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AN INORGANIC FIBROUS MATERIAL CONSISTING OF THE ASBESTOS-LIKE FORM OF AN ALKALI METAL TITANATE AND ITS PREPARATION

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This invention relates to new fibrous alkali metal titanates and to a method for their preparation. More particularly, this invention relates to new asbestos-like fibrous alkali metal titanates which are water-insoluble and to their preparation.

Titanium is known to form salts with alkali, alkaline earth and base metals. For example, alkali-metal hydroxides have been reacted with hydrous titanium dioxide at the atmospheric boiling point to produce a hydrated titanate such as $K_2TiO_3 \cdot 4H_2O$. Fusion of an alkali metal carbonate or hydroxide, e. g., potassium carbonate or potassium hydroxide, with titanium dioxide has been described as producing other titanates, such as $K_2Ti_2O_5$ and $K_2Ti_5O_{11}$. These prior art alkali metal titanates are soluble in water or either soluble or decomposed by aqueous acids or bases. However, there has been no report in the literature of an asbestos-like or fibrous alkali metal titanate which is water-insoluble.

It is an object of this invention to provide fibrous alkali metal titanates and a method for their preparation. A further object is to provide fibrous alkali metal titanates which are water-insoluble. Another object is to provide fibrous alkali metal titanates in the form of asbestos-like fibers. Other objects will appear hereinafter.

These and other objects of this invention are accomplished by providing new fibrous alkali metal titanates which are water-insoluble and wherein the alkali metal has an atomic number of at least eleven. The alkali metal titanates of this invention have a fibrous structure in which one dimension of the crystal is longer than the other dimensions by a factor of at least five and generally ten to one hundred and up to 1000 or more, i. e., the ratio of length to width of the crystal is at least 5:1 and generally 10:1 to 100:1 and up to 1000:1 or more. This fibrous product is purified and separated from any other alkali metal or titanium compounds by treatment with water or aqueous mineral acid in which the alkali metal titanates of this invention are insoluble. Their insolubility and lack of reactivity with aqueous acids and alkali also differentiates the new asbestos-like compositions of this invention from the materials described in the titanium prior art. Furthermore, the alkali metal titanates of this invention do not hydrate, i. e., do not absorb water of crystallization and thus do not contain water of crystallization.

It has now been found that fibrous as well as water-insoluble and non-hydrated alkali metal titanates can be prepared by reacting in the presence of water, a water-soluble basic oxygen-containing alkali metal compound, such as an alkali metal hydroxide, wherein the alkali metal has an atomic number of at least eleven, with an oxygen-containing titanium compound, such as titanium dioxide, in a molar ratio of 1:6 to 12:1, calculated as alkali metal oxide to titanium dioxide, at a temperature of at least 400° C. under pressure of at least

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200 atmospheres. After reaction, the mixture is then subjected to extraction, preferably with water or dilute mineral acid, until unreacted alkali, i. e., essentially no more alkali, is extracted therefrom.

The process whereby the new alkali metal titanates are formed involves the reaction in the presence of water of a titanium compound, preferably a titanium oxide or hydrated oxide, with an alkali metal oxide or a suitable basic alkali metal compound, such as the carbonate or hydroxide, at a temperature of at least 400° C. and pressure of at least 200 atmospheres. In this reaction, pressure-resistant vessels inert to the reagents present are used. The ratio of charge of alkali metal oxide, e. g., potassium oxide, to titanium oxide, can vary from 1:6 to 12:1, with the preferred ratio being from 3:1 to 8:1. The titanium compound employed is generally present in finely divided or uniformly dispersed form. The alkali metal compound is generally present in solution or suspended in water. The reaction is generally effected at temperatures of 400 to 800° C. or even higher, with temperatures of 600 to 700° C. preferred. The reaction is generally finished in times of a few hours or less. The new fibrous alkali metal titanates of this invention are readily separated from undesired products, such as unused starting materials, by virtue of their insolubility and lack of reactivity to water, dilute and concentrated mineral acids, including hydrochloric and sulfuric acid, bases such as potassium hydroxide, and aqueous salt solutions.

In the following examples, parts are by weight, and all of the reactions are conducted in sealed, collapsible platinum vessels which are subjected to the prescribed physical conditions in apparatus capable of operating under such conditions. These examples are for purposes of illustration of preferred procedures for the preparation of the novel fibrous alkali metal titanates of this invention.

Example I

A mixture of 0.1329 part titanium dioxide (anatase), 0.0665 part sodium hydroxide ($Na_2O/TiO_2=1/2$) and 0.1665 part water was heated to 625° C. at a pressure of about 2800 atmospheres. These conditions were attained in about 25 minutes at which time the heating was discontinued and the mixture allowed to return to atmospheric conditions. The entire solid product comprised fibers about 25 microns long and having a length to diameter ratio of about 100/1. The fibrous product was insoluble in aqueous solutions.

Example II

A mixture of 0.2304 part titanium dioxide (anatase) and 0.133 part 10 N sodium hydroxide aqueous solution ($Na_2O/TiO_2=1/6$) was heated 1.5 hours at 625° C. and 3000 atm. pressure. Upon returning the product to atmospheric conditions it was found to contain fibrous sodium titanate, of which at least 5% was in the form of long fibers whose properties were the same as those of the product of Example I.

Example III

A mixture of 0.0250 part titanium dioxide (rutile) and 1.05 part 10 N potassium hydroxide aqueous solution ($K_2O/TiO_2=12/1$) was heated 1.5 hours at 625° C. and 3000 atm. pressure. Upon returning the mixture to atmospheric conditions, it was found that about 85% of the potassium titanate product was in the form of long fibers which were insoluble in aqueous solutions.

Example IV

A mixture of 0.16 part titanyl sulfate and 0.35 part 10 N potassium hydroxide aqueous solution ($K_2O/TiOSO_4=1/1$)

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was heated 1 hour at 625° C. and 3000 atm. pressure. Upon cooling to room temperature, the entire solid product comprised a fluffy, light gray water-insoluble asbestos-like material. Individual fibers were about .15 microns long. The ratio of length to maximum cross sectional dimension was about 170:1.

Example V

A mixture of 0.2 part dipotassium ditanate, $K_2Ti_2O_5$, and 0.5 part water was heated 2 hours at 625° C. and 3000 atm. pressure and cooled slowly. After reaction, the aqueous medium was strongly alkaline and the solid product which was removed comprised water-insoluble fibers about 10 microns long and about 1 micron in diameter. The X-ray diffraction powder pattern of this product was the same as that given by the product of Example III.

Example VI

A mixture of 0.500 part titanium dioxide (anatase), 2.6 parts potassium carbonate ($K_2O/TiO_2=3/1$) and 4 parts water was heated 2 hours at 625° C. and 3000 atmospheres pressure. After returning to atmospheric conditions, the entire product comprising fibrous potassium titanate suspended in an aqueous alkaline medium was titrated potentiometrically with a standard solution of hydrochloric acid. It was found that 0.104 part of the alkali (as K_2O) was not available for neutralization by the acid and was therefore combined with the 0.5 part titania. This corresponds to a ratio of $K_2O/TiO_2=1/5.7$ in the product. The suspension was filtered and the solid product washed and dried to obtain 0.045 part long fibers ranging up to 1 cm. in length and about 1 micron in diameter and 0.547 part of matted short fibers less than 1 mm. in length, i. e., these flexible fibers were felted into a mat. The total weight of product from 0.5 part titania was therefore 0.592 part. On the assumption that all of the weight increase is K_2O , the K_2O/TiO_2 ratio is 1/6.4 in the product. Analysis of the fibrous potassium titanate revealed 50.3% titanium and 12.6% potassium indicating a K_2O/TiO_2 ratio of 1/6.8.

Similar preparations of potassium titanate from potassium carbonate and anatase were conducted in which the ratio of the reactants was varied. The results were as follows:

In Reactants	K ₂ O/TiO ₂ Ratio in Product Based on—		
	Non-titratable Alkali	Weight of Product	K and Ti Analyses
1/1	1/5.8	1/6.6	1/6.9
2/1	1/6.0	1/6.4	1/7.4

The products were asbestos-like water-insoluble fibers.

Example VII

A mixture of 0.1 part titanium dioxide (anatase), 0.432 part potassium pyrophosphate, $K_4P_2O_7$ ($K_2O/TiO_2=3/1$) and 0.4 part water was heated 0.5 hour at 625° C. and 3000 atm. pressure. After the reaction mixture was returned to atmospheric conditions, it was found to contain short potassium titanate water-insoluble fibers having an approximate length of 10 microns and a diameter of 1 micron.

Example VIII

A mixture of 0.1 part titanium dioxide (anatase), 0.866 part rubidium carbonate ($Rb_2O/TiO_2=3/1$) and 0.9 part water was heated 3 hours at 625° C. and 3000 atm. pressure. The product comprised in preponderant amount flexible water-insoluble fibers having diameters ranging to less than 1 micron and lengths ranging to over 1000 microns.

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Example IX

A mixture of 0.1 part titanium dioxide (anatase), 1.222 part cesium carbonate ($Cs_2O/TiO_2=3/1$) and 0.9 part water was heated 3 hours at 625° C. and 3000 atm. pressure. The product comprised, in major amounts, water-insoluble fibers of up to about 200 microns long and about 1 micron in diameter.

Example X

A mixture of 0.1336 part titania (titanium dioxide) and 1.40 part 10 N aqueous potassium hydroxide solution ($K_2O/TiO_2=3/1$) was heated 1.5 hours at 450° C. and 1000 atm. pressure. The product comprised grayish white, long water-insoluble fibers of potassium titanate.

The new products of this invention are asbestos-like fibrous, non-hydrated, alkali metal titanates which are water-insoluble and wherein the alkali metal has an atomic number of at least eleven. Chemical analysis of the fibrous alkali metal titanates of this invention indicates that they correspond in chemical composition to the general formula $M_2O \cdot (TiO_2)_n$ wherein M is an alkali metal of atomic number of at least eleven and n has a value, generally of about 6 to less than 8, and approximately 6 to 7. Determination of the non-titratable alkali in the products resulting from the process of this invention indicates that n has a value of about 6 in the fibrous alkali metal titanates corresponding in chemical composition to the formula $M_2O \cdot (TiO_2)_n$ wherein M is an alkali metal of atomic number of at least eleven. Thus, by determination of non-titratable alkali, the fibrous alkali metal titanates are indicated to have the general formula $M_2Ti_6O_{13}$, wherein M is an alkali metal having atomic number of at least eleven such as potassium, sodium, rubidium and cesium. Of the alkali metals, sodium and potassium are cheaper and more readily available than the other alkali metals and therefore most preferred.

These new products are characterized by their insolubility and lack of reactivity with water and aqueous solutions of mineral acids, bases or salts. They do not form hydrates, i. e., absorb water of crystallization. The titanates of alkali metals of atomic number of 11 or greater, i. e., sodium, potassium, rubidium and cesium, are obtained in the form of fibers, i. e., asbestos-like, and have a length to diameter ratio of at least 5:1 and usually of at least 10:1. As shown in the examples, the length is generally 10 to 1000 times the diameter of the fiber. As shown by Example VIII, there are obtained by the process of this invention alkali metal titanates in the form of water-insoluble flexible fibers having a ratio of length to diameter ranging to over 1000:1.

In the preparation of the new alkali metal titanates, an alkali metal compound such as the carbonate or hydroxide is generally employed although other water-soluble compounds can be used, e. g., an alkali metal phosphate. The alkali metal compound is preferably basic or gives a basic reaction with water. Particularly useful are the alkali metal hydroxides and carbonates, i. e., basic oxygen-containing alkali metal compounds which are soluble in water or which form the alkali metal hydroxide in aqueous solution.

The titanium source can be a titanium oxide, or salt. Particularly suitable in view of its availability is titanium dioxide. However, soluble titanium compounds such as titanyl sulfate or the lower titanates can be employed.

The ratio of alkali metal to titanium calculated as alkali metal oxide to titanium dioxide in the charge can vary from 1:6 to 12:1 with a ratio of generally at least 1:1 and preferably between 3:1 and 8:1. It is to be noted this ratio is considerably broader than the ratio of titanium dioxide to alkali metal oxide in the new compounds of this invention.

The unreacted starting materials or undesired products of reaction are removed by extraction or chemical reaction with aqueous acids or bases. The new products of this invention are insoluble in water and in aqueous acids

or bases. Advantage is taken of this property in the purification of the new titanates since alkali metal hydroxides, carbonates or other salts are water soluble. In view of the ease of removal of other alkali metal compounds than those combined with titanium in the manner required for the new products of this invention, the alkali metal starting compound can be, and usually is, employed in slight excess over the theoretical value. When titanium dioxide is present in the final product, it is generally removed by taking advantage of its greater density and higher sedimentation rate.

The reaction between the titanium and alkali metal compounds is effected at temperatures of at least 400° C. and generally less than 800° C. with the temperature preferably at 600 to 700° C. The reaction requires the presence of water. To retain water in the reaction media under these conditions necessitates the use of pressures of at least 200 atmospheres, and generally 500 atmospheres or more, as well as equipment that will withstand the conditions and reagents employed. The upper pressure limit is dependent only on the equipment employed. Although pressures of 10,000 atmospheres can be used, such pressures require strong and expensive equipment. Pressures of the order of 1000 to 4000 atmospheres are relatively easy to maintain and these pressures are preferred. The reaction time is generally short, e. g., a few minutes to a few hours.

The new asbestos-like fibrous alkali metal titanates of this invention are inert to many corrosive chemical reagents. For example, these titanates are insoluble in boiling 50% caustic, insoluble in aqueous acids such as sulfuric acid and concentrated hydrochloric acid, and unattacked by chlorine.

The fibrous alkali metal titanates are particularly useful in applications where the inertness and physical properties of an asbestos-type material are required, e. g., in reinforcing agents, in fibers or papers and as insulation material.

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.

We claim:

1. A method for preparing an asbestos-like fibrous, water-insoluble alkali metal titanate which comprise reacting in the presence of water, a water-soluble basic oxygen-containing alkali metal compound, wherein the alkali metal has an atomic number of at least eleven, with an oxygen-containing titanium compound in a molar ratio of 1:6 to 12:1, calculated as alkali metal oxide to titanium dioxide, at a temperature of at least 400° C. under a pressure of at least 200 atmospheres, and separating as the resulting product an alkali metal titanate in the form of water-insoluble, non-hydratable, flexible fibers.

2. A method for preparing an asbestos-like fibrous, water-insoluble alkali metal titanate which comprises reacting in the presence of water, an alkali metal hydroxide, wherein the alkali metal has an atomic number of at least eleven, with titanium dioxide in a molar ratio of 1:1 to 8:1, calculated as alkali metal oxide to titanium dioxide, at a temperature of 400° C. to 800° C. under a pressure of 500 to 4000 atmospheres, and separating as the resulting product an alkali metal titanate in the form of water-insoluble, non-hydratable, flexible fibers.

3. A method for preparing an asbestos-like fibrous, water-insoluble alkali metal titanate as set forth in claim 1, wherein said alkali metal compound is an alkali metal hydroxide in which the alkali metal has an atomic number of at least 11.

4. A method for preparing an asbestos-like fibrous, water-insoluble alkali metal titanate as set forth in claim 1, wherein said alkali metal compound is an alkali metal

carbonate in which the alkali metal has an atomic number of at least 11.

5. A method for preparing an asbestos-like, fibrous, water-insoluble alkali metal titanate as set forth in claim 1 wherein said titanium compound is titanium dioxide.

6. A method for preparing an asbestos-like fibrous, water-insoluble alkali metal titanate which comprises reacting in the presence of water, an alkali metal hydroxide wherein the alkali metal has an atomic number of at least 11, with titanium dioxide in a molar ratio of 1:6 to 12:1, calculated as alkali metal oxide to titanium dioxide, at a temperature of 400 to 800° C. under a pressure of 500 to 4000 atmospheres, and separating as the resulting product an alkali metal titanate in the form of water-insoluble, non-hydratable, flexible fibers.

7. A method for preparing an asbestos-like fibrous, water-insoluble sodium titanate which comprises reacting in the presence of water, sodium hydroxide with titanium dioxide in a molar ratio of 1:6 to 12:1, calculated as sodium oxide to titanium dioxide, at a temperature of 600 to 700° C., under a pressure of 1000 to 4000 atmospheres, and separating as the resulting product sodium titanate in the form of water-insoluble, non-hydratable, flexible fibers.

8. A method for preparing an asbestos-like fibrous, water-insoluble potassium titanate which comprises reacting in the presence of water, potassium hydroxide with titanium dioxide in a molar ratio of 1:6 to 12:1, calculated as potassium oxide to titanium dioxide, at a temperature of 600 to 700° C., under a pressure of 1000 to 4000 atmospheres, and separating as the resulting product potassium titanate in the form of water-insoluble, non-hydratable, flexible fibers.

9. A method for preparing an asbestos-like fibrous, water-insoluble alkali metal titanate which comprises reacting in the presence of water, an alkali metal carbonate wherein the alkali metal has an atomic number of at least 11, with titanium dioxide in a molar ratio of 1:6 to 12:1, calculated as alkali metal oxide to titanium dioxide, at a temperature of 400 to 800° C. under a pressure of 500 to 4000 atmospheres, and separating as the resulting product an alkali metal titanate in the form of water-insoluble, non-hydratable, flexible fibers.

10. A method for preparing an asbestos-like fibrous, water-insoluble sodium titanate which comprises reacting in the presence of water, sodium carbonate with titanium dioxide in a molar ratio of 1:6 to 12:1, calculated as sodium oxide to titanium dioxide, at a temperature of 600 to 700° C., under a pressure of 1000 to 4000 atmospheres, and separating as the resulting product sodium titanate in the form of water-insoluble, non-hydratable, flexible fibers.

11. A method for preparing an asbestos-like fibrous, water-insoluble potassium titanate which comprises reacting in the presence of water, potassium carbonate with titanium dioxide in a molar ratio of 1:6 to 12:1, calculated as potassium oxide to titanium dioxide, at a temperature of 600 to 700° C., under a pressure of 1000 to 4000 atmospheres, and separating as the resulting product potassium titanate in the form of water-insoluble, non-hydratable, flexible fibers.

12. As a new inorganic fibrous material, alkali metal titanate crystalline fibers each having a ratio of length to width of at least 10:1, and each being sufficiently flexible to be felted, said fibers being insoluble in water, not absorbing water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is an alkali metal having an atomic number of at least 11 and n has a value of from 6 to 7.

13. As a new inorganic fibrous material, sodium titanate crystalline fibers each having a ratio of length to width of at least 10:1, and each being sufficiently flexible to be felted, said fibers being insoluble in water, not absorbing water of crystallization to form a hydrate,

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and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is sodium and n has a value of from 6 to 7.

14. As a new inorganic fibrous material, potassium titanate crystalline fibers each having a ratio of length to width as at least 10:1, and each being sufficiently flexible to be felted, said fibers being insoluble in water, not absorbing water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is potassium and n has a value of from 6 to 7.

15. As a new inorganic fibrous material, rubidium titanate crystalline fibers each having a ratio of length to width of at least 10:1, and each being sufficiently flexible to be felted, said fibers being insoluble in water, not absorbing water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is rubidium and n has a value of from 6 to 7.

16. As a new inorganic fibrous material, cesium titanate crystalline fibers each having a ratio of length to width of at least 10:1, and each being sufficiently flexible to be felted, said fibers being insoluble in water, not absorbing water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is cesium and n has a value of from 6 to 7.

17. An inorganic flexible fiber having a ratio of length to width of at least 10:1 consisting of an alkali metal titanate fiber which is sufficiently flexible to be felted and which is insoluble in water, does not absorb water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is an alkali metal having an atomic number of at least 11 and n has a value of from 6 to 7.

18. An inorganic flexible fiber having a ratio of length to width of at least 10:1 consisting of a sodium titanate fiber which is sufficiently flexible to be felted and which is insoluble in water, does not absorb water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is sodium and n has a value of from 6 to 7.

19. An inorganic flexible fiber having a ratio of length to width of at least 10:1 consisting of a potassium titanate fiber which is sufficiently flexible to be felted and which is insoluble in water, does not absorb water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is potassium and n has a value of from 6 to 7.

20. An inorganic flexible fiber having a ratio of length to width of at least 10:1 consisting of a rubidium titanate fiber which is sufficiently flexible to be felted and which is insoluble in water, does not absorb water of crystallization to form a hydrate and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is rubidium and n has a value of from 6 to 7.

21. An inorganic flexible fiber having a ratio of length to width of at least 10:1 consisting of a cesium titanate fiber which is sufficiently flexible to be felted and which is insoluble in water, does not absorb water of crystallization to form a hydrate, and having the general formula $M_2O \cdot (TiO_2)_n$, wherein M is cesium and n has a value of from 6 to 7.

22. A new inorganic fibrous material comprising

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alkali metal titanate crystalline fibers each having a ratio of length to width of at least 10:1, and each being sufficiently flexible to be felted, said fibers being insoluble in water, not absorbing water of crystallization to form a hydrate, and having the general formula $M_2Ti_6O_{13}$, wherein M is an alkali metal having an atomic number of at least 11.

23. A new inorganic fibrous material comprising potassium titanate crystalline fibers each having a ratio of length to width of at least 10:1, and each being sufficiently flexible to be felted, said fibers being insoluble in water, not absorbing water of crystallization to form a hydrate, and having the general formula $M_2Ti_6O_{13}$, wherein M is potassium.

24. Inorganic flexible fibers, each having a ratio of length to width of at least 10:1 and consisting of an alkali metal titanate fiber which is sufficiently flexible to be felted and which is insoluble in water, does not absorb water of crystallization to form a hydrate, and having the general formula $M_2Ti_6O_{13}$, wherein M is an alkali metal having an atomic number of at least 11.

25. Inorganic flexible fibers, each having a ratio of length to width of at least 10:1 and consisting of an alkali metal titanate fiber which is sufficiently flexible to be felted and which is insoluble in water, does not absorb water of crystallization to form a hydrate, and having the general formula $M_2Ti_6O_{13}$, wherein M is potassium.

26. An insulating composition comprising a mass of metal titanate crystalline fibers which are sufficiently flexible to be felted and which are insoluble in water, do not absorb water of crystallization to form a hydrate, and have the general formula $M_2Ti_6O_{13}$, wherein M is an alkali metal having an atomic number of at least 11.

27. An insulating composition comprising a mass of potassium titanate crystalline fibers which are sufficiently flexible to be felted and which are insoluble in water, do not absorb water of crystallization to form a hydrate and have the general formula $M_2Ti_6O_{13}$, wherein M is potassium.

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