxidic compounds include the common forms in which titanium and zirconium occur naturally. Thus, titanium dioxide in the form of native rutile and artificially produced titanium silicate may be used as the source of titanium, and zirconium oxide in the form of baddeleyite and zirconium silicate in the form of naturally occurring zircon can be used effectively as the source of the zirconium. Other compounds of these metals in which substantial amounts of other elements are present may be used, although the presence of such elements generally entails the use of additional steps for the sole purpose of removing these other elements which would otherwise contaminate the desired fluotitanate or fluozirconate products. For example, ilmenite can be used as a titaniferous starting material but the presence of a relatively large amount of iron in this titaniferous ore necessitates taking a number of precautions in order to prevent interference by the iron with the formation of the alkali metal fluotitanate.

The alkali metal fluosilicates which may be used in practicing the invention include the fluosilicates of lithium, sodium, potassium, rubidium and cesium. Each of these fluosilicates is readily available and provides the full quota of fluorine for the desired fluotitanate or fluozirconate. The fluosilicate is admixed with the oxidic titanium or zirconium compound in the dry state and preferably in finely divided condition.

The relative proportions of the titaniferous or zirconiferous material and of the alkali metal fluosilicate may vary widely although it is presently preferred to use them in equimolar amounts. Variations in the relative proportions of these two components appear to have no significant effect upon the operability of the process. However, if the relative costs of the two components dictate recovering the maximum portion of the titanium or zirconium component of the starting material, then a slight excess of the fluosilicate may be used to insure this result. On the other hand, if the fluosilicate is more expensive than the titaniferous or zirconiferous starting material, then it will prove more economical to use a small excess of the latter. Where the relative costs of the two starting materials are not controlling, I have found it generally desirable to use substantially equimolar proportions of the fluosilicate and the titaniferous or zirconiferous material.

The oxidic alkali metal compound which is added to the mixture of the fluosilicate and the oxidic titaniferous or zirconiferous material pursuant to the invention should be a compound of the same alkali metal as that of the fluosilicate unless, of course, the intended use of the final product makes it permissible or even desirable to contaminate the resulting alkali metal fluotitanate or fluozirconate with the corresponding salt of another alkali metal. The oxidic compounds of the alkali metals which may be used in practicing the invention include the oxides as well as such other compounds as the carbonates, hydroxides, nitrates, sulfates, oxalates, and the like, which will decompose to the oxide form when heated to the temperature prevailing in the fusion step of my improved method.

The amount of oxidic alkali metal compound which may be used in practicing the invention ranges from about ⅙ mol to about ⅔ mol, and preferably about ⅓ mol, per mol of titanium or zirconium in the starting material. The amount of oxidic alkali metal compound which is used within the foregoing range appears to have a decided influence upon the yield of extracted fluotitanate or fluozirconate obtained by the practice of the method of my invention. For example, in the production of potassium fluozirconate by the fusion of zircon with potassium fluosilicate, the use of ⅙ mol of potassium carbonate per mol of zircon resulted in an acid-extraction yield of 84.5% whereas under otherwise identical conditions the use of ⅓ mol of potassium carbonate resulted in a yield of 93.5% and the use of ⅔ mol of potassium carbonate resulted in a yield of only about 84% of the available zirconium. Thus, although greater or lesser amounts of the oxidic alkali metal compound may be used in practicing the method of my invention, practical considerations suggest the use of an amount of the compound within the aforementioned range.

The three solid components which are fused together in the practice of my invention are preferably admixed in pulverized condition so as to facilitate intimate physical admixture. However, the method is operable when coarser starting materials are used as evidenced by the fact that successful results have been obtained when the zirconiferous material is added to the mixture in the form of zircon sand. However, I have found that fineness of particle size and intimacy of admixture are conducive to more consistent results, particularly when the method is carried out as a continuous operation. For this reason, I generally prefer to admix the starting materials in substantially pulverized form and admix these materials thoroughly in a tumbling barrel or the like.

The intimate physical admixture of the titaniferous or zirconiferous material, the alkali metal fluosilicate and the oxidic alkali metal compound is then heated to a temperature of at least about 1100° C. to effect fusion of the mass. Although there appears to be no upper limit to the temperature to which the mixture may be heated, volatilization of the salt components of the mixture becomes appreciable at temperatures in excess of about 1200° C. Fusion of the salt mixture within my presently preferred range of about 1100° to 1200° C. may be effected either in an electric furnace or in a fuel fired furnace. If an electric furnace is used, I have found it particularly advantageous to use immersed electrodes which produce at least the major portion of the furnace heat by the resistance of the conducting mixture of salts. Regardless of the type of heating employed, I have found it advantageous to carry out this fusion operation in a metal crucible such as a stainless steel shell, the use of refractory crucibles being unsatisfactory because of the corrosiveness of the fused salt mixture on such refractories.

The fusion of the salt mixture effects substantially immediately the desired formation of alkali metal fluotitanate or fluozirconate. Accordingly, there is no minimum holding time required in carrying out the process other than that required to obtain the desired fusion. It will be appreciated, accordingly, that the dry intimate mixture of the three starting compounds can be charged continuously to the furnace and that the fused product can be continuously discharged from the furnace.

The fused product must be ultimately solidified and comminuted for the subsequent leaching operation, and, as a means towards this end, I have found it advantageous to discharge the molten product in the form of a small stream into a body of water. The resulting rapid quenching of the fused salt causes it to solidify and shatter in the form of a frit which is particularly amenable to subsequent fine grinding. Thus, quenching of the fused product is a practical expedient and is not a critical feature in the practice of the method of my invention. However, when such water quenching is employed, the solubility of the alkali metal fluotitanate or fluozirconate in the quench water makes it desirable to use this water in a subsequent stage in the leaching of the remaining solid product.

Although the comminution of the solid product effected by quenching the fused salt mixture in water as aforesaid is sufficient to permit leaching of the product without further treatment, more efficient leaching and higher yields are obtained when the solid product is reduced to pulverized form. The ease with which the solid product can be subdivided makes it possible to pulverize the product in a conventional pebble mill, although any other apparatus suitable for relatively fine grinding may be used. Regardless of the apparatus used for this purpose, I have found it advantageous to minify dusting by performing the grinding as a wet operation. For this purpose the solid may be wet with water or with a portion of any quench water used in the preceding quenching operation.

The subsequent leaching operation is carried out in such manner as to yield a leach liquor having an ultimate concentration of the alkali metal fluotitanate or fluozirconate which will permit separation and recovery of this salt. For example, when separation of the fluozirconate is to be effected by crystallization from the leach liquor, I have found it to be desirable to adjust the volume of the leach liquor to that which will have an ultimate concentration of about 200 grams per liter of the fluozirconate. For this purpose, the remainder of any quench water from the preceding quenching operation may be added to the finely divided solid product and an additional quantity of water is added to make possible the aforementioned final concentration of fluotitanate or fluozirconate. Acidification of the leach liquor is effected by adding any acid, such as sulfuric, nitric or hydrochloric acid, in amount sufficient to produce a final pH within the range of about 2.5 to 4. It will be readily apparent that the amount of acid required for this purpose will depend upon the amount of the oxidic alkali metal compound admixed with the fluosilicate and titaniferous or zirconiferous material prior to the fusion step. Thus, in the case of a mixture of zircon and potassium fluosilicate further containing about ⅓ mol of potassium carbonate per mol of zircon, an amount of sulfuric acid equivalent to about 20% of the zirconium content of the mixture will result in a final pH of about 3 in the leach liquor. The acidified mixture is then thoroughly agitated while being heated, advantageously to its boiling point, and once it has attained this temperature the leaching will have been completed without requiring any further retention period. The leach liquor is subsequently filtered while hot in order to remove undissolved silica.

The resulting filtrate from the leaching operation comprises a solution of the desired fluotitanate or fluozirconate in a concentration such that the salt will crystallize from the liquor upon subsequent cooling. Accordingly, the hot filtrate is then permitted to cool to ambient temperature while maintaining agitation of the liquor to facilitate crystallization. The resulting crystals of the desired fluotitanate or fluozirconate may be removed from the mother liquor either by filtering or by centrifugal separation, or the like, and are subsequently dried in an oven at a temperature sufficient to remove entrained moisture.

The following specific example is illustrative of the practice of the method of my invention. A mixture was formed of 190 parts by weight of zircon ($ZrO_2.SiO_2$, containing about 65% by weight of ZrO_2), 220 parts by weight of potassium fluosilicate and 46 parts by weight of potassium carbonate. Each of the components of the mixture was added in finely divided form and the mixture was thoroughly dry-mixed in a tumbling barrel. The resulting mixture was then charged to a gas fired furnace provided with a stainless steel crucible wherein the mixture was fused at a temperature between 1100° and 1200° C. The fused mixture was then poured from the furnace crucible in the form of a small stream into 1500 parts by weight of water which increased from an initial temperature of 8° C. to a final temperature of 90° C. during an addition of the molten salt. The solidified material, which was obtained in the form of a frit, was then separated from the quench water by filtration. The frit was pulverized in a pebble mill with a small amount of added water to control dusting and the ground frit was combined with the quench water filtrate to form a thin slurry. To this mixture was added 46 parts by weight of 96% sulfuric acid (specific gravity 1.84) while maintaining agitation of the slurry. The entire mass was heated with continued agitation until the mass began to boil, whereupon it was filtered while still hot, the filter cake was washed with a small amount of hot water, and the filtrate and wash water were combined and cooled to ambient temperature while continuing the agitation. The resulting crystals of potassium fluozirconate which formed in the cooled liquor were separated by filtration and, without washing, were subsequently dried in an oven. The dried crystalline potassium fluozirconate represented a recovery of 94% of the zirconium content of the initial zirconiferous material.

The potassium fluozirconate (K_2ZrF_6) product obtained pursuant to the foregoing example was of sufficient purity to permit its use for all presently known purposes without further refinement. The product did contain, however, a small amount of zirconium oxyfluoride ($ZrOF_2$) which appears to have formed during the crystallization step. Although this latter compound is not an undesirable contaminant, it does represent a portion of the zirconium which is not in the desired form of the fluozirconate. Where it is desired to convert any zirconium oxyfluoride to the desired fluozirconate, this result can be obtained readily by adding a small amount of an ionizable fluorine compound such as hydrofluoric acid, ammonium bifluoride or potassium fluoride to the hot filtrate from the leaching step and prior to the crystallization step.

The efficacy of the method of the present invention is amply evidenced in the accompanying drawing wherein there is presented a plurality of curves representing the yield of extracted and crystallized potassium fluozirconate, expressed in terms of its percentage of the zirconium content of the zirconiferous starting material, plotted against the amount of acid used for the extraction or leaching liquor. In each instance, the potassium fluozirconate was obtained by fusing, at a temperature between 1100° and 1200° C., a finely divided intimate admixture of equimolar amounts of zircon ($ZrO_2.SiO_2$) and potassium fluosilicate (K_2SiF_6), by then quenching the fused product in water, pulverizing the quenched solid, and extracting the potassium fluozirconate with a uniform volume of water containing the specified amount of sulfuric acid expressed in terms of its percentage equivalent of the zirconium content of the zircon. Curve "A" represents yields from the fusion product obtained without the use of any other added salt, whereas curves "B," "C" and "D" represent the yields from fusion products obtained pursuant to the invention by the use of ⅙ mol, ⅓ mol and ⅔ mol, respectively, of potassium carbonate per mol of zirconium silicate in the zircon. From a consideration of these curves it will be seen that where the potassium carbonate was not used (a procedure representative of the aforementioned Koerner patent), the maximum yield using the optimum acid concentration in the leach liquor was approximately 53% whereas the yields obtained by the use of potassium carbonate within the preferred range pursuant to my invention were at least 84% and rose to 94% when using the optimum amount of potassium carbonate. It will be appreciated, accordingly, that the addition of an oxidic alkali metal compound to the mixture of fluosilicate and titaniferous or zirconiferous material and the use of an acidic aqueous medium in the leaching of the product of the fusion of this mixture leads to unexpectedly high yields which are not obtainable by either expedient alone. The resulting high yields obtainable by the method of my invention thus make possible a continuous operation for the production of alkali metal fluotitanates and fluozirconates.

I claim:

1. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxidic compound of a metal of the group consisting of titanium and zirconium, and an oxidic compound of an alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

2. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxidic compound of a metal of the group consisting of titanium and zirconium, and an oxidic compound of said alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

3. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal of the group consisting of sodium and potassium, an oxidic compound of a metal of the group consisting of titanium and zirconium, and an oxidic compound of an alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

4. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxide of a metal of the group consisting of titanium and zirconium, and an oxidic compound of said alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

5. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, a silicate of a metal of the group consisting of titanium and zirconium, and an oxidic compound of said alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

6. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of substantially equimolar proportions of a fluosilicate of an alkali metal and an oxidic compound of a metal of the group consisting of titanium and zirconium and from about ⅙ mol to about ⅔ mol of an oxidic compound of said alkali metal per mol of said titanium or zirconium, said oxidic alkali metal compound being one capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

7. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of substantially equimolar proportions of a fluosilicate of an alkali metal and an oxidic compound of a metal of the group consisting of titanium and zirconium and about ⅓ mol of an oxidic compound of said alkali metal per mol of said titanium or zirconium, said oxidic alkali metal compound being one capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

8. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxidic compound of a metal of the group consisting of titanium and zirconium, and an oxidic compound of said alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium such as to produce a leach liquor having a pH within the range of about 2.5 to about 4, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

9. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxidic compound of a metal of the group consisting of titanium and zirconium, and an oxidic compound of said alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium such as to produce a leach liquor having a pH of about 3, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

10. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxidic compound of a metal of the group consisting of titanium and zirconium, and an oxidic compound of said alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium containing an initial acid content approximately 20% equivalent to the metal oxide component of said titanium or zirconium compound, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

11. The method of producing a compound of the group consisting of alkali metal fluotitanates and fluozirconates which comprises forming an intimate physical admixture of a fluosilicate of an alkali metal, an oxidic compound of a metal of the group consisting of titanium and zirconium, and an oxidic compound of said alkali metal capable of thermally decomposing to the oxide, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product,

leaching the comminuted solid product with an acidic aqueous medium such as to produce a leach liquor containing about 200 grams per liter of dissolved alkali metal fluotitanate or fluozirconate, and recovering the resulting dissolved alkali metal product selected from the group consisting of the fluotitanate and fluozirconate.

12. The method of producing potassium fluozirconate which comprises forming an intimate physical admixture of potassium fluosilicate, a zirconium silicate and potassium carbonate, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an acidic aqueous medium such as to produce a leach liquor containing about 200 grams per liter of potassium fluozirconate, and recovering the resulting dissolved potassium fluozirconate from the leach liquor.

13. The method of producing a potassium fluozirconate which comprises forming an intimate physical admixture of substantially equimolar proportions of potassium fluosilicate and a zirconium silicate and about ⅓ mol of potassium carbonate per mol of zirconium silicate, heating the mixture to effect fusion thereof, cooling the resulting product to effect solidification thereof, comminuting said solid product, leaching the comminuted solid product with an aqueous medium containing sulfuric acid in an amount about 20% equivalent to the zirconium oxide content of the zirconium silicate, heating the resulting mixture to about its boiling point, separating the resulting aqueous liquor from insolubles, and cooling the separated aqueous liquor to effect crystallization therefrom of potassium fluozirconate.

HENRY C. KAWECKI.

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Number	Name	Date
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