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AUSTRALIA

PATENT 663111

NOTICE OF ENTITLEMENT

We, E.I. DU PONT DE NEMOURS AND COMPANY, of 1007 Market Street, Wilmington, Delaware 19898, United States of America, being the applicant and the person nominated for grant of patent in respect of the Application for an invention entitled ARAMID PARTICLES AS WEAR ADDITIVES

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Miriam D. Meconahey
Signature

February 4, 1994
Date

Assistant Secretary to the Patent Board
Executive Position

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(56) Prior Art Documents
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(57) Claim

1. A composite material comprising:

a) 10 to 95 percent, by weight, matrix resin;

b) 1 tc 40 percent, by weight, fiber reinforcing material;

c) 1 to 65 percent, by weight, aramid particles having no tentacle-like projections thereon, and having an average diameter of 75 to 250 microns, wherein the weight ratio of aramid particles to fiber reinforcing material is greater than 1:4.

8. A process for making a composite comprising the steps of homogeneously combining aramid particles having no tentacle-like projections thereon, and of 75 to 250 microns in average diameter and fiber reinforcing material from 1 to 6 mm in long dimension in a weight ratio of greater than 1:4 and blending that combination with a matrix resin to yield a composite having

a) 10 to 95 percent, by weight, matrix resin;

b) 1 to 40 percent, by weight, fiber reinforcing material;

c) 1 to 65 percent, by weight, aramid particles.

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(54) Title: ARAMID PARTICLES AS WEAR ADDITIVES

(57) Abstract

A composite friction or gasketting material is disclosed having a combination of thermoset or thermoplastic matrix resin, fiber reinforcing material, and aramid particles. The composite material exhibits improved wear resistance when compared with materials having no aramid particles.

Title

Aramid Particles as Wear Additives

Background of the Invention

Field of the Invention

This invention relates to composites for use as friction materials or gasketting. The composites include fibers, in the form of floc or pulp, and aramid polymer particles substantially homogeneously distributed in a matrix resin. The composites are particularly useful in high temperature applications.

Description of the Prior Art

Friction materials are well known using fibers which exhibit high temperature strength in a matrix resin and, optionally, using fillers of various kinds for other purposes. The fiber which was historically used in such friction materials was asbestos; but, recently, other fibers have been substituted therefor.

United States Patent No. 4,219,452, issued August 26, 1980 on the application of Littlefield, discloses a composite friction product comprising an elastomeric binder, an aramid fiber, and a complicated combination of additional materials. The friction product can include a thermoset resin, for example phenolic resin, but only in relatively small amount. The aramid fiber is utilized as a replacement for asbestos.

United States Patent No. 4,324,706, issued April 13, 1982, on the application of Tabe et al., discloses a friction product which includes a thermoset matrix polymer, aromatic polyamide pulp-like particles, other heat resistant fibrous materials, and friction-regulating materials. The heat resistant fibrous material may, also, be aromatic polyamides; but there is no disclosure of the use of particles of aromatic polyamides in that friction material.

United States Patent No. 4,374,211, issued February 15, 1983 on the application of Gallagher et al., discloses a friction product utilizing aramid polymer pulp as a

replacement for asbestos, aramid fibers as a reinforcing material, and thermoset polymeric matrix binder. These friction products also include inorganic particles or powders used as fillers and modifiers for the product.

Japanese Patent Publication Tokuko 1-33698, published July 14, 1989 on the application of Honma discloses a friction material which utilizes a thermoset binder resin; reinforcement fibers of glass, ceramic, organic, metallic, or carbon materials; and a significant amount of hardened polyimide powder.

Summary of the Invention

The present invention provides a composite friction or gasketting material comprising a matrix resin, a fiber reinforcing material, and aramid particles wherein the composite is 10 to 95 percent, by weight, matrix resin, 1 to 40 percent, by weight, fiber reinforcing material, and 1 to 65 percent, by weight, aramid particles and the weight ratio of aramid particles to fiber reinforcing material is greater than 1/4 and preferably from 1/4 to 4/1. The matrix resin can be thermoset or thermoplastic. The fiber reinforcing material can be pulp or floc and is preferably aramid from 1 to 6 mm in long dimension. The aramid particles are preferably poly(p-phenylene terephthalamide) and are from 10 to 250 microns and preferably 75 to 250 microns in average diameter.

For the composite friction material of this invention, as it relates to friction products such as brakes and brake shoes, the composite is generally 10 to 20 percent, by weight, matrix resin; for composite friction materials for use in wear resistant resin applications, the composite is generally 75 to 95 percent, by weight, matrix resin; and for the composite friction material of this invention for use in gaskets and gasketting, the composite is generally between that of brakes and wear resistant resins, that is, from about 15 or 20 to 75 percent, by weight, matrix resin. It can, also, be pointed out that, with regard to the weight ratio of aramid particles to fiber reinforcing material, gaskets and

gasketting material and wear resistant resins utilize a ratio which is near the low recommended range, that is, from about 1/1 to 1/4; and for brakes and friction products, the ratio of aramid particle to fiber reinforcing material is in the high recommended range, that is, from about 1/1 to 4/1 and higher.

A process is provided for making a composite which comprises a matrix resin, a fiber reinforcing material, and aramid particles wherein the aramid particles and the fiber reinforcing material, in a weight ratio of greater than 1/4 and preferably from 1/4 to 4/1, are homogeneously combined and, then, that combination is blended with the matrix resin.

Detailed Description of the Invention

The composite material of this invention comprises a matrix resin, aramid fibers, and aramid particles and is, generally, useful for friction products and gasketting. The composite material may, also, include various filler materials to accomplish any desired or desirable alternative purpose.

The composite of this invention finds use in friction materials due to its resistance to wear and high temperature stability.

Matrix resins in these composites can be selected from the broad groups of thermoplastic and thermoset, depending upon the intended use and the desired result. Thermoset materials are materials which exhibit no melting temperature and which yield high char residues. Because the usual intended uses are of a high temperature, high stress, nature, the matrix resin is usually a thermoset material. Thermoset materials are preferred for high temperature, high stress uses because they decompose rather than melt. Strength cannot be maintained if the matrix melts and flows. Eligible thermoset materials include phenolic resins, aromatic polyamides, polybenzoxadiazoles, polyimides, polybenzimidazoles and the like.

Thermoplastic materials are materials which melt and resolidify at certain temperatures under particular conditions. Thermoplastic materials are generally used in

gasketting and in relatively low temperature, low friction applications. Eligible thermoplastic materials include aliphatic polyamides such as nylon 6 and nylon 66, polyesters, acrylics, fluoropolymers such as TEF and FEP, and the like.

The matrix resin, whether thermoset or thermoplastic, serves as a carrier for the other components of the composite of this invention, as an ablative material and matrix binder in friction applications, and as a void filler, sealant and binder in gasketting applications. The matrix resin is from 10 to 95 percent, by weight, of the total composite. Composites utilizing thermoset matrix resins are generally relatively low in resin content and composites utilizing thermoplastic matrix resins are generally at the high end of the matrix resin range.

Short fibers have long been used to reinforce composite sheet structures comprising matrix resins. In some cases the short fibers have served a dual purpose of reinforcing the structure and, also, resisting frictional forces. In the present invention, the short fibers are, primarily, used to reinforce the structure, although, they may have a frictional function, also. The fibers may be made from inorganic or organic materials and may be in the form of pulp or floc. Although glass is often used, organic materials are preferred and it is preferred that the organic materials are in the form of pulp.

Fibers are generally from 0.01 to 50 mm in length, and preferably about 1 to 10 mm; and the fibers generally have a diameter of 0.01 to 200 microns and preferably about 5 to 50 microns. Additionally, it is preferred that the fibers have a surface area of greater than 5 m^2/g and a ratio of length to diameter of 10 to 10,000, preferably 20 to 1000.

Eligible inorganic fiber materials include carbon, glass, metal, mineral, asbestos and the like.

Eligible organic fiber materials include aliphatic polyamides, polyesters, polyacrylonitriles, polyvinyl alcohols, polyolefins, polyvinyl chlorides, polyvinylidene

chlorides, polyurethanes, polyfluorocarbons, phenolics, polybenzimidazoles, polyphenylenetriazoles, polyphenylene sulfides, polyoxadiazoles, polyimides, aromatic polyamides, and the like. Because friction and gasketting are often high heat, high stress, applications, the preferred fibers are strong and stable at high temperatures. Preferred fiber materials are aromatic polyamides (aramids), polybenzoxadiazole, polybenzimidazole, and the like. Fibers of aramids such as poly(p-phenylene terephthalamide) and poly(m-phenylene isophthalamide), are particularly preferred.

The fibers can be used in the form of floc or pulp. Floc is made by cutting fibers into short lengths without significant fibrillation of the fiber ends; and the lengths of floc fibers may range from 1 to 10 mm. Floc less than about 1 mm does not add significantly to the strength of the composite in which it is used; and floc more than about 6 mm often does not function well because the individual fibers may become entangled and cannot be adequately and uniformly distributed throughout the composite.

Short fibers are more effective in strengthening the composite in the form of pulp,. Pulp can be made by grinding fibers to fibrillate the ends of short pieces of the fiber material. An example of pulp and a method for making it can be found in the Research Disclosure Journal number 13675. Pulp can, also, be made by casting a polymerizing solution of polymer material and grinding the solution, once solidified, such as is disclosed in United States Patent No. 5,028,372 granted July 2, 1991 on the application of Brierre et al. In the case of pulp, the preferred material for this invention is poly(p-phenylene terephthalamide).

Aramids, the preferred material for fibers and particles in practice of this invention, are intended to refer to wholly aromatic polycarbonamide polymers and copolymers consisting essentially of recurring units of the formula

$$-HN-AR_1-NH-CO-AR_2-CO- \qquad I$$

wherein AR_1 and AR_2, which may be the same or different, represent divalent aromatic groups. Para-aramids are most preferred and refer to para-oriented aromatic polycarbonamides of Formula I, above, wherein AR_1 and AR_2, which may be the same or different, represent divalent, para-oriented, aromatic groups. By "para-oriented" is meant that the chain extending bonds from aromatic groups are either coaxial or parallel and oppositely directed, for example, substituted or unsubstituted aromatic groups including 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthalene, and 1,5-naphthalene. Substituents on the aromatic groups other than those which are part of the chain extending moieties should be nonreactive and must not adversely affect the characteristics of the polymer for use in the practice of this invention. Examples of suitable substituents are chloro, lower alkyl and methoxy groups. The term para-aramid is also intended to encompass para-aramid copolymers of two or more para-oriented comonomers including minor amounts of comonomers where the acid and amine functions coexist on the same aromatic species, for example, copolymers produced from reactants such as 4-aminobenzoyl chloride hydrochloride, 6-amino-2-naphthoyl chloride hydrochloride, and the like. In addition, para-aramid is intended to encompass copolymers containing minor amounts of comonomers containing aromatic groups which are not para-oriented, such as, for example, m-phenylene and 3,4'-biphenylene.

In accordance with a preferred form of the invention, at least about 80 mole percent of the aromatic diamine is p-phenylene diamine and at least 80 mole percent of the aromatic diacid halide is a terephthaloyl halide, for example, terephthaloyl chloride. The remainder of the aromatic diamine can be other para-oriented diamines including, for example, 4,4'-diaminobiphenyl, 2-methyl-p-phenylene diamine, 2-chloro-p-phenylene diamine, 2,6-naphthalene diamine, 1,5-naphthalene diamine, 4,4'-diaminobenzanilide, and the like. One or more of such para-oriented diamines can be employed in amounts up to about 20

mole percent together with p-phenylene diamine. The remainder of the aromatic diamine may include diamines which are not para-oriented such as m-phenylene diamine, 3,3'-diaminobiphenyl, 3,4'-diaminobiphenyl, 3,3'-oxydiphenylenediamine, 3,4'-oxydiphenylenediamine, 3,3'-sulfonyldiphenylene diamine, 3,4'-sulfonyldiphenylenediamine, 4,4'- oxydiphenylenediamine, 4,4'-sulfonyldiphenylenediamine, and the like, although it is typically necessary to limit the quantity of such coreactants to about 5 mole percent.

Similarly, the remainder of the diacid halide can be para-oriented acid halides such as 4,4'-dibenzoyl chloride, 2-chloroterephthaloyl chloride, 2,5-dichloroterephthaloyl chloride, 2-methylterephthaloyl chloride, 2,6-naphthalene dicarboxylic acid chloride, 1,5-naphthalene dicarboxylic acid chloride, and the like. One or mixtures of such para-oriented acid halides can be employed in amounts up to about 20 mole percent together with terephthaloyl chloride. Other diacid halides which are not para-oriented can be employed in amounts usually not greatly exceeding about 5 mole percent such as isophthaloyl chloride, 3,3'-dibenzoyl chloride, 3,4'-dibenzoyl chloride, 3,3'-oxydibenzoyl chloride, 3,4'-oxydibenzoyl chloride, 3,3'-sulfonyldibenzoyl chloride, 3,4'-sulfonyldibenzoyl chloride, 4,4'-oxydibenzoyl chloride, 4,4'-sulfonyldibenzoyl chloride, and the like.

Again, in a preferred form of the invention, up to 20 mole percent of para-oriented aromatic amino acid halides may be used.

The aromatic diamine and the aromatic diacid halide are reacted in an amide solvent system preferably by low temperature solution polymerization procedures (that is, less than 60C) similar to those shown in U.S. Pat. No. 4,308,374 in the names of Vollbracht et al. and U.S. Pat. No. 3,063,966 in the names of Kwolek et al. for preparing poly(p-phenylene terephthalamide). Suitable amide solvents, or mixtures of such solvents, include N-methyl pyrrolidone (NMP), dimethyl acetamide, and tetramethyl urea containing an alkali metal

halide. Particularly preferred is NMP and calcium chloride with the percentage of calcium chloride in the solvent being between about 4-10% based on the weight of NMP.

The fiber constituent of the composite of this invention represents about 1 to 40 percent, by weight, of the composite. As previously stated, the fiber is present as a reinforcement and less than about 1 percent does not provide significant improvement in the strength of the composite. More than about 40 percent causes the composite to exhibit excessive compressibility and porosity.

The element of the composite of this invention which is believed to yield a surprising benefit and which results in a composite which has not before been known, is particulate aramid polymer. Particles of aramid polymer are blended with the short fibers and the combination of particles and fibers yields a composite having extremely good wear properties and unexpectedly high wear life.

The aramid particles serve, among other things, as friction materials and, for that reason, should be stable to high temperatures. The particles are aramids, as described hereinbefore, and it is preferred that they be para-aramids, also, as described hereinbefore. The most preferred material for the para-aramids of this invention is poly(p-phenylene terephthalamide).

The aramid particles also serve as a compounding agent to assist in dispersing the fibers in the matrix resin. Particles which perform this function are often known as processing agents and it has been determined that such processing agents are preferably very small - on the order of 10 to 250 microns. Aramid particles from 10 to 250 microns are, therefore, useful as both friction materials and as processing agents in practice of this invention. Below about 50 microns, however, the particles appear to be losing effectiveness as friction additives and above about 500 microns the combination of fibers and particles is difficult to accomplish effectively. It has been determined that a

combination of fibers and particles disperses in the matrix polymer more easily and uniformly than fibers, alone; and that, as to the fibers alone, short fibers disperse more easily and uniformly than longer fibers. It has been determined that aramid particles from 125 to 150 microns (100-120 mesh) average diameter are especially preferred when the matrix resin is thermoset and that 125 to 250 microns (60-120 mesh) is an especially preferred size for use with thermoplastic matrix resins. Overall, aramid particles from about 75 to 250 microns are preferred for practice of this invention.

The aramid particles add wear resistance to the composite. It is believed that aramid particles dispersed substantially homogeneously throughout the matrix resin provide, by virtue of the high temperature characteristics of the aramid polymer, very small sites of increased wear resistance effective up to the glass transition temperature of the aramid material. It is understood that the glass transition temperature of poly(p-phenylene terephthalamide) is higher than its degradation temperature and that, therefore, aramid particles provide additional wear resistance at extremely high temperatures.

It has been determined that the excellence of the composite of this invention is, at least in part, a function of the ratio of fibers to aramid particles in the matrix resin. The weight ratio of aramid particles to fibers should be greater than 1/4 and preferably from 1/4 to 4/1 to obtain the best results for general purposes. More specifically, preferred friction products of the present invention have a weight ratio of aramid particles to fibers of about 1/4 to 1/1 using thermoset polymer matrices. Preferred gasketting compositions and friction compositions using thermoplastic polymer materials of the present invention have a weight ratio of aramid particles to fibers of about 1/4 to 1/2.

The particle constituent of the composite of this invention should be about 1 to 65 percent, by weight, aramid particles.

There are some applications for the composition of this invention wherein the total concentration of aramid fibers and aramid particles should be at the upper specified limit. It has been determined that, although there is a maximum practical concentration due to system viscosity considerations, the upper concentration limit is higher for particles than it is for fibers; and, for a combination of fibers and particles, the upper concentration limit is higher as the proportion of particles is increased. Although not completely understood, it is believed that the fiber and particle aramid concentrations and the system viscosity are related, somehow, to the bulk density of the fibers and the particles prior to distribution in the matrix polymer; -- a higher bulk density permitting a higher concentration of aramid materials.

In addition to fibers and aramid particles, the composite may include other filler materials. Such filler materials might be hard minerals added to promote friction. Such minerals might be iron grit, sand, fused silica, and the like. Also, friction modifiers might be added to the composition. Such friction modifiers might include materials such as graphite, partially cured cashew-resin solids, lead and lead compounds such as lead sulfide and the like. Friction-regulating agents can be added including alumina, silica, talc, kaolin, mica, and the like. These filler materials should generally have particle sizes of about 300 microns or less and can be added to the composite in concentrations of from 1 to as much as 50 percent, preferably from about 1 to 35 percent, by weight. There is less need for filler materials in the composite of this invention than in composites of the prior art because the aramid particles serve, to some extent, as filler materials. Filler materials are usually used for altering the coefficient of friction of

the composition. Of course, the concentration of filler materials depends entirely on the kind of filler and the reason for its use.

Aramid particles are made by comminuting aramid polymer to the desired size. For example, aramid polymer made in accordance with the teachings in previously-cited United States Patents No. 3,063,966 and 4,308,374 is finished in the form of a water-wet crumb which, for purposes of this invention, can be dried in a hammer mill to an average diameter of 100 to 250 microns. Once dried and pulverized, the aramid particles can be classified and particles of the desired size range can be isolated for use.

Inherent Viscosity (IV) is indication of the molecular weight of a polymer and is defined by the equation:

$$IV = \ln(h_{rel})/c$$

where c is the concentration (0.5 gram of polymer in 100 ml of solvent) of the polymer solution and h_{rel} (relative viscosity) is the ratio between the flow times of the polymer solution and the solvent as measured at 30°C in a capillary viscometer. The inherent viscosity values reported and specified herein for the aramid particles are determined using concentrated sulfuric acid (96% H_2SO_4). For practice of this invention, para-aramid particles should exhibit an IV of from about 4, or perhaps slightly lower, to 8 or higher. At least within that rather broad range of IV values, it appears that performance of the para-aramid particles is substantially independent of IV.

The aramid particles are combined with the fibers in such a way that the particles are intermingled with or coated on the individual fibers. Such a combination can be accomplished in a wet state by means of a hydropulper or in a dry state by means of mixing mills such as a turbulent air mill like a Turbomill, an Ultra-Rotor, or an Eirich mixer. It is often desirable to "open" the fibers by subjecting them to turbulent or shear forces before introducing the aramid particles. A Turbomill is described in United States Patent

No. 3,610,542 and is sold by Matsuzaka Company, Ltd., Tokyo. An Ultra-Rotor Mill is sold by Jackering GmbH & Co. KG, Germany. An Eirich mixer is a heavy-duty mixer with high speed blades in a closed, counter-rotating, vessel with a wall scraping bar resulting in high speed collesions of individual particles. Eirich mixers are sold by Eirich Machines, Inc., New York.

Once the combination of fibers and aramid particles has been made, that combination can be mixed with the matrix resin. Mixing with the matrix resin can be accomplished by a dry dispersion of all of the components, a liquid dispersion (such as in water) of all undissolved components, a dispersion of the fiber and particle components in a solution of the matrix resin, or by any other means utilized to make mixtures of materials. When the matrix resin is a thermoset resin, the combination of fibers and aramid particles can be blended with the components of the thermoset matrix resin recipe and subjected to a curing cycle appropriate for the particular matrix resin being used. It is, also, possible to use "staged" systems, such as in the case of phenolic resins wherein a blend can be made of an "A-stage" phenolic and the fiber/particle combination prior to finally and completely curing the composition.

When the matrix resin is a thermoplastic resin, the combination of fibers and aramid particles can be blended at a high concentration with the thermoplastic resin to make a concentrate for later blending with additional thermoplastic resin. The concentrate can be provided in some convenient size and shape such as by being formed into pellets; and then the pellets can be used as a source of fiber and particles in later applications. The concentrate is usually made having 5-35 weight percent particles and 5-20 weight percent fibers.

Description of the Preferred Embodiments

EXAMPLE 1

In this example, aramid particles of poly(p-phenylene terephthalamide) (PPD-T) were combined with other components to make friction materials of this invention; and those friction materials were compared with known friction materials using pulp of PPD-T and with a control material using no aramid at all (no fibers and no particles).

Novolac phenolic resin was used as a thermoset matrix resin for the friction materials of this example; and the composition recipes were as follow:

Compositions

	Example 1a (%)	Example 1b (%)	Comparative Ex. 1 (%)	Control (%)
Novolac Resin	16	16	16	16
Dolomite	50	50	50	52
Barite	15	15	15	16
Friction Particles	15	15	15	16
Aramid Particles	4	2	0	0
Pulp	0	2	4	0

The Dolomite had a particle size of less than 75 microns; the Barite had a particle size of less than 45 microns; and the Friction Particles had a particle size of less than 400 microns. The Friction Particles were made from cashew oil and were sold by Cardolite Corp. under the trade designation Cardolite NC104-40.

The Aramid Pulp was refined poly(p-phenylene terephthalamide) (PPD-T) fiber having a length of about 5 millimeters and a diameter of about 12 microns and sold by E. I. du Pont de Nemours & Co. under the trade designation KEVLAR aramid pulp.

The Aramid Particles were particles of PPD-T polymer having an inherent viscosity of about 6 g/dL and a variety of

average diameters from 75 to 250 microns. The particles were sized by sieving and the sizes are denoted as the maximum size in a range extending from 75 microns as the minimum.

The components of each composition were mixed to yield a substantially homogeneous mass of material. The aramid particles, the dolemite particles, the barite particles, and the friction particles were combined, dry, in a Littleford mixer, identified as Model 130D; and that was combined with the phenolic resin in a dry, particulate form. That composition was molded into composite articles for testing.

The molding was conducted by preforming the articles at room temperature at 2000 psi for one minute, heating from room temperature to 180°C at 2000 psi for 15 minutes and postcuring the molded article at 350°C at no pressure for 16 hours. The articles were tested in accordance with SAE-J-661-a - Brake Lining Quality Control Test Procedure (Chase Test for Friction and Wear). Results of the tests are set out in the table below.

TABLE 1

Examples	Wear (inch)	Thickness Loss (%)	Mass Loss (%)
Example 1a particle sizes			
210 microns (H)	0.008	3.20	3.28
150 microns (H)	0.010	2.69	1.77
125 microns (L)	0.005	1.97	2.08
125 microns (L)	0.004	1.57	1.79
Example 1b particle size			
250 microns (H)	0.005	1.91	1.89
150 microns (H)	0.004	1.58	1.65
125 microns (L)	0.003	1.20	1.68
125 microns (L)	0.005	1.99	1.68
Comparative (pulp only)			
pulp	0.008	3.83	1.02
pulp	0.007	2.89	3.12
pulp	0.007	2.71	1.97
Control	0.009	3.63	3.13

In the above table, example designation of "H" means that the PPD-T particles had a high inherent viscosity of at least 6.3 g/dL and designation "L" indicates the PPD-T particles had a low inherent viscosity of slightly less than about 5.5 g/dL. It appears that there is no significant difference between the high viscosity material and the low viscosity material.

EXAMPLE 2

In this example, as in Example 1, above, aramid particles of poly(p-phenylene terephthalamide) (PPD-T) were combined with other components to make friction materials of this invention. In this example, combinations of pulp and particles were used; and friction materials using those

2b	1.0	0.003	1.20
2c	1.6	0.003	1.19
2d	2.4	0.002	0.80
2e	3.0	0.003	1.18
2f	3.2	0.002	0.79
Control	0	0.007	2.89

EXAMPLE 3

In this example, compositions similar to those of the previous examples were made and tested in accordance with a Friction And Wear Test named the Kraus Test. The compositions were as set out below.

Compositions

Components	Examples 3a (%)	3b (%)	3c (%)	3d (%)	Control (%)
Novolac Resin	18	18	18	18	18
Filler	54	54	54	54	54
Fibers	19	19	19	19	19
Friction Modifiers	4	4	4	4	4
Aramid Particles	2.5	4.0	3.5	2.5	0
Pulp	2.5	1.0	1.5	2.5	5

The Novolac Resin composition included dry novolac and particulate rubber. The filler included magnesium oxide, barium sulfate, lime, graphite, zinc oxide, talc, and coke. The fibers included glass and mineral wool. The friction modifiers included alumina and particulate brass.

The aramid particles had a particular size of 125 microns and the aramid pulp was the same as that used in Example 1, above.

The Kraus Test and the Kraus Test Bench are described by A. Heiss et al. in "Technisches Messen atm" 43 (1976), issue 3, pages 91-100 in an article titled Automatic Test Bench for Determining The Coefficient of Friction of Brake Linings for Disk Brakes of Passenger Cars and Trucks.

TABLE 3

KRAUS TEST

Example	Pressure	Thickness Loss (mm)			Flexural Strength (N/mm)	
	(Kg/cm^2)	Front	Back	Total	Cold	180°C
3a	4	0.07	0.06	0.13	23	10
	6	0.16	0.13	0.24		
	8	0.27	0.21	0.48		
	TOTAL			0.85		
3b	4	0.07	0.05	0.12	27	12
	6	0.18	0.11	0.29		
	8	0.29	0.19	0.48		
	TOTAL			0.89		
3c	4	0.07	0.06	0.13	26	11
	6	0.17	0.13	0.30		
	8	0.30	0.22	0.52		
	TOTAL			0.95		
3d	4	0.07	0.05	0.12	28	11
	6	0.17	0.11	0.28		
	8	0.28	0.22	0.50		
	TOTAL			0.90		
Control	4	0.07	0.06	0.13	26	12
	6	0.16	0.13	0.29		
	8	0.30	0.22	0.52		
	TOTAL			0.94		

EXAMPLE 4

In this example, the effect of polymer particles was tested in composites utilizing thermoplastic matrix materials.

The composites of this invention were compared with a composite using floc of PPD-T about 1/2 inch long.

The thermoplastic matrix material was nylon 66 such as that sold under the trademark designation "Zytel 801" by E. I. du Pont de Nemours & Co. The particles were PPD-T as described in Example 1, above, with a size of 125 microns.

To prepare the composition of this invention and make test specimens for this example, the PPD-T particles were extruded with nylon in concentrations which varied from 5 to 30 percent based on the total weight of the composition.

In order to obtain a homogeneous dispersion of the floc in the matrix, for comparative purposes, the floc was extruded as a concentrate in the nylon at a concentration of about 15 to 35, weight, percent and that extruded product was cut into pellets for use in making the comparative test specimens for this example. The pellets were then extruded with nylon to overall floc fiber concentrations ranging from 5 to 30 percent based on the total weight of the composition.

The materials of this example were extruded into plaques 0.25" x 3" x 5"; and, using those extruded plaques, test washers were machined and tested in accordance with ASTM D3702-78 - Standard Test Method for Wear Rate of Materials in Self-Lubricating Rubbing Contact Using a Thrust Washer Testing Machine. The wear surface of the washers was maintained at least 0.020" below the molded surface of the plaques. Tests were conducted without lubrication in ambient room air against AISI 1018 carbon steel at 250 lb/in^2 and 10 ft/min. In these tests, there was, also, a variety of PPD-T particle sizes used to make the test compositions. The test results are shown in the Table, below.

TABLE 4

	Composition		Thrust Washer Wear		
Example	PPD-T (wt%)	Particle Size (μ)	Wear Factor* Mass	Wear Factor* Volume	Wear Rate **
4a	10	120	143	134	3.58
4b	17.5	60	143	144	3.57
4c	17.5	100	110	113	2.75
4d	17.5	120	53	41	1.33
4e	15	120	111	120	2.89
Control 1	20	floc	239	--	5.98
Control 2	33	glass	917	--	22.93
Control 3	0	--	785	806	19.60

* Units for the Wear Factor are $\frac{(in^3\text{-min})}{(ft\ lbs\text{-hr})} \times 10^{-10}$

** Units for the Wear Rate are (in/hr) X 10^{-5}

EXAMPLE 5

In this example, the effect of a combination of PPD-T polymer particles and 1 mm long PPD-T floc was tested in composites of this invention utilizing thermoplastic matrix materials. The composites of this invention were compared with a composite using 1 mm long floc of PPD-T, only.

The thermoplastic matrix material was the same nylon 66 as was used in Example 4. The particles were PPD-T as described in Example 1, above, with a size of 125 microns.

The composition of polymer particles and floc was made using particles and a concentrate of floc, prepared as described in Example 4. The composition was made and extruded with a particle concentration of 10% and a floc concentration of 5%, based on the total weight of the composition.

The materials of this example were extruded into plaques and the plaques were made into test washers and tested as described and under the conditions used, in Example 4.

The test results of the washers made in this example were that the Thrust Washer Wear was 5.2 for the mass wear factor, 13.0 for the volume wear factor, and 0.225 for the wear rate. Control washers of the matrix polymer with no additives exhibited a Wear Rate of 22.

In this example, it is seen that the combination of particles with short floc, only 1 mm long, yields especially good results. The short floc can be compounded directly into the matrix polymer and can be, thereby, more uniformly distributed. Uniform fiber distribution results in increased heat deflection temperatures.

EXAMPLE 6

In this example, compositions of this invention using glass fibers and PPD-T polymer particles in a thermoplastic matrix were tested against compositions using glass fibers, only, in a thermoplastic matrix.

The thermoplastic matrix material was the same nylon 66 as was used in Example 4. The particles were PPD-T as described in Example 1, above, with a size of 120 microns. The glass fibers were about 3 mm long.

The composition using the glass fibers and the particles was made by the same process as was used in Example 4. Several compositions of this invention were made and extruded with a particle concentration of 15 weight percent with 13 and 43 weight percent glass fibers. The control compositions were made and extruded having no particles and glass concentrations of 13 and 43 weight percent, based on the total weight of the composition.

The materials of this example were extruded into plaques and the plaques were made into test washers and tested as described, and under the conditions used, in Example 4. The test results are shown in the Table, below.

TABLE 5

Example	Composition PPD-T (Wt %)	Composition Glass (Wt %)	Wear Factor Mass	Wear Factor Volume	Wear Rate
6a	15	13	118	125	3.03
Control	0	13	240	237	5.96
6b	15	43	222	224	5.57
Control	0	43	245	243	6.10
6c	15	0	111	120	2.89

EXAMPLE 7

In this example, compositions of PPD-T particles in a thermoplastic matrix were tested with a wide range of PPD-T particle concentrations.

The thermoplastic matrix material was nylon 66 from a product sold under the trademark designation "Zytel 103HS" by E. I. du Pont de Nemours & Co. The particles were PPD-T, as described in Example 1, above, with a size of 120 microns.

The composition using the particles was made by the same extruding process as was used in Example 4. Compositions having wide range of PPD-T particle concentrations were made and extruded into plaques and the plaques were made into test washers and tested as described, and under the conditions used, in Example 4. The test results are shown in the table below.

TABLE 6

Example	Composition PPD-T (Wt %)	Wear Factor Mass	Wear Factor Volume	Wear Rate
7a	0	911	921	22.9
7b	1	490	498	12.35
7c	3	381	352	9.16
7d	5	408	397	10.06
7e	15	111	120	2.89
7f	30	131	117	3.10

EXAMPLE 8

In this example, compositions of this invention were tested using PPD-T polymer particles in a thermoplastic matrix. Those compositions were compared with controls of the matrix, alone, and compositions using PPD-T floc in the matrix.

The thermoplastic matrix material was acetal resin such as that sold under the trademark designation "Celon M90" by Celanese. The particles were PPD-T as described in Example 1, above, with a size of 125 microns. The floc was about 4 mm long; and the composition using floc was made from a concentrate prepared in the same way as was described in Example 4.

The composition of the invention was made and extruded with a particle concentration of 17.5%, based on the total weight of the composition. The composition of the control using PPD-T floc, alone, was made and extruded with a floc concentration of 15%, based on the total weight of the composition.

The materials of this example were extruded into plaques and the plaques were made into test washers and tested as described, and under the conditions used, in the Example 4. The test results are shown in the Table, below. Thrust Washer Wear tests were conducted without lubrication in ambient room air against AISI 1018 carbon steel at 500 lb/in^2 and 10 ft/min. In these tests, there were, also, two PPD-T particle sizes used to make the test compositions

TABLE 7

	Composition		Thrust Washer Wear		
	PPD-T	Particle			Wear
Example	(wt%)	Size (u)	Wear Factor		Rate
			Mass	Volume	
8a	17.5	250	40	42	2.00
8b	17.5	150	29	33	1.45
Control 1	15.0	(floc)	78	--	3.90
Control 2	0	--	44	44	2.20

The claims defining the invention are as follows:

1. A composite material comprising:

a) 10 to 95 percent, by weight, matrix resin;

b) 1 to 40 percent, by weight, fiber reinforcing material;

c) 1 to 65 percent, by weight, aramid particles having no tentacle-like projections thereon, and having an average diameter of 75 to 250 microns, wherein the weight ratio of aramid particles to fiber reinforcing material is greater than 1:4.

2. The composite of Claim 1 wherein the weight ratio of aramid particles to fiber reinforcing material is 1:4 to 4:1.

3. The composite of Claim 1 wherein the matrix resin is selected from the group consisting of thermoset resin and thermoplastic resin.

4. The composite of Claim 1 wherein the fiber reinforcing material selected from the group consisting of aramid and aramid floc from 1 to 6 mm in long dimension.

5. The composite of Claim 1 wherein the aramid particles are poly(p-phenylene terephthalamide).

6. The composite of Claim 1 wherein the matrix resin is a thermoset phenolic material and the fiber reinforcing material is poly(p-phenylene terephthalamide).

7. The composite of Claim 6 wherein the aramid particles are poly(p-phenylene terephthalamide).

8. A process for making a composite comprising the steps of homogeneously combining aramid particles having no tentacle-like projections thereon, and of 75 to 250 microns in average diameter and fiber reinforcing material from 1 to 6 mm in long dimension in a weight ratio of greater than 1:4 and blending

combinations were compared with known friction materials using pulp of PPD-T, only. The particles used in this example had a particle size of 125 microns.

Novolac phenolic resin was used as a thermoset matrix resin for the friction materials of this example; and the composition recipes were as follow:

Compositions

EXAMPLE

	2a (%)	2b (%)	2c (%)	2d (%)	2e (%)	2f (%)	Control (%)
Novolac Resin	16	16	16	16	16	16	16
Dolomite	50	50	50	50	50	50	50
Barite	15	15	15	15	15	15	15
Friction Particles	15	15	15	15	15	15	15
Aramid Particles	0.8	1.0	1.6	2.4	3.0	3.2	0
Pulp	3.2	3.0	2.4	1.6	1.0	0.8	4

The components for this example were the same as those used in Example 1, above.

The components of each composition were mixed and molded as in Example 1, above.

The articles were tested in accordance with SAE-J-661 - the Chase Test for Friction and Wear. Results of the tests are set out in the table below.

that combination with a matrix resin to yield a composite having

a) 10 to 95 percent, by weight, matrix resin;

b) 1 to 40 percent, by weight, fiber reinforcing material;

c) 1 to 65 percent, by weight, aramid particles.

9. The process of Claim 8 wherein the weight ratio of aramid particles to fiber reinforcing material is 1:4 to 4:1.

D A T E D this 2nd day of August, 1995.

E.I. DU PONT DE NEMOURS AND COMPANY

By their Patent Attorneys:

CALLINAN LAWRIE

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/06802

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 F16D69/02; C09K3/10; C08J5/14

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	F16D ; C09K ; C08J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	DE,A,3 637 022 (AKEBONO) 7 May 1987 see page 1, line 40 - line 66	1-9
Y	FR,A,2 532 243 (BORG WARNER) 2 March 1984 see page 3, line 15 - page 4, line 17 see examples 2,4 see page 8, line 6 - line 13	1-9
Y	FR,A,2 532 385 (BORG WARNER) 2 March 1984 see page 4, line 25 - line 31 see page 5, line 7 - page 6, line 4	1-9

-/--

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
18 NOVEMBER 1992	25. 11. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BOULON A.F.J.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	EP,A,0 034 258 (TEIJIN LTD) 26 August 1981 see page 3, line 17 - line 34 see page 9, line 17 - line 30 see page 11, line 18 - line 37 see page 12, line 24 - line 29 see page 14, line 7 - line 13	1-9
Y	EP,A,0 074 838 (THIOKOL) 23 March 1983 cited in the application see page 5, line 19 - line 27 see page 10, line 28 - page 11, line 23	1-9
A	DE,A,3 735 634 (GOETZE AG) 3 May 1989 see claims 1-6	1-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9206802 SA 63990

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 18/11/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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FR-A-2532243	02-03-84	GB-A- 2125451	07-03-84
		DE-A- 3231254	23-02-84
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