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PROCESS FOR PREPARING FIBROUS AND WATER-INSOLUBLE ALKALI METAL TITANATES AND NEW FIBROUS CRYSTALLINE ALKALI METAL TETRATITANATES OBTAINED THEREBY

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This invention relates to a new and improved process for the preparation of fibrous and water-insoluble alkali metal titanates and to certain new fibrous alkali metal titanates. More particularly this invention relates to a new and improved process for preparing fibrous and water-insoluble alkali metal titanates which can be carried out at atmospheric pressure and to certain new fibrous alkali metal titanates prepared therein.

This application is a continuation-in-part of my U. S. patent application Serial No. 490,425, filed February 24, 1955, now abandoned.

Water-soluble or water-sensitive alkali metal titanates have been reported in the titanium literature. These titanium compounds are generally prepared by fusion of an alkali metal hydroxide or carbonate with titanium dioxide and generally have the formula $M_2Ti_nO_{2n+1}$ where M is an alkali metal such as sodium or potassium and n is 1, 2, or 3.

Recent investigation in the chemistry of alkali metal titanates has revealed that water-insoluble and fibrous titanates are obtained when an alkali metal hydroxide or carbonate is reacted with titanium dioxide under aqueous conditions at elevated temperatures and pressures, particularly above the critical temperature and pressure of water. The alkali metal is one that has an atomic number of at least 11, i. e., sodium, potassium, rubidium, and cesium, and the titanate thus obtained has the value of n in the above formula of substantially 6. These new titanates have unusual stability to aqueous solutions of acids, alkalies and to halogens. The fibrous character is useful in applications of reinforcement or insulation which require the inertness and physical properties of an asbestos-like material.

The process of obtaining these novel fibrous titanates has heretofore required conditions wherein water is present above its critical temperature and pressure as described by Gier, Salzberg and Young in their U. S. patent application Ser. No. 458,279, filed September 24, 1954. This process makes special demands upon apparatus for effecting the reaction since pressures of the order of 1000–4000 atmospheres at temperatures of 400° to 700° C. are employed.

It is an object of this invention to provide a new and improved process for the preparation of fibrous and water-insoluble alkali metal titanates. A further object is to provide a new process for preparing fibrous and water-insoluble alkali metal titanates which does not require high pressure equipment but can be carried out at atmospheric pressure. A still further object is to provide a novel process for preparing fibrous and water-insoluble alkali metal titanates which can be carried out in a continuous manner in relatively simple equipment. Another object is to provide a novel and improved process for increasing the rate of formation of fibrous and water-insoluble alkali metal titanates. An important object is to provide new fibrous alkali metal titanates, particularly fibrous potassium tetratitanates. Other objects will appear hereinafter.

These and other objects of this invention are accomplished by the following process for preparation of fibrous and water-insoluble alkali metal titanates which comprises heating an alkali metal chloride or fluoride or a mixture thereof to a molten state at a temperature of generally not higher than 1200° C., the alkali metal in the alkali metal halide having an atomic number of at least 11, dissolving in said molten alkali metal halide titanium dioxide or a non-fibrous alkali metal titanate of the general formula $M_2Ti_nO_{2n+1}$, i. e., $M_2O\cdot(TiO_2)_n$ wherein n is 4 or 6 (i. e., corresponds to the formula $M_2O\cdot(TiO_2)_{2m}$ wherein m is an integer of value 2–3) and M is an alkali metal having an atomic number of at least 11, maintaining at least a portion of said molten alkali metal halide saturated with dissolved titanium dioxide or non-fibrous alkali metal titanate as fibrous alkali metal titanate is formed therein, and separating the thus formed fibrous and water-insoluble alkali metal titanate from said alkali metal halide. Among the fibrous alkali metal titanates prepared by the novel process of this invention are new fibrous metal tetratitanates of an alkali metal having an atomic number of at least 11 and particularly fibrous potassium tetratitanates and fibrous water-extracted potassium tetratitanates.

In a preferred embodiment of this invention the hottest portion of the molten alkali metal chloride or fluoride or mixture thereof is maintained at a temperature no higher than 1200° C. and there is maintained a cooler portion in the molten alkali metal halide at a temperature of at least 5° C. lower than said hottest portion. At least the cooler portion of the molten alkali metal halide is maintained saturated with dissolved non-fibrous alkali metal titanate so that fibrous alkali metal titanate is crystallized out in said cooler portion. Addition to the molten alkali metal chloride of the corresponding alkali metal fluoride increases the rate of formation of the fibrous alkali metal titanate.

When the amount of fluoride in the bath does not exceed 20%, the fibrous titanate produced is the hexatitanate, i. e., $M_2O\cdot6TiO_2$ wherein M is an alkali metal having an atomic number of at least 11. When the alkali metal fluoride content of the bath is higher, e. g., 35–100%, the fibrous titanate consists generally of the tetratitanate, i. e., $M_2O\cdot4TiO_2$ or $M_2Ti_4O_9$ wherein M is an alkali metal having an atomic number of at least 11. It is particularly preferred that the bath contain 10–65% of the alkali metal fluoride, i. e., 10–20% for the fibrous hexatitanate and 35–65% for tetratitanate fiber production. The fibrous titanates are preferably separated from the alkali metal halides by dissolving the latter in water. Long treatment with hot water of the fibrous tetratitanate lowers the alkali metal content of the latter and converts it to a new fibrous product characterized by different X-ray diffraction pattern, lower alkali metal content, and superior fiber characteristics.

In effecting the preparation of the fibrous alkali metal titanates, the non-fibrous titanate can be charged into

the molten halide, i. e., chloride or fluoride, or mixture thereof, or the titanium dioxide (TiO_2) and a source of the alkali metal oxide (M_2O), such as the carbonate (M_2CO_3), can be introduced into the molten halide. When the latter method is employed the ratio of titanium dioxide to alkali metal oxide is at least 1:1 and less than 12:1 and preferably between 2:1 and 8:1.

The following examples, in which the parts are by weight, and ratios are generally molar ratios of the indicated effective reactant compounds, further illustrate the preparation of the fibrous titanates through treatment with molten alkali metal halide.

Example I

Fibrous crystals of potassium hexatitanate

($K_2O/TiO_2=1/6$)

prepared from potassium hydroxide/titanium dioxide reaction (mol ratio=3/1) by heating 1.5 hours at 450° C. and 1000 atmospheres in the presence of water (the process of Gier, Salzberg and Young U. S. patent application Serial No. 458,279, filed September 24, 1954) were melted at 1450° C. and cooled slowly. By this melting and cooling treatment, the fibrous character was destroyed and a coherent crystalline mass was obtained in which the crystals were rod-like needles up to about 0.1 mm. long and about 0.1 mm. thick with no fibers present.

One part of this non-fibrous crystal mass was placed in about 50 parts fused potassium chloride at about 800–850° C. Most of the potassium titanate remained as an insoluble solid phase in the potassium chloride melt. The melt was solidified by cooling and placed in 500 parts of water to dissolve the potassium chloride. Fibers of potassium titanate were suspended in the aqueous solution. The potassium hexatitanate needles which remained undissolved in the potassium chloride melt and in water had fibers protruding from their surfaces particularly at the ends of the needles.

Example II

Twenty-five parts of potassium chloride was melted by heating to 900–1000° C., 0.7 part of potassium carbonate was dissolved in the melt and over a period of 3 hours, 1.125 parts of titanium dioxide

($K_2O/TiO_2=1/2.8$)

was added in small increments. Between each addition, the melt was heated momentarily to about 1200° C.

After completion of the titanium dioxide addition, the melt was cooled slowly to room temperature and added to 300 parts of water to dissolve potassium chloride. The 1.328 part (83% yield) which was insoluble in the water contained fibers ranging up to 0.5 mm. in length and about 1 micron in thickness. Treatment of this product with 1/1 hydrochloric acid/water at 100° C. left 0.303 part (22.8% of the water-insoluble product) of fibers which gave the same X-ray diffraction pattern as the corresponding fibrous titanates prepared by the use of water as indicated in the introductory portion of Example I (i. e. by the process of Gier, Salzberg and Young, U. S. patent application Serial No. 458,279).

Example III

A mixture of 0.659 part of titanium dioxide, 0.362 part of 85% potassium hydroxide ($K_2O/TiO_2=1/3$) and 30 parts of potassium chloride was heated in a vertical tubular vessel in such a manner that the temperature was 1075° C. at the bottom and 925° C. at the top. The potassium titanate from reaction of the potassium hydroxide and titanium dioxide fell to the bottom of the melt in the hottest zone and fibers of potassium titanate formed continuously in the top or coolest part of the melt from the potassium titanate which dissolved at the bottom of the melt and migrated to the top. These were withdrawn about every hour over a period of 32 hours. During this withdrawal, the fibers displayed a tendency to spin into fine threads in which the individual filaments were about 1 micron in thickness and up to 3–4 mm. long.

The fibrous product was suspended in water, filtered, washed free of potassium chloride with water, and dried to obtain 0.250 part of a colorless fiber mass. This contained by analysis 45.03% titanium and 13.1% potassium. Its X-ray diffraction pattern was identical with that of the fibrous product of Example II. The residual potassium titanate was isolated from the melt by freezing and water washing and comprised 0.523 part of a blue coherent mass of non-fibrous needles.

Example IV

A mixture of 1.891 part of titanium dioxide, 1.039 part 85% potassium hydroxide ($K_2O/TiO_2=1/3$) and 70 parts potassium chloride was heated in a vertical tube so that the temperature of the melt was 1050° C. at the bottom and 900° C. at the top. Fibers of potassium titanate which formed in the top of the melt were withdrawn intermittently during 40 hours. The product was pressed at about 850° C. to remove most of the potassium chloride and then heated 3 hours at 1200° C. in an air stream to evaporate the remaining potassium chloride. There remained 1.3 parts of potassium titanate fibers. The latter contained 48.9% titanium and 13.4% potassium corresponding to the formula $K_2Ti_6O_{13}$. Characteristic X-ray diffraction pattern corresponding to that of Example II was obtained on the fibers.

Example V

Titanium dioxide and potassium carbonate in 5:1 molar proportions, respectively, were reacted by melting at 1400° C. A colorless mass of needlelike non-fibrous crystals was obtained on cooling. This material (6.476 parts) was placed in approximately 100 parts of molten potassium chloride contained in a vertical tubular vessel which was heated so that the temperature was 1090–1115° C. at the bottom and 980–1040° C. at the top.

Fibrous crystals grew continuously in the top of the melt and were removed intermittently during 69 hours. Potassium chloride was added to the melt to replace that occluded to the removed fibrous product. Potassium chloride was removed from the fibers by expressing the major part at 850° C. and evaporating the remainder during 3 hours in an air stream at 1200° C. leaving 3.98 parts of fine fibers. The starting material which remained in the melt was 1.836 parts. The fibers contained 50.04% titanium, 12.5% potassium. The X-ray diffraction pattern of the product indicated that it comprised mostly $K_2Ti_6O_{13}$.

Example VI

The process of Example V was repeated except that the starting alkali metal compound was 5 parts of the corresponding sodium compound instead of potassium titanate and sodium chloride was substituted for potassium chloride. The fibrous product was removed intermittently from the melt during 80 hours and showed a tendency to spin to fine threads when withdrawn from the melt. The fibrous product was washed free of sodium chloride with water, dried and found to comprise 3.35 parts.

Example VII

Five parts of preformed non-fibrous potassium titanate as employed in Example V was placed in the hottest zone, at about 1100° C., of 180 parts of a molten mixture of 90% by weight potassium chloride and 10% potassium fluoride.

Fibrous crystals were deposited rapidly in the coolest zone of the melt (at about 850–1050° C.) and were removed almost continuously during 4 hours. This material was extracted and washed with water, dried and found to comprise 4.55 parts, 84% of which was fibrous and insoluble in 4 N hydrochloric acid at 100° C. These contained 49.63% titanium and 13.2% potassium corresponding to $K_2O/TiO_2=1/6.1$. The fibrous products contained substantially no halogen.

Example VIII

A mixture of 4.794 parts of titanium dioxide and 1.382 parts potassium carbonate ($K_2O/TiO_2=1/6$) was fused at 1500–1600° C. and the non-fibrous potassium titanate product crystallized to needles by cooling.

One hundred and twenty parts of potassium chloride was added and the process of Examples III–VII conducted. During 94 hours, 5.4 parts of a product were removed from the melt, of which 94% were fibers insoluble in 4 N hydrochloric acid at 100° C.

Example IX

This example illustrates a substantially continuous process for the relatively large scale production of the fibrous titanate.

The reaction vessel was of graphite, had an inside diameter of 6½" and was 10" deep. A ¾" thick graphite baffle was positioned vertically such that it extended from the top of the vessel to 2" from the bottom and approximately 1½" from a side wall, thus providing a small and large compartment. The total working volume of the vessel was 4 liters (about 0.14 cu. ft.). The vessel was heated by means of an electric arc struck between a graphite electrode outside of the vessel and the central portion of the bottom of the vessel.

To the smaller chamber of the vessel was charged a quantity of non-fibrous potassium titanate (containing 48.2% Ti and 13.5% K, equivalent to a molar ratio of about $TiO_2:K_2O$ of 5.8:1) made by the solid state reaction of finely divided potassium carbonate with titanium dioxide at 800–1000° C. A vibrating feeder was used to add substantially continuously to the smaller chamber of the vessel a solid mixture of potassium chloride (90%) and potassium fluoride (10%). The mixed salt was added through-out the run at a rate sufficient to maintain the level of the liquid salt near the top of the graphite vessel. More non-fibrous potassium titanate was added at intervals as needed to replace material removed as fibers.

The net movement of materials through the vessel was downward in the smaller chamber and upward in the larger chamber. Thus, in the smaller chamber, solid salt was converted to liquid salt at the top of the vessel and solid non-fibrous potassium titanate dropped through the liquid salt to the bottom of the vessel when it passed under the baffle and slowly dissolved in molten salt at a temperature of 1100 to 1150° C. In the larger chamber a semicircular horizontal baffle 3" in radius and ½" thick was attached at right angles to the vertical baffle at a point 4" from the bottom of the vessel. In this chamber, the molten salt containing dissolved potassium titanate at 1100–1150° C. diffused around the horizontal baffle into the upper portion of the chamber. The surface of the liquid salt in the larger chamber was at a temperature of 900–950° C., and in this region the melt became supersaturated with potassium titanate. Here fibrous potassium titanate crystallized from the melt on the walls and at the surface of the larger chamber and was collected from the melt almost continuously.

In 32 hours of continuous operation, 275 lbs. of mixed salt (90% KCl, 10% KF) and 4.0 lbs. of non-fibrous potassium titanate were added to the smaller chamber of the vessel. In this same period salt and fibrous potassium titanate with a combined weight of 263 lbs. were removed. Most of this 263 lbs. represents salt entrained by the sponge-like mass of fibrous potassium titanate.

A 249.5 lb. portion of the recovered fibers in the salt matrix was leached with water until the effluent water gave no test for chloride ion. The salt-free fibrous potassium hexatitanate was then collected in a basket centrifuge, washed with water and dried. The dry fibers weighed 3.5 lbs. They were further purified by extraction with hydrochloric acid. Finally, carbon from the vessel entrained by the fibers was burned out during 24 hours at 600° C. to leave a nearly white product. In this experiment fibers were produced at the rate of 0.85 lb./cu. ft./hour or 13.7 g./l./hour.

Example X

A mixture of completely anhydrous potassium carbonate (3.46 parts), titanium dioxide (12 parts), potassium fluoride (76.7 parts) and potassium chloride (64.7 parts) in respective molar proportions of 1/6/48/32 (corresponding to weight proportions of 1/3.3/22/18 and to weight ratio of KF/KCl of 54/46) was heated in a platinum vessel to 1020° C. to obtain a clear homogeneous melt. The melt was cooled slowly and fiber formation started at about 975° C. The melt was cooled to room temperature. Loss of the halides by volatilization amounted to 10.6 parts. The product comprised a hard white solid mass containing long fine fibers embedded and distributed uniformly in the matrix. The X-ray diffraction pattern indicated the presence of KCl and KF. In addition the following lines were present which were assigned to the new titanate $K_2Ti_4O_9$.

Interplanar spacings (Angstroms):	Relative intensity
8.75	18
6.9	11
2.95	7
2.88	8
2.72	8
2.18	7
2.09	7

A portion of the product obtained was heated in an air stream for 120 hours at 875–950° C. Potassium chloride and fluoride were evaporated completely from the solid mass leaving a deposit of fibrous material containing 49.1% titanium and having an X-ray diffraction pattern corresponding to that of $K_2Ti_6O_{13}$.

In support of the tetratitanate structure, a mixture of 13.82 parts of predried potassium carbonate and 31.96 parts of predried titanium dioxide (1/4 molar ratio) was ball milled for 39 hours. A portion of this mixture (13.325 parts) was heated for 7.3 hours in a platinum vessel at 840–900° C. There was obtained 12.019 parts of potassium tetratitanate with traces of potassium dititanate and potassium hexatitanate.. Further heating for 40.7 hours at 850–900° C. gave no further change in weight. This essentially non-fibrous titanate exhibited the following X-ray diffraction pattern.

Interplanar spacings (Angstroms):	Relative intensity
8.80	21
6.23	7
3.7	4
3.2	14
2.95	16
2.88	11
2.72	8
2.66	12
2.18	7
2.09	9
1.90	12

The differences in the curves obtained for the preceding compositions are probably due to orientation of the fibers. The similarities are, however, sufficient to show that both products are tetratitanates.

By the latter method, i. e., fusion of K_2CO_3 and tiO_2 in 1/1 and 1/2 and 1/6 molar ratios, the monotitanate, K_2TiO_3, dititanate, $K_2Ti_2O_5$, and hexatitanate, $K_2Ti_6O_{13}$, were prepared. These titanates had the following X-ray diffraction patterns:

K_2TiO_3

Interplanar spacings (Angstroms):	Relative intensity
7.02	20
5.71	49
3.02	26
2.94	59
2.73	14
2.64	100
2.26	40
2.02	26
1.90	27
1.80	19
1.74	10
1.67	20
1.60	16
1.46	20
1.38	11

$K_2Ti_2O_5$

Interplanar spacings (Angstroms):	Relative intensity
6.65	100
4.72	5
3.79	33
3.08	20
2.82	11
2.76	2
2.66	5
2.64	9
2.59	3
2.44	3
2.38	2
2.18	50
1.92	7
1.89	6

$K_2Ti_6O_{13}$

Interplanar spacings (Angstroms):	Relative intensity
8.93	10
7.69	100
6.41	69
4.48	8
3.83	4
3.77	4
3.67	18
3.2	7
3.04	47
2.98	60
2.97	66
2.90	7
2.79	23
2.70	28
2.64	7
2.58	23
2.10	32
2.08	32
1.90	26

Example XI

A mixture of completely anhydrous potassium carbonate, titanium dioxide, potassium fluoride, and potassium chloride in respective molar proportions of 1/6/83/95 corresponding to respective weight proportions of 1/3.43/34.3/50.5 and a potassium halide salt composition of 40/60% by weight KF/KCl was heated in a platinum vessel to 1050° C. to obtain a clear homogeneous melt. This melt was cooled slowly at a rate of approximately 25° C./hr. until fiber formation started as evident by the appearance of turbidity at approximately 1000° C. This temperature was held essentially constant for approximately two hours until the melt had apparently turned solid as a result of fiber formation of the potassium titanate component. The temperature was decreased at a rate of 50° C./hr. to approximately 950° C. and thereafter lowered rapidly to room temperature. There resulted a hard white solid mass containing long fibers firmly embedded in and distributed throughout a white matrix and comprising 80.5 parts by weight. The 8.7 parts lost by volatilization consisted of carbon dioxide, potassium fluoride, and potassium chloride. The product mass was treated 27 hrs. in about 400–500 parts of boiling distilled water with frequent replacements of the water by fresh portions. The duration of this boiling water extraction was determined by completion of the removal of potassium chloride and fluoride. The extracted, water-insoluble material was dried at 120° C. in a vacuum oven and comprised 4.1 parts by weight of a matted mass of fibers having very low bulk density. This mass was readily pulled apart revealing individual fibers up to about 3 cm. long and having cross sectional axis dimensions ranging from less than one to several microns. It contained by analysis 48.7% Ti. It gave an X-ray diffraction pattern characteristic of a crystal structure obtained by the water extraction of $K_2Ti_4O_9$. The diffraction pattern had the following lines and relative intensities from analysis of which it appeared that tetratitanate contained both the dipotassium salt and a further tetratitanate having decreased potassium content.

Interplanar spacings (Angstroms):	Relative intensity
8.75	10
6.55	3
3.95	1
2.93	1
2.68	3
2.18	1
2.07	1
1.94	1

The product was subjected to differential thermal analysis and showed no changes evident by heat absorption or evolution until the temperature reached approximately 1330° C. where melting started. After this heat treatment at the melting point, the product was found by X-ray diffraction to comprise largely $K_2Ti_6O_{13}$ and a small amount of rutile.

Example XII

The general procedure of Example XI was repeated except that the charge consisted of $K_2CO_3/TiO_2/KF/KCl$ in molar proportions of 1/6/48/32. The potassium fluoride content of the bath was 54% on a weight basis. The charge was melted at 1000° C. and fiber formation started at 980° C. The fibrous product was extracted in boiling water for 6 days. The resulting fibers were 3–4 mm. in length and on analysis had 12.7% potassium and 48.9% titanium. The following X-ray diffraction

pattern was obtained for this tetratitanate having low potassium content.

Interplanar spacings (Angstroms):	Relative intensity
8.66	40
6.70	17
3.95	5
2.95	14
2.68	10
2.18	6
2.07	8
1.95–7	5
1.88	7

Example XIII

The general process of Example XI was repeated with the exception that no potassium chloride was present, the molar ratio of $K_2CO_3/TiO_2/KF$ being 1/6/10. The initial temperature of the melt was about 1010° C. with fiber formation taking place at 970° C. There was obtained fibrous potassium tetratitanate, which upon extraction of the fluoride by water had a diffraction pattern corresponding to that of the product of Example XI.

When this general procedure was repeated except that the molar ratio of $K_2O/TiO_2/KF$ was 1/6/5.5 and the temperature of the melt was 1150° C., X-ray diffraction pattern indicated the major fibrous product was the hexatitanate with some tetratitanate present. This shows that higher temperatures, e. g., 1150° C. or higher, favor hexatitanate formation.

Example XIV

Following the general procedure of Example XI, with the molar ratio of K_2CO_3 to TiO_2 at 1/6, the amount of KF in the KF/KCl bath was in each case 25, 44, and 54%. The bath was heated to about 1000–1020° C. Upon cooling there was obtained in each case long fibers of the tetratitanate which were subjected to water extraction.

Example XV

Following the general procedure of Example XI, with the molar ratio of K_2CO_3 to TiO_2 at 1/5, the amount of KF in the potassium halide bath was varied from 100% KF through 50/50, 39/61 and 33/67 of KF/KCl. Fibrous product was obtained in each case after heating to about 1000° C.

Example XVI

The following general procedure has been employed numerous times for the production of potassium tetratitanate fibers:

A platinum vessel was charged with 9.05 parts of potassium carbonate, 21.25 parts of titanium dioxide (1:4 mole ratio of $K_2O:TiO_2$), 185.3 parts of potassium fluoride, and 289.8 parts of potassium chloride (KF/KCl eutectic 39/61% by weight). The vessel was then heated to 1070° C. in a crucible-type electric resistance furnace. The furnace was arranged so that heat was added through the vertical walls but not through the well-insulated top or bottom sections. At 1070° C. the melt was stirred. It was determined visually that the clear melt contained no undissolved titanium dioxide or potassium titanates. The melt was allowed to cool from 1070° to 995° (as determined by a thermocouple at the outside bottom of the platinum dish) in 1.5 hours. In an additional 40 minutes of cooling, the temperature fell to 980° C. and in another 50 minutes to 970° C. The first separation of fibers from the clear melt was observed through a small opening in the top of the furnace at 970° C. Then a few minutes after fiber formation started, the entire melt appeared to solidify, and in 20 minutes the temperature at the thermocouple registered 978° C. At the end of 2.25 hours the temperature had returned to 970°. Cooling was continued slowly until the temperature of 940° C. was reached 1.83 hours later. Power to the furnace was turned off at 940° C., and the furnace was allowed to cool to room temperature.

During this process 18.7 parts of salt were lost from the vessel through evaporation. The fibers of potassium tetratitanate in salt matrix were removed from the dish and transferred to a blowcase. In the blowcase, the salt-fiber cake was repeatedly leached with hot distilled water on an hourly cycle. At the end of 70 hours, the aqueous discharge from the blowcase gave no test for chloride ions with silver nitrate reagent or for fluoride ions with cerium nitrate reagent.

The wet salt-free fibers were finally dried 45 hours at 150° C. to a constant weight of 24.9 parts. They contained 49.6% titanium and about 14.4% potassium.

The X-ray diffraction pattern of the fibers corresponded to that of potassium tetratitanate which had been subjected to water extraction until no more potassium was removed (Ex. XII).

Example XVII

A graphite crucible was charged with 300 parts of non-fibrous potassium hexatitanate (obtained as shown for the non-fibrous starting potassium titanate in Example IX), 2,223 parts of potassium fluoride, and 3,477 parts of potassium chloride (KF/KCl eutectic). The graphite crucible was placed in a silicon carbide muffle heated in a gas-fired furnace. The charge gave a clear liquid melt at 1040–1045° C. The melt was slowly cooled while fiber formation took place. After removal of salt from the product as in Example XVI above, the dry fibers of hydrolyzed potassium tetratitanate weighed 268 parts and contained 49.0% titanium. These fibers were faintly blue in color but were readily converted to white fibers by heating 2 hours at 565° C. in air.

Example XVIII

A premelt of the composition given in Example XVI above was made by rapidly cooling the clear melt from 1050° C. to room temperature. The salt cake containing potassium tetratitanate was micronized under dry nitrogen and the resulting powder converted to dense wafers ¾ inch in diameter by ⅛ inch thick. A platinum tube ¾ inch i. d. was packed solidly with these pellets (263.5 parts) for a length of 83 cm. and the ends of the platinum tube were sealed, leaving only a small opening for escape of gases. The platinum tube was placed inside a porcelain tube mounted on rollers in a manner such that the porcelain tube could be passed through a horizontal tube furnace.

The platinum tube and its contents were thus passed through a melting zone, a liquid region, and finally through a solidification zone at the rate of 2 linear cm./min. The furnace temperature in the latter zone decreased approximately 19° C. per cm. of length. The maximum temperature in the furnace was approximately 1035° C.

The salt cake and fibers from the platinum tube were leached with water in the blowcase as in Example XVI above to give water-extracted potassium tetratitanate fibers.

Example XIX

Following the general procedure of Example XVI, fibrous potassium titanates C—M were prepared in a molten potassium halide bath with titanates A—B prepared by the procedure of Example IX. The temperature at which fiber formation first occurred was noted. The following table shows the composition of the bath, reactants and fibrous product. The potassium carbonate is expressed as oxide in the table. The fibers were ob-

tained by water extraction of the product and charactered by X-ray diffraction studies.

	Composition of Charge			Temp. °C., Fibers Formed	Product
	Molar Ratio, K_2O/TiO_2/ KF/KCl	Molar Ratio, $K_2O:TiO_2$	Wt. Percent KF in KF/KCl		
A	<0.1/<0.3/12.3/87.6	1:3	10	>1,100	Hexatitanate.
B	<0.1/<0.6/12.3/87.6	1:6	10	>1,100	Do.
C	0.115/0.467/24.1/75.3	1:4	20	993	Hexa- and tetratitanate.
D	0.138/0.558/24.1/75.2	1:4	20	1,000	Primarily hexatitanate.
E	0.301/1.23/35/63.5	1:4	30	995	tetratitanate.
F	0.88/3.58/43.1/52.5	1:4	40	970–980	Do.
G	0.845/3.44/61.1/34.6	1:4	58	875	Do.
H	0.804/3.27/80.3/15.6	1:4	80	795	Do.
I	1.56/6.32/92.1/0	1:4	100	814	Do.
J	0.688/3.59/43.2/52.6	1:5.2	40	980	hexa- and tetratitanate.
K	0.568/3.64/43.2/52.6	1:6.1	40	985	Do.
L	0.442/3.69/43.2/52.7	1:8.1	40	995	hexatitanate.
M	0/3.61/43.5/52.9	0	40	1,027	Do.

In the above table it is seen that the tetratitanate formation is favored by molar ratios of K_2O/TiO_2 approaching 1:4 while ratios of 1:6–8 favor the hexatitanate. Higher temperatures increase the amount of hexatitanate. The last item in the table shows that a fibrous potassium titanate can be formed wherein the potassium must come from the halides since no other source of potassium was employed.

Example XX

The general procedure of Example XVI was repeated except that the fiber formation started at 962° C. The product was extracted for only 48 hours by water. The resulting fibers had 17.9% K, 48.14% Ti and 0.19% Cl. The X-ray diffraction pattern had bands for both the dipotassium tetratitanate of Example X and the potassium deficient tetratitanate of Example XII.

Example XXI

Repetition of the general procedure of Example XVI with the exception that 6 parts of potassium carbonate (molar ratio of $K_2CO_3:TiO_2$ of 1:6.12) was used with a fiber formation temperature of 984° C. gave a fibrous product which was extracted for 24 hours by water. The X-ray diffraction pattern indicated the presence of both tetratitanate and potassium deficient tetratitanate with perhaps more of the latter.

Example XXII

Potassium titanate was preformed in the manner described in the first part of Example V (1/5 ratio of K_2O/TiO_2). To 10 parts of molten potassium fluoride in a platinum vessel was added in increments a total of 10 parts of the preformed titanate. The solution on cooling solidified to a white glistening cake containing fibrous potassium titanate.

Example XXIII

A mixture of potassium fluoride and titanium dioxide in a molar ratio of 1/2.24 was melted in a tube and cooled. Fiber bundles, which formed across the mouth of the tube, were identified as potassium hexatitanate by their X-ray diffraction pattern.

Example XXIV

Potassium chloride (50 parts) was fused in a platinum vessel which was heated by a flame in such a manner that the bottom surface of the vessel in contact with the melt was at a temperature of 1025–1030° C. and the top outer regions of the melt farthest from the area of heating were at a temperature of 850–860° C. as determined by means of an optical pyrometer. One part of titanium dioxide was added to the melt. It aggregated and settled to the bottom at the hottest zone. After about 12 minutes, a growth of flocculent, colorless fibrous crystals started forming upward from the titanium dioxide. Thereafter the growth was more rapid and quite voluminous. After about one hour, the fibers filled most of the melt volume and a preponderant part was removed mechanically leaving the residual titanium dioxide and some seed fibrous crystals of the product. This cropping was repeated intermittently during two hours. The isolated product containing occluded potassium chloride was dispersed in water to dissolve the potassium chloride, filtered, washed free of chloride ions with water, and dried to obtain 0.1 part of fine fibrous product which had an X-ray diffraction pattern characteristic of potassium hexatitanate.

The process of this invention thus provides the production of fibrous alkali metal titanates by the use of molten alkali metal chloride or fluoride or mixtures thereof (MCl or MF or mixtures thereof), on non-fibrous alkali metal titanates of the general formula $M_2Ti_nO_{2n+1}$ wherein n is 4 or 6, i. e., $M_2O\cdot(TiO_2)_{2m}$ where m is an integer of value 2 to 3 and M is an alkali metal of atomic number of at least 11. This new process for the preparation of fibrous alkali metal titanates comprises introducing, generally to the point of saturation, a non-fibrous alkali metal titanate of the general formula $M_2Ti_nO_{2n+1}$ wherein n is subtantially 4 or 6 and M is an alkali metal of atomic number of at least 11, into the chloride or fluoride of the alkali metal or mixture thereof (MCl or MF or mixture thereof) which is molten but which is maintained at a temperature of generally less than 1200° C. above which the metal halide evaporates at a substantial rate, followed by separation of the fibrous titanate from the alkali metal halide. It is preferred that a zone is present in the molten chloride or fluoride or mixture thereof that is at least 5° C. below that of the remainder of the molten halide and that the molten halide in this zone is maintained saturated with the non-fibrous alkali metal titanate so that crystallization of fibrous alkali metal titanate occurs therefrom.

When the alkali metal is potassium and sodium the general formulas are respectively $K_2O\cdot(TiO_2)_{2m}$ and $Na_2O\cdot(TiO_2)_{2m}$ where m is 2 or 3. These alkali metal titanates can be previously obtained in non-fibrous form by the fusion of alkali metal oxide or preferably an equivalent source thereof, such as the carbonate or hydroxide, with titanium dioxide at temperatures of above 1200° C., e. g., 1200–1500° C. Alternatively, non-fibrous alkali metal titanates may be made by the dry solid state reaction of a metal carbonate with titanium dioxide at temperatures considerably below the melting point of the reactants, e. g., 800–1000° C. The non-fibrous titanates are then charged into the molten alkali metal halide as required by the process of this invention. A further method involves the preparation of the titanate and its separation in fibrous form by the action of molten alkali metal halide on titanium dioxide and alkali metal oxide.

In the latter embodiment of this invention whereby the fibrous titanate is prepared from titanium dioxide and an alkali metal oxide, the alkali metal oxide can be employed as such or from any alkali metal compound that is basic or gives a basic reaction with water. Included are the alkali metal phosphates; however, the carbonates and hydroxides, particularly the potassium and sodium carbonates and hydroxides, are generally cheaper, more readily available and are preferred as sources of the alkali metal oxide.

The titanium source can be a titanium oxide or a salt, such as titanyl sulfate, which gives rise to titanium dioxide under the reaction conditions. Titanium dioxide is generally employed since it is readily available and reacts readily under the conditions of reaction.

The ratio of titanium to alkali metal calculated as titanium dioxide to alkali metal oxide in the charge added to the molten halide can vary in wide limits, usually from 1:1 to 12:1 with the ratio preferably between 2:1 and 8:1. The tetratitanate is generally formed when the ratio of alkali metal oxide to titanium dioxide is about 1:1 to 1:5, preferably about 1:4 at temperatures of about 1000° C. When less alkali metal is present, i. e., ratios of 1:6 to 1:8 and preferably about 1:6, the hexatitanate is the major product, particularly if somewhat higher temperatures are employed.

The fibrous titanates can thus be obtained by introducing titanium dioxide and the alkali metal oxide (M_2O) or their equivalents as previously defined, into the molten chloride or fluoride of the alkali metal or mixture thereof (MCl or MF or mixture thereof) at least to the point of saturation and effecting the formation of the fibrous alkali metal titanate followed by separation from the metal halide. The metal halide employed is of the same alkali metal as that of the oxide and the titanate to be obtained. The alkali metal halides thus useful include sodium chloride, potassium chloride, rubidium chloride, cesium chloride, sodium fluoride, potassium fluoride, cesium fluoride and rubidium fluoride.

The temperature of the molten halide should be no higher than 1200° C. during the preparation of the fibrous titanate. Temperatures above 1200° C., particularly if maintained for substantial times not only bring about evaporation of the volatile metal halides, but inhibit the growth of highly fibrous crystals. Higher temperatures, however, can be used for short times for the preparation and solution of non-fibrous titanates. Furthermore, the fibrous form of the metal hexatitanate is not stable at temperatures of the order of 1400° C. while the tetratitanates decompose at lower temperatures. The preferred temperatures are from about 750 to 1150° C. The lowest temperature employed necessary to maintain a molten bath depends upon the halide used but must be at least 600° C. and generally is over 700° C.

A particularly effective method for obtaining the alkali metal titanate fibers involves maintaining the temperature of the molten chloride or fluoride or mixture thereof in a manner such that one zone is at a higher temperature of at least 5° C. and preferably at least 25° C. or more than a cooler zone to permit solution of the titanate at the warmer portion. This warmer solution of the alkali metal titanate moves by convection to the cooler zone where it becomes supersaturated with respect to said alkali metal titanate and deposits the latter as fibrous crystals. It is evident, therefore, that rapid recrystallization is favored by the widest temperature differences, and by high temperatures in the hotter zone to favor the highest solubility and rate of solution of the non-fibrous alkali metal titanate. Highest yields of fibrous titanates are obtained if the metal oxide and titanium dioxide, or their equivalents, are introduced during the process in such a manner as to maintain saturation of the non-fibrous titanate or its precursors throughout the molten alkali metal halide bath. Optimum yields of fibrous alkali metal titanates in shorter times are obtained when the molten halide bath contains both alkali metal chloride and alkali metal fluoride.

The fibrous metal titanates obtained by the halide bath fusion process of this invention include those of the formula $M_2Ti_nO_{2n+1}$ wherein M is an alkali metal of atomic number of at least 11 and n is an integer having a value of substantially either 4 or 6, i. e., titanates of the formula $M_2O\cdot(TiO_2)_{2m}$ wherein m is an integer of 2 to 3, as determined by X-ray and chemical analysis. Sodium and potassium are cheaper and more readily available than cesium and rubidium and are preferred more than the latter. Potassium is especially preferred since fibrous titanates containing it have superior fiber properties.

The fibrous tetratitanates are formed only in the presence of an alkali metal fluoride. They are less stable than the hexatitanate and upon heating to temperatures above about 1100° C. change to the hexatitanate. The exact transition temperature is difficult to define since the time factor is dependent upon the temperature. Some of the potassium content of potassium tetratitanate can be removed by treatment with water, e. g., water at 20 to 100° C. for 2 to 100 hours with higher temperatures being more effective. The exact time and temperature employed are interdependent and dependent upon the amount of water used and amount of chloride or fluoride to be removed. The resulting tetratitanate can contain as low as about 60% of the potassium content of the original tetratitanate, e. g., extraction for 129 days gave a titanate having 9.8% K and 53.7% Ti. Exact analysis of the alkali metal is difficult since the presence of titanium makes the flame photometry method less accurate. The extracted tetratitanate is less stable to temperature than the other fibrous titanates. Heating at above 700° C., especially at 900–1000° C. converts it to the hexatitanate. In general, however, the extracted tetratitanate has superior flexibility and fiber length.

The fibrous alkali metal titanates and particularly the potassium titanates have good thermal stability, inertness and low bulk density. Mats or felts of the fibers are readily obtained by filtration, e. g., by suspending the fibers in a viscous liquid such as glycerine followed by removal of the dispersing liquid. The mats are useful as filters, e. g., in air to remove solids or to remove bacteria from solutions. They are also good thermal insulators. Potassium titanate fibers give increased stiffness and tear strength when incorporated in plastic laminates. They are also useful as reinforcing agents for fibers or papers. Finely ground fibers when incorporated with oils such as silicone oil have produced thick greases useful as lubricants.

The fibrous alkali metal titanates do not dissolve in water. They generally do not react with aqueous solutions of mineral acids, such as sulfuric or hydrochloric acid, bases or salts at room temperatures. These titanates, and particularly the hexatitanates are insoluble in boiling 50% caustic, and are not attacked by chlorine. They do not form hydrates, i. e. absorb water of crystallization. The fibrous titanates as obtained by the process of this invention are asbestos-like in the general appearance of their fibers. They have a length to diameter ratio of at least 5:1 and usually at least 10:1 with the length generally 10 to more than 1000 times the diameter of the fibers. The fibers are flexible.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A fibrous dialkali metal tetratitanate wherein the alkali metal has an atomic number of at least 11, said

fibrous dialkali metal tetratitanate exhibiting by X-ray diffraction analysis a definite pattern of crystalline structure.

2. Fibrous dipotassium tetratitanate exhibiting by X-ray diffraction analysis a definite pattern of crystalline structure.

3. A fibrous water-extracted potassium tetratitanate containing a potassium content of at least 9.8%, exhibiting by X-ray diffraction analysis a definite pattern of crystalline structure, and which is the product obtained by water-extracting fibrous crystalline dipotassium tetratitanate.

4. A mixture of fibrous dipotassium tetratitanate and its fibrous water-extracted potassium tetratitanate product containing a potassium content of at least 9.8%, said mixture exhibiting by X-ray diffraction analysis a definite pattern of crystalline structure.

5. Fibrous alkali metal tetratitanates exhibiting by X-ray diffraction analysis a definite pattern of crystalline structure and which are selected from the class consisting of fibrous dialkali metal tetratitanates wherein the alkali metal has an atomic number of at least 11, fibrous water-extracted potassium tetratitanates containing a potassium content of at least 9.8% which is the product obtained by water-extracting fibrous crystalline dipotassium tetratitanate, and mixtures of fibrous dipotassium tetratitanate with its fibrous water-extraced poassium tetratitanate product.

6. As a new inorganic fibrous material, the asbestos-like form of a dialkali metal tetratitanate characterized in that it is in the form of flexible crystalline fibers having a ratio of length to width of at least 10:1, which are water-insoluble, and corresponds in chemical composition to the general formula $M_2Ti_4O_9$ wherein M is an alkali metal having an atomic number of at least 11.

7. As a new inorganic fibrous material, the asbestos-like form of dipotassium tetratitanate characterized in that it is in the form of flexible crystalline fibers having a ratio of length to width of at least 10:1, which are water-insoluble, and corresponds in chemical composition to the formula $K_2Ti_4O_9$.

8. As a new inorganic fibrous material, the asbestos-like form of potassium tetratitanate, having a potassium content of at least 9.8%, characterized in that it is in the form of flexible crystalline fibers having a ratio of length to width of at least 10:1, which are water-insoluble, and is the product obtained by water-extracting the fibrous form of crystalline dipotassium tetratitanate having the formula $K_2Ti_4O_9$.

9. An inorganic flexible crystalline fiber having a ratio of length to width of at least 10:1, consisting of the asbestos-like form of a crystalline dialkali metal tetratitanate, which is water-insoluble, and corresponds in chemical composition to $M_2Ti_4O_9$ wherein M is an alkali metal having an atomic number of at least 11.

10. An inorganic flexible crystalline fiber having a ratio of length to width of at least 10:1 consisting of the asbestos-like form of crystalline dipotassium tetratitanate, which is water-insoluble, and corresponds in chemical composition to $K_2Ti_4O_9$.

11. An inorganic flexible crystalline fiber having a ratio of length to width of at least 10:1, which is water-insoluble, consists of a fibrous potassium tetratitanate having a potassium content of at least 9.8%, and is the product obtained by water-extracting the fibrous form of crystalline dipotassium tetratitanate having the formula $K_2Ti_4O_9$.

12. An insulating composition comprising a mass of asbestos-like crystalline fibers of a dialkali metal tetratitanate corresponding in chemical composition to $M_2Ti_4O_9$ wherein M is an alkali metal having an atomic number of at least 11.

13. An insulating composition comprising a mass of asbestos-like crystalline fibers of dipotassium tetratitanate corresponding in chemical composition to $K_2Ti_4O_9$.

14. An insulating composition comprising a mass of asbestos-like crystalline fibers of potassium tetratitanate having a potassium content of at least 9.8% and which is the product obtained by water-extracting the fibrous form of crystalline dipotassium tetratitanate having the formula $K_2Ti_4O_9$.

15. An insulating composition comprising a mass of asbestos-like crystalline fibers of dipotassium tetratitanate corresponding in chemical composition to $K_2Ti_4O_9$ and of its fibrous water-extracted product containing a potassium content of at least 9.8%.

16. Process for preparation of fibrous and water-insoluble alkali metal titanates which comprises heating an alkali metal halide from the group consisting of alkali metal chlorides and fluorides and mixtures thereof to a molten state at a temperature not higher than 1200° C., the alkali metal in said alkali metal halide having an atomic number of at least 11, dissolving in said molten alkali metal halide a compound from the class consisting of titanium dioxide and non-fibrous alkali metal titanates of the general formula $M_2O\cdot(TiO_2)_{2m}$ wherein m is an integer of 2 to 3 and M is an alkali metal having an atomic number of at least 11, maintaining at least a portion of said molten alkali metal halide saturated with the dissolved compound from the class consisting of titanium dioxide and non-fibrous alkali metal titanates of said general formula as fibrous alkali metal titanate is formed therein, and separating the fibrous and water-insoluble alkali metal titanate from said alkali metal halide.

17. Process for preparation of fibrous and water-insoluble alkali metal titanates which comprises heating an alkali metal halide from the group consisting of alkali metal chlorides and fluorides and mixtures thereof to a molten state at a temperature not higher than 1200° C., the alkali metal in said alkali metal halide having an atomic number of at least 11, dissolving in said molten alkali metal halide a non-fibrous alkali metal titanate of the general formula $M_2O\cdot(TiO_2)_{2m}$ wherein m is an integer of 2 to 3 and M is an alkali metal having an atomic number of at least 11, maintaining at least a portion of said molten alkali metal halide saturated with dissolved non-fibrous alkali metal titanate of said general formula as fibrous alkali metal titanate is formed therein, and separating the fibrous and water-insoluble alkali metal titanate from said alkali metal halide.

18. Process for preparation of fibrous and water-insoluble alkali metal titanates as set forth in claim 17 wherein said fibrous and water-insoluble alkali metal titanate is separated from said alkali metal halide by treatment with hot water.

19. Process for preparation of fibrous and water-insoluble potassium titanate which comprises heating potassium chloride to a molten state at a temperature not higher than 1200° C., dissolving in said molten potassium chloride a non-fibrous potassium titanate of the general formula $K_2O\cdot(TiO_2)_{2m}$ wherein m is an integer of 2 to 3, maintaining at least a portion of said molten potassium chloride saturated with dissolved non-fibrous potassium titanate of said general formula as fibrous potassium titanate is formed therein, and separating the fibrous and water-insoluble potassium titanate from said potassium chloride.

20. Process for preparation of fibrous and water insoluble sodium titanate which comprises heating sodium chloride to a molten state at a temperature not higher than 1200° C., dissolving in said molten sodium chloride a non-fibrous sodium titanate of the general formula $Na_2O\cdot(TiO_2)_{2m}$ wherein m is an integer of 2 to 3, maintaining at least a portion of said molten sodium chloride saturated with dissolved non-fibrous sodium titanate of said general formula as fibrous sodium titanate is formed therein, and separating the fibrous and water-insoluble sodium titanate from said sodium chloride.

21. Process for preparation of fibrous and water-insoluble alkali metal titanates as set forth in claim 17

wherein said non-fibrous alkali metal titanate is formed in situ in said molten alkali metal chloride by introducing therein an alkali metal compound that gives a basic reaction with water and in which the alkali metal has an atomic number of at least 11 and a titanium compound selected from the class consisting of titanium dioxide and titanium salts which give rise to titanium dioxide under the reaction conditions, in a molar ratio of 1:1 to 1:12 calculated as alkali metal oxide to titanium dioxide.

22. Process for preparation of fibrous and water-insoluble potassium titanate which comprises heating potassium chloride to a molten state at a temperature not higher than 1200° C., introducing potassium hydroxide and titanium dioxide into said molten potassium chloride in a molar ratio of 1:2 to 1:8 calculated as potassium oxide to titanium dioxide thereby forming potassium titanate in solution in said molten potassium chloride, maintaining at least a portion of said molten potassium chloride saturated with dissolved potassium titanate as fibrous potassium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble potassium titanate from said potassium chloride.

23. Process for preparation of fibrous and water-insoluble potassium titanate which comprises heating potassium chloride to a molten state at a temperature not higher than 1200° C., introducing potassium carbonate and titanium dioxide into said molten potassium chloride in a molar ratio of 1:2 to 1:8 calculated as potassium oxide to titanium dioxide thereby forming potassium titanate in solution in said molten potassium chloride, maintaining at least a portion of said molten potassium chloride saturated with dissolved potassium titanate as fibrous potassium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble potassium titanate from said potassium chloride.

24. Process for preparation of fibrous and water-insoluble sodium titanate which comprises heating sodium chloride to a molten state at a temperature not higher than 1200° C., introducing sodium hydroxide and titanium dioxide into said molten sodium chloride in a molar ratio of 1:2 to 1:8 calculated as sodium oxide to titanium dioxide thereby forming sodium titanate in solution in said molten sodium chloride, maintaining at least a portion of said molten sodium chloride saturated with dissolved sodium titanate as fibrous sodium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble sodium titanate from said sodium chloride.

25. Process for preparation of fibrous and water-insoluble sodium titanate which comprises heating sodium chloride to a molten state at a temperature not higher than 1200° C., introducing sodium carbonate and titanium dioxide into said molten sodium chloride in a molar ratio of 1:2 to 1:8 calculated as sodium oxide to titanium dioxide thereby forming sodium titanate in solution in said molten sodium chloride, maintaining at least a portion of said molten sodium chloride saturated with dissolved sodium titanate as fibrous sodium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble sodium titanate from said sodium chloride.

26. Process for preparation of fibrous and water-insoluble alkali metal titanates which comprises heating an alkali metal chloride containing up to 65% by weight of the corresponding alkali metal fluoride to a molten state at a temperature not higher than 1200° C., dissolving in said molten alkali metal chloride a non-fibrous alkali metal titanate of the general formula $M_2O \cdot (TiO_2)_{2m}$ wherein m is an integer of 2 to 3 and M is an alkali metal having an atomic number of at least 11, the alkali metal in said alkali metal chloride and fluoride being the same as in said alkali metal titanate, maintaining at least a portion of said molten alkali metal chloride saturated with dissolved non-fibrous alkali metal titanate of said general formula as fibrous alkali metal titanate is formed therein, and separating the fibrous and water-insoluble alkali metal titanate from said alkali metal chloride and fluoride.

27. Process for preparation of fibrous and water-insoluble potassium titanate which comprises heating potassium chloride containing up to 65% by weight of potassium fluoride to a molten state at a temperature not higher than 1200° C., dissolving in said molten potassium chloride a non-fibrous potassium titanate of the general formula $K_2O \cdot (TiO_2)_{2m}$, wherein m is an integer of 2 to 3, maintaining at least a portion of said molten potassium chloride saturated with dissolved non-fibrous potassium titanate of said general formula as fibrous potassium titanate is formed therein, and separating the fibrous and water-insoluble potassium titanate from said potassium chloride and fluoride.

28. Process for preparation of fibrous and water-insoluble sodium titanate which comprises heating sodium chloride containing up to 65% by weight of sodium fluoride to a molten state at a temperature not higher than 1200° C., dissolving in said molten sodium chloride a non-fibrous sodium titanate of the general formula $Na_2O \cdot (TiO_2)_{2m}$, wherein m is an integer of 2 to 3, maintaining at least a portion of said molten sodium chloride saturated with dissolved non-fibrous sodium titanate of said general formula as fibrous sodium titanate is formed therein, and separating the fibrous and water-insoluble sodium titanate from said sodium chloride and fluoride.

29. Process for preparation of fibrous and water-insoluble alkali metal titanates which comprises heating an alkali metal chloride to a molten state, dissolving in said molten alkali metal choride a nonfibrous alkali metal titanate of the general formula $M_2O \cdot (TiO_2)_{2m}$, wherein m is an integer of 2 to 3 and M is an alkali metal having an atomic number of at least 11, the alkali metal in said alkali metal chloride being the same as in said alkali metal titanate, maintaining the hottest portion of said molten alkali metal chloride at a temperature not higher than 1200° C., and a cooler portion thereof at a temperature at least 5° C. below said hottest portion, maintaining the molten alkali metal chloride in said cooler portion saturated with dissolved non-fibrous alkali metal titanate of said general formula as fibrous alkali metal titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble alkali metal titanate from said alkali metal chloride.

30. Process for preparation of fibrous and water insoluble potassium titanate which comprises heating potassium chloride to a molten state, dissolving in said molten potassium chloride a non-fibrous potassium titanate of the general formula $K_2O \cdot (TiO_2)_{2m}$, wherein m is 3, maintaining the hottest portion of said molten potassium chloride at a temperature not higher than 1200° C. and a cooler portion thereof at a temperature at least 5° C. below said hottest portion, maintaining the molten potassium chloride in said cooler portion saturated with dissolved non-fibrous potassium titanate of said general formula as fibrous potassium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble potassium titanate from said potassium chloride.

31. Process for preparation of fibrous and water-insoluble sodium titanate which comprises heating sodium chloride to a molten state, dissolving in said molten sodium chloride a non-fibrous sodium titanate of the general formula $Na_2O \cdot (TiO_2)_{2m}$ wherein m is 3, maintaining the hottest portion of said molten sodium chloride at a temperature not higher than 1200° C., and a cooler portion thereof at a temperature at least 5° C. below said hottest portion, maintaining the molten sodium chloride in said cooler portion saturated with dissolved non-fibrous sodium titanate of said general formula as fibrous sodium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble sodium titanate from said sodium chloride.

32. Process for preparation of fibrous and water-

insoluble alkali metal titanates which comprises heating an alkali metal chloride containing up to 65% by weight of the corresponding alkali metal fluoride to a molten state, dissolving in said molten alkali metal chloride a non-fibrous alkali metal titanate of the general formula $M_2O \cdot (TiO_2)_{2m}$, wherein m is an integer of 2 to 3 and M is an alkali metal having an atomic number of at least 11, the alkali metal in said alkali metal chloride and fluoride being the same as in said alkali metal titanate, maintaining the hottest portion of said molten alkali metal chloride at a temperature not higher than 1200° C., and a cooler portion thereof at a temperature at least 5° C. below said hottest portion, maintaining the molten alkali metal chloride in said cooler portion saturated with dissolved non-fibrous alkali metal titanate of said general formula as fibrous alkali metal titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble alkali metal titanate from said alkali metal chloride and fluoride.

33. Process for preparation of fibrous and water-insoluble potassium titanate which comprises heating potassium chloride containing up to 65% by weight of potassium fluoride to a molten state, dissolving in said molten potassium chloride a non-fibrous potassium titanate of the general formula $K_2O \cdot (TiO_2)_{2m}$, wherein m is an integer of 2 to 3, maintaining the hottest portion of said molten potassium chloride at a temperature not higher than 1200° C. and a cooler portion thereof at a temperature at least 5° C. below said hottest portion, maintaining the molten potassium chloride in said cooler portion saturated with dissolved non-fibrous potassium titanate of said general formula as fibrous potassium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble potassium titanate from said potassium chloride and fluoride.

34. Process for preparation of fibrous and water-insoluble sodium titanate which comprises heating sodium chloride containing up to 65% by weight of sodium fluoride to a molten state, dissolving in said molten sodium chloride a non-fibrous sodium titanate of the general formula $Na_2O \cdot (TiO_2)_{2m}$, wherein m is an integer of 2 to 3, maintaining the hottest portion of said molten sodium chloride at a temperature not higher than 1200° C. and a cooler portion thereof at a temperature at least 5° C. below said hottest portion, maintaining said molten sodium chloride in said cooler portion saturated with dissolved non-fibrous sodium titanate of said general formula as fibrous sodium titanate is crystallized therefrom, and separating the crystallized fibrous and water-insoluble sodium titanate from said sodium chloride and fluoride.

35. Process for preparation of fibrous and water-insoluble potassium tetratitanate which comprises heating potassium chloride containing 20 to 65% by weight of potassium fluoride to a molten state at a temperature not higher than 1200° C., dissolving in said molten potassium chloride a non-fibrous potassium titanate of the general formula $K_2O \cdot (TiO_2)_{2m}$ wherein m is 2, maintaining at least a portion of said molten potassium chloride saturated with dissolved non-fibrous potassium titanate of said general formula as fibrous potassium tetratitanate is formed therein, and separating the fibrous and water-insoluble potassium tetratitanate from said potassium chloride and fluoride.

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