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(64) Friction material composites containing crystalline phosphate fibers and a process for the preparation thereof.

(67) Asbestos-free friction material composites containing asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof, are useful as brake pads, brake linings, clutch facings, and the like where friction material composites are needed. Such composites are prepared by (a) blending asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof, a thermosetting resin-based binder, a particulate friction modifier, and a particulate inorganic filler to form a uniform mixture; (b) placing the mixture within a mold cavity having a shape approximately that of the desired composite; and (c) compressing the mixture at a temperature and a pressure, and for a time, sufficient to form the asbestos-free friction material composites.

FRICTION MATERIAL COMPOSITES CONTAINING
CRYSTALLINE PHOSPHATE FIBERS AND A PROCESS FOR
THE PREPARATION THEREOF

BACKGROUND OF THE INVENTION

5 Field of the Invention

 This invention relates to asbestos-free friction material composites and a process for the preparation of such composites. More particularly, this invention relates to asbestos-free friction material composites containing asbestiform crystal-
10 line calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof and a process for the preparation. The friction material composites are
15 suitable for use as brake pads, brake linings, clutch facings, and other similar uses where friction material composites are needed.

Description of the Prior Art

 Friction material composites for use as
20 brake elements in automotive, truck, bus, or similar vehicles are known in the art. In general, such composites contain asbestos fibers as an inorganic fibrous reinforcement material. The popularity enjoyed by asbestos fibers for such uses resides in
25 the fact that asbestos has been considered to be relatively inexpensive, is easily preformed, and provides a brake element having excellent wear, durability, friction, and strength properties. However, asbestos has recently been found to expose workers
30 making or installing the brake elements as well as the public to a potentially serious health hazard. It has been determined that the inhalation of small asbestos fibers can result in a disease known as asbestosis in which these fibers accumulate in the
35 lungs, scar lung tissue, and cause many respiratory problems. It has become increasingly clear that

inhalation of asbestos fibers over an extended period of time can lead to a cancer of the lining of the lungs known as mesothelioma as well as lung cancer.

5 In addition, in the operation of conventional asbestos-based brake elements, as the brake element wears away, some of the asbestos discharges into the atmosphere in its fibrous form to thereby pose a potential hazard. In view of the potential hazard of asbestos material, it has become increasingly desirable to find substitutes for asbestos in those applications involving the
10 manufacture and use of materials containing asbestos, and more specifically, for manufacturers of friction materials such as asbestos-based brake elements to find suitable substitutes for asbestos.

15 U.S. Patent 4,137,214 discloses friction compositions containing nonasbestos fibrous materials. Suitable nonasbestos materials include, for example, fiber glass, mineral wool, silica fibers, carbon fibers, boron fibers, and the like; and tungsten
20 fibers or steel fibers and the like.

In U.S. Patent 4,278,584, an asbestos-free organic friction material reportedly having favorable mechanical, thermal, and frictional properties is described. Such materials contain phenolic resins,
25 carbon fibers, steel fibers, and filler materials, and are useful as brakes and clutches of automobile and brake blocks of railroad (railway) vehicles.

U.S. Patent 4,374,211 discloses a non-asbestos friction material composite. Such composites
30 are comprised of a thermosetting binder, a nonasbestos fibrous material such as, for example, those disclosed in U.S. Patent 4,137,214 discussed hereinabove, and an effective amount of an aramid polymer (an aromatic polycarbonamide) pulp fiber. Such friction material

reportedly results in good structural integrity of preforms made therefrom.

Although these prior art friction materials are effective to eliminate asbestos in products
5 utilizing such friction materials, none have been found to provide strength, wear resistance, and frictional properties comparable to those provided by asbestos-containing friction materials, coupled with economical materials and manufacturing costs. For
10 example, glass fibers have a tendency to fracture in the mixing procedures used to prepare the friction compositions with the result that they contribute poor reinforcement. Furthermore, glass fibers are brittle and tend to break down at the braking interface during
15 service of the brake element and high wear rates are thereby encountered. Moreover, the nonporous glass fibers have a low surface area as compared with asbestos, and the glass fibers do not absorb products of decomposition of the organic components caused by
20 heat which occurs during braking. As a result, when glass fibers are used as the reinforcing material, friction drops precipitously at the temperatures generated during braking. This friction drop due to poor absorption by the reinforcing fibers is known in the
25 brake industry as "fade". Similarly, organic fibers such as cotton, wood pulp, and rayon, synthetic fibers composed of such organic polymers as polyacrylonitrile, polyamide, polyester, and the like have low surface area and exhibit poor heat resistance. These latter
30 fiber materials tend to lose strength at temperatures in the range of 93° C - 149° C (240° F - 300° F) and break down in the same manner as the binder material. The discovery of the friction material composites of the instant invention, which exhibits properties comparable to, and in many instances superior to,
35 conventional asbestos-containing friction material in

wear, durability, friction, and strength, while at the same time presenting no health hazard and a process for their preparation, therefore, is believed to be a decided advance in the asbestos-free friction material composite art.

SUMMARY OF THE INVENTION

It is an object of this invention to provide novel asbestos-free friction material composites containing asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof, which exhibit wear, durability, friction, and strength characteristics comparable to or exceeding those of conventional asbestos-type friction material composites, and at the same time present no health hazard.

It is also an object of this invention to provide an asbestos-free friction material composite which can be shaped into brake pads, brake lining segments, clutch facings, and the like using conventional processes.

Another object of this invention is to provide a process for preparing novel asbestos-free friction material composites containing asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof, which exhibit wear, durability, friction, and strength characteristics comparable to or exceeding those of conventional asbestos-type friction material composites, and at the same time present no health hazard.

Yet another object of this invention is to provide a process for preparing an asbestos-free friction material composite which can be shaped into

brake pads, brake lining segments, clutch facings, and the like using conventional processes.

These and other objects will become apparent from the accompanying description and claims. The provision of the friction material composites objects is achieved by friction material composites which comprise:

- (a) asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof;
- (b) a thermosetting resin-based binder;
- (c) a particulate friction modifier; and
- (d) a particulate inorganic filler.

The provision of the process for the preparation of such friction material composites objects is achieved by a process which comprises:

- (a) blending asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof, a thermosetting resin-based binder, a particulate friction modifier, and a particulate inorganic filler to form a uniform mixture;
- (b) placing the mixture within a mold cavity having a shape approximately that of the desired composite; and
- (c) compressing the mixture at a temperature and a pressure, and for a time, sufficient to form the asbestos-free friction material composites.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, novel asbestos-free friction material composites, and a process for the preparation thereof, are provided.

5 The friction material composites exhibit wear, durability, friction, and strength characteristics comparable to, or exceeding, those of conventional asbestos-type friction materials, while at the same time present no health hazard. Such composites
10 comprise:

- (a) asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof;
- 15 (b) a thermosetting resin-based binder;
- (c) a particulate friction modifier; and
- (d) a particulate inorganic filler.

The composites are prepared by a process
20 which comprises:

- (a) blending asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof, a thermosetting resin-based binder, a particulate friction modifier, and a particulate inorganic filler to form a uniform mixture;
- 25 (b) placing the mixture within a mold cavity having a shape approximately that of the desired composite; and
- (c) compressing the mixture at a temperature and a pressure, and for a time,
30 sufficient to form the asbestos-free friction material composites.

It is contemplated that, in use, the asbestos-free friction material composites of the instant invention may be fastened unto standard brake shoe members by conventional means, either by integral molding, riveting or bonding with a rubber solvent-based adhesive, as desired, for installation into conventional brake assemblies.

The asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof, are high molecular phosphates $[\text{CaM}(\text{PO}_3)_3]_n$ wherein n is a number representing the number of repeating $\text{CaM}(\text{PO}_3)_3$ units. Advantageously, such fibers have an aspect ratio (length-to-average diameter ratio, L/D) of at least 30:1 and an average diameter in the range of from about 0.5 micron (μm) to about 20 μm . Preferred fibers are those having an aspect ratio of from about 40:1 to about 100:1 and an average diameter from about 1 micron to about 10 microns. Among such fibers, particularly preferred are calcium M phosphate fibers wherein M is sodium.

Details of the preparation, crystallinity, and other characterizing properties of asbestiform crystalline calcium M phosphate fibers are described in U.S. Patent 4,346,028, the disclosure of which is herein incorporated by reference.

It is contemplated within the scope of the instant invention that the asbestiform crystalline calcium M phosphate fibers may be used alone as the fibrous reinforcement material or in combination with suitable auxiliary fibers. When employed, the auxiliary fibers preferably will be present in an amount such that the phosphate fiber/auxiliary fiber weight ratio will be about 2/1 or higher, that is, at least 2/1. Representative of suitable auxiliary fibers are

glass fibers, mineral wool fibers, aramid fibers, steel fibers, and the like, and mixtures thereof.

The thermosetting resin-based binder materials suitable to prepare the asbestos-free friction material composites of the instant invention are those which provide the desired physical properties and characteristics in the final product, and, in general, may be any thermosetting resin generally known to be useful in the production of brake pads, brake lining segments, clutch facings, and the like. Representative thermosetting resins include phenol-formaldehyde resins, phenol-furfural resins, melamine-formaldehyde resins, epoxy resins, cross-linked alkyd resins, diallyl phthalate resins, and urea-formaldehyde resins. Preferred resins are phenol-formaldehyde resins. A phenol-formaldehyde resin suitable for use in the instant invention is available commercially from Schenectady Chemicals Co., Inc. as SP6416.

As will be apparent to those skilled in the friction-material art, the thermosetting resins suitable for use in the instant invention may be used alone or in combination with a heat and chemical resistant vulcanized rubber. Examples of such rubber include nitrile rubber, butyl rubber, styrene-butadiene copolymer rubber, acrylonitrile rubber, and chlorinated butyl rubber. A preferred rubber is nitrile rubber.

When a rubber is used in the instant invention, it preferably constitutes less than 50% of the thermosetting resin-based binder. It may be incorporated into the asbestos-free friction material composite in the form of a solution in an organic solvent such as trichlorethylene or, more preferably, in the form of a powder, and a vulcanizing agent -- sulfur, 2-mercaptobenzothiazole, tetramethylthiuram

disulfide, and mixtures thereof, for example -- also can be used.

5 The particulate friction modifier component employed in the instant invention is incorporated to stabilize the coefficient of friction of the composite materials under a variety of operating and climactic conditions to which a typical brake element will be exposed during use so as to provide wear resistance for such composites. The particulate friction modifier preferably is a cashew-based material such as cashew nut shell oil-based friction particles. Suitable cashew-based friction particles are an aldehyde condensation product of cashew nut shell liquid and are available commercially from Colloid Chemicals Laboratories, Inc. as Collan 10A-40.

10 Particulate inorganic filler materials employed in the instant invention may be crystalline or amorphous in structure as long as they are able to maintain stability at temperatures up to 538° C (1000° F), and higher. Representative of suitable particulate inorganic filler materials include barytes (barium sulfate), carbon or graphite, calcium carbonate, silica, and the like. In general, however, dolomite, a conventional filler, is not preferred for use in the instant invention due to low normal friction exhibited by such composites. It will be recognized, of course, that this characteristic may vary, depending to some extent upon the remaining components of such composites.

0 The particle size of the particulate materials (that is, the particulate friction modifier and the particulate inorganic filler) is not particularly critical. The particle sizes normally employed in friction materials are satisfactory but wide deviations therefrom will have no substantial effect on

performance. Particle sizes from about 0.5 μm to about 500 μm may be used.

In the practice of the instant invention, the components of the asbestos-free friction material composites are blended in the desired proportions in a mixer such as a Waring blender. The mixed components are then placed in a preform mold cavity having approximately the desired product shape. The mixture is then compressed at ambient temperatures and at a pressure of about 18.0 MPa (2600 psi) for a period of about one minute. The preform is then cured by heating to a temperature of about 171° C (340° F) for about one hour while maintaining the pressure at about 18.0 MPa. Alternatively, the preform step may be omitted and the mixture immediately subjected to the 171° C curing step. For larger test pieces, which may be trimmed to any desired size by conventional means known to the art, the formed pieces are subjected to a post cure in a drying oven at about 177° C (350° F) for about four hours.

Any convenient concentration (on a weight basis) of the components of the asbestos-free friction material composites may be used. In general, the composites of the instant invention will comprise (on a weight basis) from about 5% to about 20% of the phosphate fibers, from about 10% to about 30% of the thermosetting resin-based binder, from about 5% to about 25% of the particulate friction modifier, and from about 40% to about 70% of the particulate inorganic filler. In a preferred embodiment, the concentration for the phosphate fiber will range from about 10% to about 17.5%, for the thermosetting resin-based binder, from about 15% to about 25%, for the particulate friction modifier, from about 10% to about 15%, for the particulate inorganic filler, from about 45% to about 65%. In a most preferred embodiment, the

concentration for the phosphate fiber will be, as previously noted, about 10% to about 17.5%, for the thermosetting resin-based binder, about 15%, for the particulate friction modifier, about 10%, with the balance being particulate inorganic filler. If desired, an auxiliary fiber may be substituted for a portion of the particulate inorganic filler and employed in combination with the phosphate fibers in an amount such that the auxiliary fibers will constitute about 2% to about 10% of the friction material composite (so long as the aforementioned phosphate fiber/auxiliary fiber weight ratio is at least 2/1). In a similar manner, a rubber (with nitrile rubber being preferred) may be substituted for a portion of the particulate inorganic filler and employed in combination with the thermosetting resin of the thermosetting resin-based binder in an amount such that the rubber will constitute about 0.5% to about 5% of the friction material composite.

The asbestos-free friction material composites of, and prepared in accordance with, the instant invention exhibit excellent wear, durability, friction, and strength characteristics, and at the same time present no health hazard.

The following specific examples illustrating the best presently-known methods of practicing this invention are described in detail in order to facilitate a clear understanding of the invention. It should be understood, however, that the detailed exposition of the application of the invention, while indicating preferred embodiments, are given by way of illustration only and are not to be construed as limiting the invention since various changes and modifications within the spirit of the invention will become apparent to those skilled in the art from this detailed description.

EXAMPLES 1-14

(a) Calcium Sodium Phosphate Fibers - Asbestiform crystalline calcium sodium phosphate fibers were prepared in five batches of 29.0 kg to 70.3 kg (64 lb to 155 lb) each by scale-up of the general procedures described in the previously referenced U.S. Patent 4,346,028. In a typical preparation, 20.452 parts 85.2% phosphoric acid, 4.880 parts calcium carbonate, 3.241 parts sodium carbonate, and about 8.1 parts distilled water, providing an anhydrous basis mole percent ratio of 50.60% P_2O_5 , 32.45% CaO, and 16.95% Na_2O , were placed in a large alumina crucible and heated slowly in a furnace at a rate of 5° C/hr up to 1000° C, at which point essentially all the water and CO_2 had been driven off and the contents were molten. The melt was held at 1000° C for 24 hr, cooled to 740° C, at which time several small seed crystals of $[CaNa(PO_3)_3]_n$ were added to the surface of the melt which was held at 740° C for 72 hr to crystallize. The temperature was reduced to 720° C and held for an additional 72 hr to complete the crystallization, after which the crystallized mass was slowly cooled to room temperature and removed from the crucible. The crystallized mass was broken apart, passed through a mechanical jaw crusher, and then fiberized by dry milling in an air classification mill. The fibers had an average aspect ratio of 64.5, an average diameter of 2.09 μm , and a surface area of 6773 cm^2/g .

(b) Friction Material Composite Preparation - Sample asbestos-free friction material composites were prepared in two sizes -- 1.27 cm wide x 15.24 cm long x 0.64 cm thick (0.5 in x 6 in x 0.25 in), with a weight of about 20.0 g and 5.08 cm x 15.24 cm long x 0.64 cm thick (2 in x 6 in x 0.25 in), with a weight of about 100.0 g.

Dry ingredients in the amount of either 20.0 g or 100.0 g, depending upon the composite size desired, and having the desired composition were dry blended thoroughly in a Waring blender. The blended material was loaded into a rectangular steel mold having a shape approximately that of the desired product and pressed for one hour at 18.3 MPa (2650 psi) and a temperature of 171° C (340° F). The 5.08 cm wide pressed pieces were subjected to a post cure in a drying oven at 177° C (350° F) for a period of four hours. For green flexural strength tests, the samples were compressed at 18.3 MPa (2650 psi) at ambient temperature for one minute. The parameters and property data for the asbestos-free friction material composites are tabulated in Table 1.

	EXAMPLE	COMPOSITION ¹ , wt. %	FLEXURAL STRENGTH ² , MPa	
			GREEN ³	CURED ⁴
5	2	45.0 Barytes 10.0 PF ⁹	---	69912.84
	3	"	86.18	64638.35
	4 ¹⁰	55.0 Asbestos	---	69175.10
	5 ¹⁰	55.0 Fiberglass	---	51662.42
		.		
10	6 ¹⁰	55.0 Dolomite	33.09	37107.58
	7 ¹⁰	45.0 Dolomite 10.0 PF ⁹	29.65	48042.67
	8 ¹⁰	50.0 Dolomite 5.0 Kevlar Ara-	406.79	45850.14
15		mid Fiber Pulp		
	9	45.0 Barytes	87.56	69933.52

TABLE 1

SWELL/GROWTH ⁵ , %	FRICTION COEFFICIENT, μ /- FRICTION CLASS ⁶	
	NORMAL	HOT
0.58/0	0.372/F	0.391/F
0.38/0	0.330/E	0.382/F
0.75/0	0.290/E	0.321/E
0.18/0	0.530/G	0.380/F
0/0	0.448/F	0.313/E
0.80/0.80	0.220/D	0.293/E
0.20/0	0.330/E	0.320/E
0.57/0	0.332/E	0.428/F

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TABLE 1

	EXAMPLE	WEAR, %		MINIMUM REQUIREMENTS ⁷
		WT.	THICKNESS	
	2	5.99	3.49	Pass
5				
	3	6.75	4.04	Pass
10	4 ¹⁰	9.11	7.65	Pass
	5 ¹⁰	11.81	10.66	Pass
	6 ¹⁰	3.04	1.93	Pass
15	7 ¹⁰	4.55	10.53	Fail
	8 ¹⁰	2.11	2.27	Fail
	9	6.69	2.98	Pass

(cont'd)

QUALITY CONTROL⁸

Good standard test;
high fade in extended
test.

Good standard test;
excessive fade in
extended test.

Acceptable performance

Excessive fade; high
pitched screech.

Excessive variation in
friction coefficient.

Low normal friction.

Excessive variation in
friction coefficient.

Good standard test;
excessive fade in
extended test.

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TABLE 1 (cont'd)

	EXAMPLE	COMPOSITION ¹ , wt. %	FLEXURAL STRENGTH ² , MPa		SWELL/GROWTH ⁵ , %	FRICTION COEFFICIENT, μ /- FRICTION CLASS ⁶	
			GREEN ³	CURED ⁴		NORMAL	HOT
5	10	53.5 Barytes 1.5 NR ¹⁰	248.21	37790.16	0.20/0	0.668/H	0.546/G
	11	43.5 Barytes 1.5 NR ¹⁰ 10.0 PF ⁹	386.11	64245.35	0.55/0.18	0.368/F	0.396/F
10	12	36.0 Barytes 1.5 NR ¹⁰ 17.5 PF ⁹	434.37	70436.84	1.24/0.53	0.312/E	0.367/F
	13 ¹⁰	Commercial Asbestos Pad	---	---	0.91/0.26	0.438/F	0.467/G
15	14 ¹⁰	Commercial Semi- metallic Pad	---	---	1.23/0.96	0.338/E	0.334/E

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TABLE 1 (cont'd)

	EXAMPLE	WEAR, %		MINIMUM REQUIREMENTS ⁷	QUALITY CONTROL ⁸
		WT.	THICKNESS		
	10	5.31	3.76	Pass	Excessive fade.
5	11	6.03	3.35	Pass	Good standard test; excessive fade in extended test.
	12	4.74	2.82	Pass	Good standard test; excessive fade in extended test.
10	13 ¹⁰	11.77	8.45	Pass	Acceptable performance.
	14 ¹⁰	---	0.91	Pass	Excellent performance; low wear.

1 A base formulation was employed which had a weight
% composition as follows:

33.33[15%] phenol-formaldehyde thermosetting
resin (containing hexamethylene-
tetramine as curing agent),
available commercially from
Schenectady Chemicals, Inc.

22.22[10%] particulate friction modifier, which
was an aldehyde condensation product
of cashew nut shell liquid available
commercially from Colloid Chemicals
Laboratories, Inc. as Collan 10A-40.

44.44[20%] barytes (barium sulfate) available
commercially from Pfizer Minerals,
Pigments & Metals Div.

[55% fiber/filler/additive material.]

In use, the fiber (and other additives, if em-
ployed) to be tested was added to the base
formulation in an amount sufficient to consti-
tute 55% by weight of the final composition.
This resulted in the 33.33%, 22.22%, and
44.44% in the base formulation being reduced
to 15%, 10%, and 20%, respectively, all by
weight, in the final composition. If less
than 55% fiber was used, the balance was made
up with filler material, for example, barytes,
and/or rubber, for example, nitrile rubber.

2, 3, 4 The test was carried out according to ASTM
D790-80 test method for plastics on a flexural
jig on an Instron Universal testing instrument.
The 15.24 cm long green (uncured) strength
samples were cut in half to provide two 7.62
cm (3 in) test pieces and each piece was
tested with a 50.8 mm (2 in) span. The cured
samples were broken with a 101.60 mm (4 in)

span and the two resulting pieces were rebroken with a 50.8 mm (2 in) span.

5 The test was carried out according to SAE Test J160.

5 6 The test was carried out according to SAE Test J661a by Greening Testing Laboratories, Inc., and the classifications were made in accordance with SAE Test J866a. The standard J661a test has 343° C (650° F) as the upper temperature limit. The
10 extended test has an upper temperature limit of 454° C (850° F), a more severe test.

7 This test was carried out according to SAE Test J998.

8 Qualitative observations and comments regarding
15 performance of test pieces during the SAE Test J661a.

9 Phosphate fibers.

10 Comparative example.

11 Nitrile rubber.

Thus, it is apparent that there has been provided in accordance with the instant invention, asbestos-free friction material composites containing crystalline phosphate fibers and a process for preparing same that fully satisfy the objects and advantages set forth hereinabove. While the invention has been described with respect to various specific examples and embodiments thereof, it is understood that the invention is not limited thereto and that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the invention.

WHAT IS CLAIMED IS:

1. An asbestos-free friction material composite containing phosphate fibers comprising:
 - (a) asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and lithium, and mixtures thereof;
 - (b) a thermosetting resin-based binder;
 - (c) a particulate friction modifier; and
 - (d) a particulate inorganic filler.
2. The asbestos-free friction material composite of Claim 1 wherein M is sodium.
3. The asbestos-free friction material composite of Claim 1 wherein the phosphate fibers have an aspect ratio of at least 30:1.
4. The asbestos-free friction material composite of Claim 3 wherein the phosphate fibers have an aspect ratio of from about 40:1 to about 100:1.
5. The asbestos-free friction material composite of Claim 1 wherein the phosphate fibers have an average diameter of from about 0.5 μm to about 20 μm .
6. The asbestos-free friction material composite of Claim 5 wherein the phosphate fibers have an average diameter of from about 1 μm to about 10 μm .
7. The asbestos-free friction material composite of Claim 1 wherein the composite further comprises an auxiliary fiber selected from the group consisting of glass fibers, mineral wool fibers, aramid fibers, steel fibers, and mixtures thereof.
8. The asbestos-free friction material composite of Claim 1 wherein the thermosetting

resin-based binder comprises a phenol-formaldehyde thermosetting resin.

5 9. The asbestos-free friction material composite of Claim 8 wherein the thermosetting resin-based binder further comprises a rubber.

10 10. The asbestos-free friction material composite of Claim 9 wherein the rubber is a nitrile rubber.

15 11. The asbestos-free friction material composite of Claim 1 wherein the particulate friction modifier is an aldehyde condensation product of cashew nut shell liquid.

20 12. The asbestos-free friction material composite of Claim 1 wherein the particulate inorganic filler is selected from the group consisting of barytes, calcium carbonate, silica, and mixtures thereof.

25 13. The asbestos-free friction material composite of Claim 11 wherein the particulate inorganic filler is barytes.

30 14. The asbestos-free friction material composite of Claim 1 wherein the particulate friction modifier and the particulate inorganic filler have an average particle size from about 0.5 μm to about 500 μm .

35 15. The asbestos-free friction material composite of Claim 1 wherein the composite comprises

(a) from about 5% to about 20% by weight of the phosphate fibers;

(b) from about 10% to about 30% by weight of the thermosetting resin-based binder;

(c) from about 5% to about 25% by weight of the particulate friction modifier; and

- (d) from about 40% to about 70% by weight of the particulate inorganic filler.

5 16. An asbestos-free friction material composite containing phosphate fibers comprising:

- (a) from about 10% to about 17.5% by weight of asbestiform crystalline calcium sodium phosphate having an aspect ratio of from
10 about 40:1 to about 100:1 and an average diameter of from about 1 μm to about 10 μm ;
- (b) from about 15% to about 25% by weight of a phenol-formaldehyde
15 thermosetting resin-based binder;
- (c) from about 10% to about 15% by weight of a particulate aldehyde-cashew nut shell liquid
20 condensation product; and
- (d) from about 45% to about 65% by weight of particulate barytes.

25 17. A process for the preparation of an asbestos-free friction material composite containing phosphate fibers which comprises:

- (a) blending asbestiform crystalline calcium M phosphate fibers wherein M is a metal cation selected from the group consisting of sodium and
30 lithium, and mixtures thereof, a thermosetting resin-based binder, a particulate friction modifier, and a particulate inorganic filler to form a uniform mixture;

- (b) placing the mixture within a mold cavity having a shape approximately that of the desired composite; and
- (c) compressing the mixture at a temperature and a pressure, and for a time, sufficient to form the asbestos-free friction material composites.

5

18. The process of Claim 17 wherein M is sodium.

10

19. The process of Claim 17 wherein the phosphate fibers have an aspect ratio of at least 30:1.

20. The process of Claim 19 wherein the phosphate fibers have an aspect ratio of from about 40:1 to about 100:1.

15

21. The process of Claim 17 wherein the phosphate fibers have an average diameter of from about 0.5 μm to about 20 μm .

20

22. The process of Claim 21 wherein the phosphate fibers have an average diameter of from about 1 μm to about 10 μm .

25

23. The process of Claim 17 wherein the composite further comprises an auxiliary fiber selected from the group consisting of glass fibers, mineral wool fibers, aramid fibers, steel fibers, and mixtures thereof.

24. The process of Claim 17 wherein the thermosetting resin-based binder comprises a phenol-formaldehyde thermosetting resin.

30

25. The process of Claim 24 wherein the thermosetting resin-based binder further comprises a rubber.

26. The process of Claim 25 wherein the rubber is a nitrile rubber.

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27. The process of Claim 17 wherein the particulate friction modifier is an aldehyde condensation product of cashew nut shell liquid.

28. The process of Claim 17 wherein the particulate inorganic filler is selected from the group consisting of barytes, calcium carbonate, silica, and mixtures thereof.

5 29. The process of Claim 28 wherein the particulate inorganic filler is barytes.

 30. The process of Claim 17 wherein the particulate friction modifier and the particulate inorganic filler have an average particle size from
10 about 0.5 μm to about 500 μm .

 31. The process of Claim 17 wherein the composite comprises:

- (a) from about 5% to about 20% by weight of the phosphate fibers;
- 15 (b) from about 10% to about 30% by weight of the thermosetting resin-based binder;
- (c) from about 5% to about 25% by weight of the particulate friction modifier; and
- 20 (d) from about 40% to about 70% by weight of the particulate inorganic filler.

25 32. The process of Claim 17 wherein the mixture is compressed at ambient temperature and a pressure of about 18.0 MPa for about one minute.

 33. The process of Claim 32 wherein the mixture is further compressed for a period of about one hour at a temperature of about 171° C and a pressure
30 of about 18.0 MPa.

 34. The process of Claim 17 wherein the mixture is compressed at a temperature of about 171° C and a pressure of about 18.0 MPa for about one hour.

35 35. The process of Claim 17 wherein the composite is subjected to a post cure at a temperature of about 177° C for about four hours.

36. A process for the preparation of an asbestos-free friction material composite containing phosphate fibers which comprises:

- 5 (a) blending from about 10% to about 17.5% by weight of asbestiform crystalline calcium sodium phosphate having an aspect ratio of from about 40:1 to about 100:1 and an average diameter of from
10 about 1 μm to about 10 μm , from about 15% to about 25% by weight of a phenol-formaldehyde thermo-setting resin-based binder, from
15 about 10% to about 15% by weight of a particulate aldehyde-cashew nut shell liquid condensation product, and from about 45% to about 65% by weight of particulate barytes to form a uniform
20 mixture;
- (b) placing the mixture within a mold cavity having a shape approximately that of the desired composite;
- 25 (c) compressing the mixture at a temperature and a pressure, and for a time, sufficient to form the asbestos-free friction material composite.

30 37. The process of Claim 36 wherein the mixture is compressed at ambient temperature and a pressure of about 18.0 MPa for about one minute.

35 38. The process of Claim 37 wherein the mixture is further compressed for a period of about one hour at a temperature of about 171° C and a pressure of about 18.0 MPa.