

[54] **COMPOSITE FIBERS OF ALKALI METAL
HEXATITANATE AND RUTILE TiO_2**

3,703,357 11/1972 Surls et al. 106/300

[75] Inventor: **Robert Steele Emslie, deceased**, late
of Chadds Ford, Pa. by Jean
McPhaul Emslie, administratrix

Primary Examiner—Curtis R. Davis
Attorney—Donald A. Hoes

[73] Assignee: **E. I. DuPont de Nemours and
Company, Wilmington, Del.**

[22] Filed: **Apr. 6, 1972**

[21] Appl. No.: **241,681**

[52] U.S. Cl. **106/300, 106/308 B**

[51] Int. Cl. **C09c 1/36**

[58] Field of Search **106/300, 308 B**

[56] **References Cited**

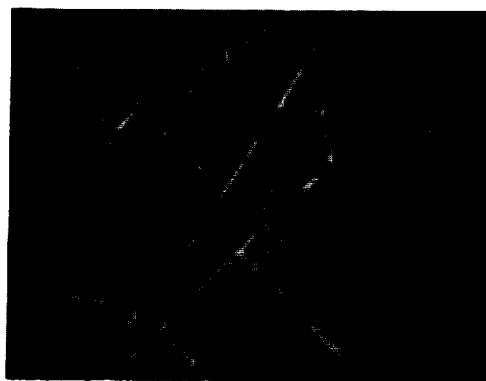
UNITED STATES PATENTS

3,338,677 8/1967 Berry 106/300

[57] ABSTRACT

A fibrous material is provided which is composed of composite fibers having a number average diameter of up to about 10 microns and an average length/diameter ratio of at least about 5/1. The fibers have a core of alkali metal hexatitanate encapsulated by a shell of rutile TiO_2 and are essentially inert to aqueous 5% by weight HF solution. The fibrous material is particularly useful in the reinforcing of plastics.

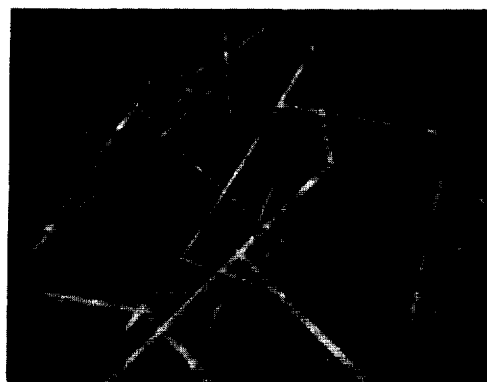
1 Claim, 1 Drawing Figure



15 MICRONS

PATENTED DEC 18 1973

3,779,784



15 MICRONS

COMPOSITE FIBERS OF ALKALI METAL HEXATITANATE AND RUTILE TiO₂

BACKGROUND OF THE INVENTION

Water-insoluble, fibrous alkali metal titanates having the formula $M_2O(TiO_2)_n$ where M is an alkali metal of atomic number of at least 11, and n is a number of from 4 to 8 and their preparations are disclosed in U.S. Pat. Nos. 2,833,620, Gier et al.; 2,841,470, Berry; 3,328,117, Emslie et al.; and 3,331,658, Lewis et al.

The preparation of fibrous titanium dioxide is described in U.S. Pat. Nos. 3,012,857, Pease; 3,065,091, Russell; 3,241,928, Pease; and 3,244,481, Berry.

Also mixtures of pigmentary titanium dioxide and fibrous alkali metal titanates are disclosed in U.S. Pat. No. 3,484,260, Emslie et al.

These fibrous materials are useful as reinforcing components for plastics, ceramics and cermets. Other uses include insulation materials and additives during paper manufacture.

It is known that fibrous titanates will tend to deteriorate in certain acid atmospheres and that improvements in this and other properties would be desirable.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a fibrous material composed of composite fibers having a number average diameter of up to about 10 microns and an average length/diameter ratio of at least about 5/1, said fibers having a core composition corresponding to the formula



wherein M is an alkali metal of atomic number of at least 11, said core being encapsulated by a shell of rutile TiO_2 thereby rendering the fibers essentially inert to aqueous 5 % by weight HF solution.

The individual composite fibers possess the combined strength of the alkali metal hexatitanate and rutile components. In addition they tend to be less expensive to prepare, more dense, and more stable to acid and elevated temperatures than are the alkali metal titanates. It is known, for example, that when ordinary potassium titanate fibers are heated to a temperature over 900° C., they start to lose potassium oxide and some strength. The rutile titanium dioxide shell of the composite fibers of the present invention minimizes the loss of alkali at high temperatures. Since the outer shell of these composite fibers is rutile titanium dioxide, the fibers are characterized by the higher refractive index of titanium dioxide, i.e. the refractive index of rutile TiO_2 is about 2.71 compared to the refractive index of potassium titanate which is about 2.35. This higher refractive index of the composite fibers is important when the fibers are to be used in a system where high opacity is a desired characteristic.

The presence of the alkali metal hexatitanate and rutile TiO_2 components in the composite fibers can be readily confirmed by X-ray analysis techniques as both components are characterized by distinct X-ray diffraction patterns. The existence of the core/shell composite structure is readily confirmed by treating the fibers with a 5% by weight HF solution. A true composite is virtually unaffected by the treatment since rutile TiO_2 is essentially inert to the action of 5% or even 10% HF solution. If the fibers were a homogeneous mixture of alkali metal hexatitanate and rutile TiO_2 or if the alkali

metal hexatitanate was otherwise in the shell portion, considerable dissolution and weight loss would occur.

The actual percentage of rutile TiO_2 as a shell about the core of alkali metal hexatitanate is not critical provided that the amount be such as to ensure inertness to the action of 5% by weight HF solution. Normally the alkali metal titanate should constitute at least 10% and, preferably at least 50%, by weight of the composite fibers.

The fact that the TiO_2 shell about the alkali metal hexatitanate core is in the rutile crystalline phase serves to distinguish the products of the invention from prior art products in which alkali metal titanate fibers may have been leached with acid to remove a portion of the alkali metal oxide from the surface; i.e. such leaching would not result in a distinct TiO_2 shell of the rutile crystalline phase.

Various processes can be used for preparing the composite fibers. One technique, to be described in Example I hereinafter, involves the preparation of alkali metal titanate fibers in the usual way. This may be accomplished, for example, by calcining a dry blended mixture of anatase TiO_2 , alkali metal carbonate and alkali metal halide followed by leaching of the calcined product to remove soluble salts. The resultant alkali metal titanate fibers can then be converted to composite fibers by calcining, for example, at 1,000° C., in the presence of a boron- or silicon-containing compound such as $Na_2B_4O_7$, $K_2B_4O_7$, B_2O_3 , Na_2SiO_3 , muscovite mica, or feldspar. The composite fibers form directly, apparently as a result of the reaction of the boron- or silicon-containing compound with the alkali metal oxide in the surface portion of the alkali metal titanate fibers.

Alternatively, alkali metal titanate fibers may be initially formed by the procedure described above but with the inclusion of one of the aforementioned boron- or silicon-containing compounds in the dry blended mix before calcining. This method is illustrated in Example II hereinafter.

Still a third method, and one which will be illustrated in Examples III through V hereinafter, involves direct formation of the composite fibers from a mixture of an alkali metal hydroxide, titanium oxychloride, and one of the silica- or boron-containing compounds described above. In this case, a salt-gel is formed of the various components, which is calcined at a temperature of 850° C. to 1,050° C. More particularly, the salt-gel is prepared by admixing concentrated aqueous alkali metal hydroxide solution, e.g. KOH or NaOH, and aqueous titanium oxychloride solution (e.g. as prepared from the reaction of $TiCl_4$ and ice), the mixing preferably being carried out by means of a high speed, high shear mixer. In the process, one solution is conveniently added to the other in relative amounts such that a pH of at least 9, preferably of 10-10.5, is reached, at which point a thick salt-gel is formed. The salt-gel is then cast in a suitable container and, preferably, dried. The resultant porous brick is subsequently calcined at a temperature in the range from 850° C. to 1,050° C. and then leached, e.g. with water or aqueous liquids, to produce the composite fibers.

Regardless of the method employed, simple leaching of the resultant fibers appears to remove essentially all residual compounds containing boron or silicon. Thus, borates tend to be converted to higher borates in the process and these are generally soluble in the water

used as a leaching agent. Where a silicon-containing compound has been employed, the use of an aqueous HF leaching solution may be necessary to remove undesired silicate by-products.

The amount of boron- or silicon-containing compound that need be so employed will vary depending upon which particular process is selected. Moreover, the amount will affect, at least to some extent, the thickness of the TiO_2 shell which is formed. Too little may result in an unduly thin TiO_2 shell, which in turn may fail to give the requisite inertness to a 5% HF solution. Large quantities of the boron- or silicon-containing compound will, conversely, tend to produce a relatively thick shell of TiO_2 . This is not particularly detrimental, however, except from the standpoint that the economics may be less favorable. In general, it is satisfactory to employ some 5 to 50% by weight of the boron- or silicon-containing compound based on the weight of the composite fiber which is formed.

Each of the processes results in a composite fiber in which the titanate is essentially in the hexa-crystalline form, apparently because that species is the most thermally stable species.

The utility of the composite fibers will depend, at least in part, upon their particle size. Smaller size particles, say of 0.1 to 0.6 micron in diameter, are useful for the pigmentation of paper, plastics, fibers and the like. Larger size particles, most commonly of 0.6 to 3 microns in diameter, but occasionally up to 10 microns in diameter, are useful in the reinforcement of plastics or as insulation materials. In general the composite fibers should have aspect ratios, i.e. L/D ratios of at least 5 to 1 but more preferably 15 to 1. Aspect ratios of 100-1,000 to 1 are not uncommon.

DESCRIPTION OF THE DRAWING

FIG. 1 is a photomicrograph at 4,200X of composite $\text{K}_2\text{Ti}_6\text{O}_{13}$ — rutile fibers prepared by the salt-gel method of Example IV with the incorporation of both potassium borate and paper pulp in the reaction mixture.

EXAMPLES

To illustrate the invention more completely, the following examples are given. These are for purposes of illustration only and are not to be construed as limitation of the invention.

EXAMPLE I

Pigmentary size fibers of potassium titanate are produced by the general procedure described in Emslie et al. U.S. Pat. No. 3,328,117 involving the calcination of potassium carbonate, anatase TiO_2 and KCl.

A 0.4 gr. portion of the potassium titanate fibers are wet mixed with 0.6 gr. of wet ground plate glass (silicate glass). The mixture is then dried and placed in a furnace. The temperature is raised to 900° C. over a period of about 2 hours and kept at that temperature for ½ hour. The product is removed from the furnace, and leached in 5% by weight HF with agitation for 3 days. After settling, decanting the clear liquor, filtering, washing with water and drying, the product is subjected to analysis.

X-ray analysis demonstrates that the product is composed of $\text{K}_2\text{Ti}_6\text{O}_{13}$ and rutile TiO_2 in a ratio estimated to be about 1/1. Microscopically the fibers are found to have an L/D ratio of about 100:1. They are in the pig-

mentary range, i.e. with a fiber diameter of about 0.1 to 0.6 microns. The core/shell structure is confirmed by the inertness to 5% by weight HF solution in water.

EXAMPLE II

A blend is prepared by micronizing together the following components:

300 grams	anatase TiO_2
100 grams	K_2CO_3
200 grams	KCl
75 grams	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

The mixed powder is then added to wet paper pulp (100 grams total weight — 20% paper pulp fibers) and rolled in a four liter vessel for 1 hour. Balls form that are about 1-2 cm. in diameter and are made up of the paper pulp-ingredient mixture. These balls are calcined for 2 hours at 1,000° C. The composite fibers are then recovered by leaching away the soluble salts with dilute sulfuric acid.

Microscopically the product is found to have an average length of about 10 microns, an average diameter of about 0.1 to 0.2 micron and a surface area of 7.3 M^2/g . The fibers are found to be composed of a predominately potassium hexatitanate core and an outer rutile TiO_2 shell.

EXAMPLE III

Fifty grams of KOH is added to 50 cc. distilled water to prepare a concentrated KOH solution which is then placed in a Waring Blendor along with 15 grams $\text{K}_2\text{B}_4\text{O}_7$. While agitation is maintained, a titanium oxychloride solution (considered to be represented by the formula $\text{TiOCl}_2 \cdot 2\text{HCl}$) is added until a pH of 10 is reached. The titanium oxychloride solution is prepared by mixing TiCl_4 and ice in a 3:7 weight ratio. The amount of titanium oxychloride solution so required is 150 grams.

The salt-gel thus prepared is cast into a glass vessel lined with polytetrafluoroethylene and dried for 4 hours at 200° C. A porous brick is formed which is then calcined for 90 minutes at 900° C.

The calcined brick is leached free of soluble salts by washing with hot distilled water. Fourteen grams of a fibrous product are thereby obtained. X-rays reveal that the product, which has a surface area of 9.5 M^2/gr ., contains both rutile and potassium hexatitanate. Examined microscopically, the composite fibers are found to have an average diameter of about 0.1 micron and an L/D ratio of about 200.

Five grams of the product is placed in 10% aqueous hydrogen fluoride solution in a polyethylene beaker. After 2 hours of stirring, the fibrous product is recovered, washed with distilled water, and dried. It is found to be essentially unchanged. This demonstrates that the rutile effectively encapsulates a potassium hexatitanate core since it is known that potassium titanate alone would be completely soluble in 10% hydrogen fluoride solution.

EXAMPLE IV

The procedure is the same as that of Example III except that 10 grams of wet paper pulp (20% solids) is added to the KOH solution along with the 15 grams of $\text{K}_2\text{B}_4\text{O}_7$. In this case the potassium hexatitanate/ TiO_2 composite fibers have a surface area of 17 M^2/gr . and length and diameter dimensions similar to the fibers of

Example III. FIG. 1 is a photomicrograph of the fibers at 4,200X.

EXAMPLE V

Fifty grams of KOH is added to 50 cc. distilled water to prepare a concentrated KOH solution. The concentrated KOH solution is placed in a Waring Blendor along with 10 grams of wet paper pulp (20% solids) and 10 grams of a titanium oxychloride solution prepared as in Example III. While agitation is maintained, more of the titanium oxychloride solution is added until a pH of 10 is reached, this requiring 15 grams of the solution.

The salt-gel thus prepared is cast and dried as in Example III. The porous brick thus formed is subsequently calcined for 1 hour at 950° C.

The calcined brick is leached free of soluble salts by washing with hot distilled water. A 10% hydrogen fluoride solution is then used over a period of 2 hours to dissolve away the silicates generated in the calcination step. The treatment otherwise leaves the fibers essentially unchanged.

The recovered composite fibers have a surface area of 15 M²/gr. and X-rays reveal the presence of both rutile and potassium hexatitanate components. The fibers have length and diameter dimensions similar to those of Example III.

EXAMPLE VI

Composite fibers prepared by the methods described in Examples II and III are tested for their reinforcing strength in a commercial, high density, linear polyeth-

ylene resin of melt index 17.5.

Each test sample is prepared at 20% loading, i.e. 20% by weight composite fibers and 80% by weight resin. The fibers are incorporated in the polyethylene on a two-roll mill according to standard polyethylene test procedures and molded into flex bars measuring about 5.7 cm × 2.7 cm. × 0.3 cm.

The standard test for flex strength and flex modulus, ASTM-D-790, is performed on the samples. A control containing no reinforcing fibers is included.

FLEX TEST RESULTS

Sample	Flex Strength-psi	Flex Modulus-psi
Control — No fiber reinforcement	4,500	150,000
Example II fibers	7,320 ± 290	594,000 ± 40,000
Example III fibers	6,450 ± 230	427,000 ± 17,000

What is claimed is:

1. A fibrous material composed of composite fibers having a number average diameter of up to about 10 microns and an average length/diameter ratio of at least about 5/1, said fibers having a core composition corresponding to the formula



wherein M is an alkali metal of atomic number of at least 11, said core being encapsulated by a shell of rutile TiO₂ thereby rendering the fibers essentially inert to aqueous 5% by weight HF solution.

* * * * *

35

40

45

50

55

60

65