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(54) Title: SLURRY TECHNIQUE FOR PRODUCING FLUOROPOLYMER COMPOSITES

FIG. 1A

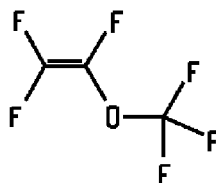


FIG. 1B

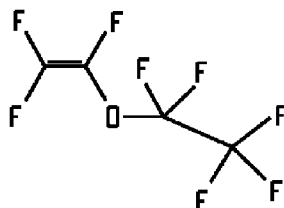
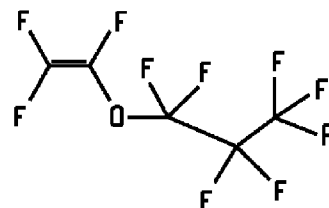


FIG. 1C



(57) Abstract: A fluoropolymer composite comprising at least one fluoropolymer and particulate filler material is formed using a slurry process, in which the particulate filler material is first dispersed in a polar organic liquid, which is then combined with a suitable particulate fluoropolymer. The combination is dried to form a composite powder material. The composite powder material, with optional addition of another fluoropolymer, is processed to form a fluoropolymer composite body. The process can be carried out with either melt-processible or non-melt-processible fluoropolymers.



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TITLE**Slurry Technique for Producing
Fluoropolymer Composites**

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CROSS-REFERENCE TO RELATED APPLICATION

The present application claims benefit of US Provisional Patent Application Serial No. 61/486,083, filed May 13, 2011, which is incorporated
10 herein in the entirety for all purposes by reference thereto.

Technical Field

This invention relates to composite materials and, more particularly, to a process for producing a powder composite material comprising a
15 fluoropolymer matrix and particulate filler material dispersed therein using a slurry technique, as well as a fluoropolymer composite body produced with the powder composite material.

Background

20 The low-friction properties of many fluoropolymers have long been known and have led to application of these materials as one or both of the facing surfaces of a low-friction couple. Fluoropolymers are attractive for a variety of applications because they are relatively inert against a wide variety of chemical substances, have high melting points, and are generally
25 biocompatible. Fluoropolymers, often in the form of finely divided powders that may be dispersed in liquid or solid carriers, also have been used as lubricants for other bearing surfaces.

However, known fluoropolymers used as lubricants and bearing surfaces generally have been found to exhibit very poor wear resistance, which often mitigates the benefit of their low friction characteristics and other desirable physical and chemical properties. For example, an operating
5 mechanism that includes a bearing surface made of a material having low wear resistance may have to be given frequent maintenance, often involving down-time and replacement of parts, to prevent actual failure and potentially catastrophic consequences. Production efficiency and machine utilization may be adversely affected. In some cases, the critical nature of some
10 function precludes use of a fluoropolymer bearing surface that might fail in favor of a more expensive approach that may involve other detriments.

In the case of a friction couple of the widely-used polymer polytetrafluoroethylene (PTFE) and a hard surface such as a metal, it is found that the PTFE often acts as a transfer lubricant. Relative mechanical motion
15 between the PTFE and the facing hard surface causes a transfer layer of PTFE to be continually built up on the hard surface, so that the immediate bearing contact effectively is between PTFE on both surfaces. However, as soon as the transfer layer reaches a modest thickness, flake-like portions of the transfer surface typically begin to break off as wear debris. As
20 mechanical motion continues, additional material is transferred from the bulk PTFE member, only to be shed as additional wear debris, signaling poor durability and a high wear rate of the PTFE bearing material.

The sliding friction and wear resistance characteristics of materials are frequently specified quantitatively by a coefficient of friction μ (sometimes
25 termed a coefficient of sliding friction) and a coefficient of wear resistance k . These quantities are conventionally defined by the following equations:

$$\mu = \frac{F_d}{F_n} \quad (1)$$

$$k = \frac{V}{F_n \times d} \quad (2)$$

wherein F_d is the frictional resistance force that must be overcome in moving

an object subjected to a force F_n applied in a direction normal to the motion direction. V is the volume of material removed and d is the total sliding distance over the course of a wear exposure. Typically k is reported in units of $\text{mm}^3/\text{N}\cdot\text{m}$, whereas μ is inherently a dimensionless ratio. In many cases, it is found that an initially high wear rate is followed by steady-state behavior corresponding to a relatively constant wear rate, so that reported values of k ordinarily refer to the steady-state behavior. Ideally, a bearing surface material has a low value of μ and a low value of k , signaling low friction and good wear resistance.

There have been numerous attempts to incorporate particulate and fibrous materials into fluoropolymer matrices to improve their friction and wear resistance characteristics. In some cases, modestly improved wear resistance results, but often at the cost of an increased coefficient of friction. The portion of particulate filler required to improve wear resistance is often substantial.

Among the particulate fillers that have been considered for PTFE are particles of hard materials such as refractory metal oxides. Typically, these additions have improved wear resistance by at most a factor of about a hundred over that of pure PTFE. However, in many cases the wear surface after use is decorated with the hard particles, which are large enough and protrude sufficiently to scratch the facing surface. These particulate fillers also typically increase μ .

It has been found that incorporation of particles of certain types in PTFE reduces the propensity for the material to scratch the facing surface, but there are conflicting results as to how much the wear resistance can be improved. There is no basis presently for identifying and predicting the effect of particulate fillers on the critical physical properties, including wear resistance, as many of the additions tried have led to only a modest improvement, generally at most about one to two orders of magnitude, in wear resistance k over that of the PTFE matrix without any such additions.

One of the persistent problems in creating composites comprising particulate fillers in a polymer matrix is the difficulty of assuring that the filler is distributed in the matrix with sufficient uniformity, especially in matrices that are not melt-processible. The difficulty of dispersing particles is widely
5 regarded as increasing as the particle size decreases. Small particles readily agglomerate, especially when in dry form. It often requires significant energy and/or a surfactant to disperse them adequately.

Consequently, there remains a need for processes capable of uniformly dispersing small particles in a wide range of polymer systems, especially
10 fluoropolymer systems.

Summary

In an aspect, there is provided a process for forming a composite
15 powder material comprising: (a) creating a particle dispersion of particulate filler material in a polar organic liquid; (b) mixing the particle dispersion with fluoropolymer particles to form a precursor slurry; and (c) drying the precursor slurry by removing the polar organic liquid to form the composite powder material, wherein the particulate filler material is associated with a surface of
20 the fluoropolymer particles.

Another aspect provides a process for manufacturing a fluoropolymer composite body comprising: (a) creating a composite powder material by a process comprising: (i) creating a particle dispersion of particulate filler material in a polar organic liquid, (ii) mixing the particle dispersion with
25 fluoropolymer particles to form a precursor slurry, and (iii) drying the precursor slurry by removing the polar organic liquid to form the composite powder material, wherein the particulate filler material is associated with a surface of the fluoropolymer particles; and (b) forming the composite powder material into the fluoropolymer composite body.

30 Still another aspect provides a process for manufacturing a

fluoropolymer composite body comprising: (a) creating a composite powder material by a process comprising: (i) creating a particle dispersion of particulate filler material in a polar organic liquid, (ii) mixing the particle dispersion with particles of a first fluoropolymer to form a precursor slurry, and
5 (iii) drying the precursor slurry by removing the polar organic liquid to form the composite powder material, wherein the particulate filler material is associated with the surface of the particles of the first fluoropolymer; (b) combining particles of a second fluoropolymer with the composite powder material; and (c) melt processing the composite powder material and second fluoropolymer
10 particles to form the fluoropolymer composite body.

Further provided are fluoropolymer composite bodies made by any of the foregoing processes.

15 Brief Description of the Drawings

The invention will be more fully understood and further advantages will become apparent when reference is had to the following detailed description of the preferred embodiments of the invention and the accompanying drawing, in which:

20 FIGS. 1A – 1C are structures of certain perfluoroolefin monomers useful in the practice of the present process; and

FIGS. 2A and 2B are microradiographs of fluoropolymer composite bodies created by the present slurry process and a jet-milling process, respectively.

25

Detailed Description

An aspect of the subject matter hereof provides a slurry-based technique for dispersing particulate filler material in a fluoropolymer matrix and
30 the composite powder material produced thereby. In an embodiment, the

particulate filler material is first dispersed in a polar organic liquid. The particle dispersion is then mixed with fluoropolymer particles and the combination is processed to create a precursor slurry in which the particulate filler material is substantially uniformly dispersed. The slurry is then dried,
5 typically vacuum and/or heating, to form a composite powder material, in which the filler particles are associated with the surface of the fluoropolymer particles. The composite powder material preferably is free flowing. In some embodiments, the filler particles may be submicron or nanoscale particles.

The foregoing composite powder material may then be employed to
10 create a fluoropolymer composite body. In different implementations, the fluoropolymer particles in the composite powder material may be either melt-processible or not melt-processible. The fluoropolymer composite body may be formed directly from the composite powder material; or alternatively, the composite powder material may be combined with additional fluoropolymer
15 particles of the same or different type for processing into the final fluoropolymer composite body. Typically a molding and sintering operation is used for bodies that contain all non-melt processible fluoropolymer particles. Bodies containing a sufficient amount of melt processible fluoropolymer can be formed using known melt processing techniques.

20 In an implementation of one of the processes hereof, the particle dispersion is formed by combining the particulate filler material and the polar organic liquid in a suitable vessel and then imparting mechanical energy to the combination. In an embodiment, the mechanical energy is provided by sonication, meaning an exposure to a source of ultrasonic energy.
25 Preferably, the intensity and time of the exposure is sufficient to cause the particulate filler material to become substantially fully dispersed in the polar organic liquid. Alternatively, the energy may be supplied by any other suitable high-energy mixing technique, including without limitation high vortex or high shear mixing.

30 A variety of polar organic liquids are useful in creating the particle

dispersion and precursor slurry from which the present composite powder material and fluoropolymer composite body are produced. Suitable polar organic liquids include, but are not limited to, lower alcohols, such as methanol, ethanol, isopropanol (IPA), *n*-butanol, and *tert*-butanol. In some
5 embodiments, IPA is preferred. Other polar organic liquids are useful as well, including *N,N*-dimethylacetamide (DMAc), esters, or ketones.

 Ideally, the particle dispersion remains stable for a time sufficient for the formation of the dried composite powder material. Various effects, including filler particle shape, size, and composition, and the polar organic liquid used,
10 alter the forces governing particle interactions, and thus the stability of the particle dispersion.

 The present slurry-based process is found to promote better dispersion of particles in a composite powder material than previous techniques such as jet-milling and typically does not have a deleterious effect on the fluoropolymer
15 itself.

 A precursor slurry is then formed by combining the particulate filler dispersion and particles of a desired fluoropolymer. The term "particle," as used herein with reference to fluoropolymer compositions, refers to any divided form, including, without limitation, powder, fluff, granules, shavings,
20 and pellets. The fluoropolymer particles may have any characteristic dimensions consistent with adequate blending and dispersion of the particulate filler material in a final composite body produced using the composite powder material. In an embodiment, the fluoropolymer particles may have characteristic dimensions ranging from about 100 nm to several
25 mm. It has been found that in some embodiments smaller fluoropolymer particles are beneficially employed to promote good dispersion of the particulate filler material. It is believed that initially improving the dispersion of the particulate filler on the starting fluoropolymer particles ultimately results in a more uniform dispersion of the particulate filler material in the final
30 composite body. Attaining a good dispersion of the particulate filler material

in the polar organic liquid (by sonication or other like mixing technique) permits the particulate filler then to be well dispersed on the fluoropolymer particles with minimal agglomeration. Ordinarily a good dispersion then can be maintained through subsequent processing, including production of the composite powder material and the final fluoropolymer composite body. The present slurry technique is believed to be particularly effective when used to disperse submicron and nanoscale particulate filler material.

The microradiographs of FIGS. 2A and 2B provide evidence of the improvement in dispersion attained by using the present slurry process. The images were obtained by placing specimens of fluoropolymer composite bodies between an x-ray source and a two-dimensional detector, which records the intensity of the beam transmitted through each sample as a function of position in a projected plane perpendicular to the vector connecting the center of the source to the center of the detector. The intensity recorded at any point is governed by the x-ray absorption of the object along the path from the source to the detector. The x-ray absorption is in turn affected by three variables: the length of the path through the object, the mass density, and the elemental composition along the propagation path. Thus, a body that is completely homogeneous and uniform at a length scale comparable to the detector area resolution will give rise to a microradiograph that has no contrast or intensity variation. A body that is not homogenous or not uniform at this length scale will produce an image having perceptible intensity variation. (The images of FIGS. 2 were acquired with a configuration and conditions that gave a resolution of about 800 nm.)

The samples producing the images of FIGS. 2 were prepared as fluoropolymer composite bodies using composite powder materials combining the same starting materials, i.e. TEFLON® PTFE 7C with 5.0 wt.% of alumina addition. The additive and PTFE of the FIG. 2B sample were combined by a jet milling process, whereas the materials for the FIG. 2A sample were combined by an IPA slurry process according to the present disclosure.

Comparison of the images, which both represent about a 2 mm × 2 mm projection, reveals significant intensity variation across the FIG. 2B image for the jet milled sample, whereas the FIG. 2A image of the IPA slurry sample shows far less intensity variation. The large intensity variation in the FIG. 2B
5 image establishes that different volumes of the sample have different radiographic density, in turn indicating the presence of different proportions of the polymer and the filler at the length. The relatively uniform intensity of the FIG. 2A image indicates that there are few if any regions in which there are different proportions, thus demonstrating that a far better dispersion was
10 obtained in the consolidated, composite body comprising material made with the slurry technique.

The initial particle dispersion may be formed with any concentration of the particle substance in the polar organic liquid that is consistent with adequate dispersion. However, for the sake of minimizing the energy
15 consumed in the process, the amount of particulate filler material in the polar organic liquid is preferably maximized, consistent with adequate dispersion. Such a choice of formulation minimizes the amount of the polar organic liquid that must later be removed. In an implementation, the particle dispersion may contain particulate filler material in an amount up to about 10 wt.%, up to about
20 8 wt.%, up to about 5 wt.%, or up to about 2 wt.%, based on the total liquid dispersion. A higher concentration of the particulate filler material can alternatively be used, consistent with maintaining a good dispersion and avoiding gelation for filler types prone to this phenomenon. It is desirable for there to be sufficient solvent in the particle dispersion to achieve adequate
25 wetting of the fluoropolymer particles after the components are mixed to form the slurry. The removed liquid may be recycled, burned to recover its latent energy, or otherwise disposed.

The particle dispersion is then combined with an amount of fluoropolymer required to produce the desired loading of the particulate filler
30 material in the dried composite powder material. Depending on the end use,

particulate filler material is present in the dried composite powder material in an amount such that the final loading of the filler particles in the composite fluoropolymer body may range from about 0.1 wt.% to about 50 wt.%. In another embodiment, the final loading of filler material in the fluoropolymer
5 may be about 0.1 to 30 wt.%. In still other embodiments, the final loading of the filler material may be about 0.1 to 20 wt.%, about 0.1 to 10 wt.%, about 0.5 to 10 wt.%, or about 1 to 8 wt.%. Too high a loading may compromise mechanical properties of the composite body, such as tensile strength and toughness. While a low loading may beneficially improve such strength
10 properties, the loading may be chosen to produce concomitantly a sufficient improvement in wear properties over an unloaded fluoropolymer body. Specific loading ranges of the particulate filler material consistent with good mechanical properties and wear properties are of course dependent on the type of filler and fluoropolymer used.

15 The processes hereof may be carried out using a wide variety of materials as the particulate filler. Non-limiting examples of particulate filler material that may be incorporated in the present composite powder material include both metals and inorganic substances, which may be prepared by a wide variety of techniques that either produce the desired particle
20 conformation directly or entail post-processing to alter the initial conformation. Suitable processes include, but are not limited to, chemical synthesis, gas-phase synthesis, condensed phase synthesis, high speed deposition by ionized cluster beams, consolidation, deposition and sol-gel methods, as well as processes that use grinding, crushing, milling, or other mechanical
25 processes to make small particles from larger precursors.

Exemplary metals include, but are not limited to, iron, nickel, cobalt, chromium, vanadium, titanium, molybdenum, aluminum, the rare earth metals, and alloys thereof, including steels and stainless steels. Non-limiting
examples of inorganic substances include: oxides of silicon, aluminum,
30 titanium, iron, zinc, zirconium, alkaline earth metals, and boron; nitrides of

boron, aluminum, titanium, and silicon; borides of rare earth metals such as lanthanum; carbides of silicon, boron, iron, tungsten, and vanadium; sulfides of molybdenum, tungsten, and zinc; fluorides of alkaline earth and rare earth metals; submicron and nanoscale carbon-based materials, including graphitic materials such as graphenes and graphite oxides that are optionally chemically functionalized, carbon black, carbon fiber, nanotubes, and spherical, C₆₀-based materials; and mixed oxides and fluorides, by which are meant compounds containing at least two cations other than the oxygen or fluorine. Exemplary mixed oxides include silicates, vanadates, titanates, and ferrites, as well as natural or synthetic clays in either platy or rod-like forms. Either a single particulate material or a combination of more than one particulate material may be incorporated as the particulate filler material, and it is to be understood that the materials herein enumerated may include dopants or incidental impurities.

The particles of the filler material may have any shape, including irregular particles and high or low aspect ratio particles such as needles, rods, whiskers, fibers, or platelets. In some embodiments, the particles have a size distribution with at least one submicron dimension. The particle shapes may be round or faceted and may be substantially fully dense or have some degree of porosity. Faceted shapes may include needle-like sharp points or multiple, substantially planar faces.

In some embodiments, the particulate fillers are composed of individual primary particles, while in other embodiments, some or all of the particulate filler comprises aggregated or agglomerated primary particles. As used herein, the term “aggregated particle” refers to a structure comprising smaller particles that are relatively strongly associated by chemical bonding, such as by fusion or the like. For example, such an aggregation may result from the techniques used to prepare particulate filler material.

The term “agglomerated particle” refers to a structure in which smaller particles are relatively weakly bound together by physical forces. As known to

one of ordinary skill, individual particles in an ensemble tend to agglomerate due to physical forces such as electrostatic and van der Waals interactions. The propensity for such agglomeration depends on the particle type and environmental conditions, but typically is heightened as the particle size
5 decreases.

Ensembles containing either agglomerated or aggregated particles can often be processed to break some or all of the linkages by imparting sufficient energy, resulting in a change in particle size distribution. For example, the particle ensemble may be placed in a suitable solvent and subjected to
10 ultrasonication, high-shear mixing, or the like. Upon increasing the energy imparted, the apparent minimum particle size generally decreases until it reaches a limiting minimum value. A surfactant is sometimes included in the solvent to impede re-agglomeration of the particles. Operationally, the smallest particles thus obtained are frequently regarded as "primary particles"
15 and their size may be termed "primary particle size." The measurement of this size is commonly obtained from static or dynamic light scattering measurements, which are described below.

The present process may be used to disperse additive particles having a wide range of sizes in the composite powder material. A number of
20 techniques are known in the art for characterizing the size of small particles, whether as primary particles, agglomerates, or aggregates, by either direct or indirect measurements.

In one approach to particle characterization, direct imaging, e.g. using scanning or transmission electron microscopy, permits individual particles to
25 be imaged and sized directly. Image analysis techniques can be applied to electron micrographs to quantify size distributions and shape characteristics, such as the departure from sphericity. However, skilled interpretation may be needed to establish that the images observed are representative of a larger amount of material, to identify other crucial features, such as porosity, and to
30 ascertain whether the object being visualized is a primary particle or an

association of multiple primary particles, e.g. particles that have agglomerated or are joined more rigidly.

Other approaches may be used to characterize larger amounts of sample to determine ensemble averages and size distributions. For example, various radiation scattering techniques, including small-angle x-ray and neutron scattering and static and dynamic light scattering also can be used, although broad or multimodal distributions and irregular shaped particles or distributions of shape complicate interpretation of the scattering data.

Various statistical characterizations can be derived from particle distribution data obtained using either dynamic or static light scattering. The d_{50} or median particle size by volume is commonly used to represent the approximate particle size. Other common statistically derived measures of particle size include d_{10} and d_{90} . It is to be understood that 10 vol.% and 90 vol.% of the particles in the ensemble have a size less than d_{10} and d_{90} , respectively. These values can provide additional characterization of a particle distribution, which is especially useful for a distribution that is not symmetrical, or is multimodal, or complex.

Still other approaches for characterizing particle size rely on even more indirect methods. For example, a widely-used indirect method is the Brunauer-Emmett-Teller (BET) technique, which provides a determination of the aggregate effective surface area of a known mass of particles, based on a measurement of the amount of gas that can be adsorbed on the surface of the ensemble of particles. The amount of gas is used to calculate a specific surface area of the ensemble (area per unit mass). By assuming the ensemble to consist of monodisperse, fully dense spheres, a characteristic size may be inferred. It will be appreciated that for BET measurements, the larger the surface area the smaller the equivalent or characteristic size. However, particle sizes inferred from a BET measurement will be smaller than values obtained from other direct or indirect techniques for particles that feature porosity or jagged or otherwise irregular surfaces.

In some embodiments, the filler used in the present composition and method comprises submicron particles or nanoparticles. As used herein, the term "submicron particle" refers to a particle that is part of an ensemble of like particles having a size distribution, as measured in at least one dimension, that is characterized by a d_{50} value (median size) of at most 0.5 μm (500 nm). The term "nanoparticle" refers to a particle that is part of an ensemble of like particles having a size distribution in at least one dimension that is characterized by a d_{50} value of at most 0.1 μm (100 nm). Nanoparticles thus fall within the larger class of submicron particles.

It is to be noted that different techniques can give different apparent size results for the same particles. In some instances, the differences are subtle, but in others, more pronounced, e.g., for ensembles in which the particles are non-spherical, irregularly shaped, multi-modal, or not fully dense. For example, dynamic light scattering measurements of submicron particle ensembles typically are insensitive to the presence of particles above 1 μm , such as particles resulting from the aggregation or agglomeration of smaller primary particles, which may be revealed in micrographs or in static light scattering. Particles in such ensembles are nevertheless regarded as submicron particles useful in the practice of the present invention, provided that their d_{50} values are less than 500 nm.

Fluoropolymers

Fluoropolymers are used herein to prepare a polymeric composite by admixture with a metal oxide or other suitable particulate filler material. For that purpose an individual fluoropolymer can be used alone; mixtures or blends of two or more different kinds of fluoropolymers can be used as well. Fluoropolymers useful in the practice of this invention are prepared from at least one unsaturated fluorinated monomer (fluoromonomer). A fluoromonomer suitable for the present processing preferably contains at least about 35 wt.% fluorine, and preferably at least about 50 wt.% fluorine, and can

be an olefinic monomer with at least one fluorine or fluoroalkyl group or fluoroalkoxy group attached to a doubly-bonded carbon. In one embodiment, a fluoromonomer suitable for use herein is tetrafluoroethylene (TFE).

An especially useful fluoropolymer is thus polytetrafluoroethylene (PTFE), which refers to (a) polymerized tetrafluoroethylene by itself without any significant comonomer present, *i.e.* a homopolymer of TFE, and (b) modified PTFE, which is a copolymer of TFE with such small concentrations of comonomer that the melting point of the resultant polymer is not substantially reduced below that of PTFE (reduced, for example, by less than about 8%, less than about 4%, less than about 2%, or less than about 1%). Modified PTFE contains a small amount of comonomer modifier that improves film forming capability during baking (fusing). Comonomers useful for such purpose typically are those that introduce bulky side groups into the molecule, and specific examples of such monomers are described below. The concentration of such comonomer is preferably less than 1 wt.%, and more preferably less than 0.5 wt.%, based on the total weight of the TFE and comonomer present in the PTFE. A minimum amount of at least about 0.05 wt.% comonomer is preferably used to have a significant beneficial effect on processability. The presence of the comonomer is believed to cause a lowering of the average molecular weight.

PTFE (and modified PTFE) typically have a melt creep viscosity of at least about 1×10^6 Pa•s and preferably at least about 1×10^8 Pa•s. With such high melt viscosity, the polymer does not flow in the molten state and therefore is not a melt-processible polymer. The measurement of melt creep viscosity is disclosed in col. 4 of U.S. Patent 7,763,680. The high melt viscosity of PTFE arises from its extremely high molecular weight (Mw), *e.g.* at least about 10^6 . Additional indicia of this high molecular weight include the high melting temperature of PTFE, which is at least 330 °C, usually at least 331 °C and most often at least 332 °C (all measured on first heat). The non-melt flowability of the PTFE, arising from its extremely high melt viscosity,

manifests itself as a melt flow rate (MFR) of 0 when measured in accordance with ASTM D 1238-10 at 372 °C and using a 5 kg weight. This high melt viscosity also leads to a much lower heat of fusion obtained for the second heat (e.g. up to 55 J/g) as compared to the first heat (e.g. at least 75 J/g) to melt the PTFE, representing a difference of at least 20 J/g. The high melt viscosity of the PTFE reduces the ability of the molten PTFE to recrystallize upon cooling from the first heating. The high melt viscosity of PTFE enables its standard specific gravity (SSG) to be measured by forming a solid body, termed an SSG sample. A measurement procedure appointed for measurement of SSG is set forth in ASTM Standard D 4894-07 and also described in U.S. Patent 4,036,802. The technique includes sintering the SSG sample in a free standing configuration (without containment) above its melting temperature without change in dimension of the SSG sample. The SSG sample does not flow during the sintering.

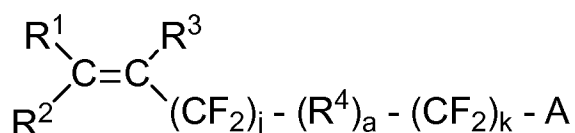
Low molecular weight PTFE, commonly known as PTFE micropowder, is distinguished from the PTFE described above. The molecular weight of PTFE micropowder is low relative to PTFE, *i.e.* the molecular weight (M_w) is generally in the range of 10^4 to 10^5 . The result of this lower molecular weight of PTFE micropowder is that it has fluidity in the molten state, in contrast to PTFE which is not melt flowable. The melt flowability of PTFE micropowder can be characterized by a melt flow rate (MFR) of at least about 0.01 g/10 min, preferably at least about 0.1 g/10 min, more preferably at least about 5 g/10 min, and still more preferably at least about 10 g/10 min., as measured in accordance with ASTM Standard D 1238-10, at 372 °C using a 5 kg weight on the molten polymer.

While PTFE micropowder is characterized by melt flowability because of its low molecular weight, the micropowder by itself is not melt fabricable, *i.e.* an article molded from the melt of PTFE micropowder has extreme brittleness, and an extruded filament of PTFE micropowder is so brittle that it breaks upon flexing. Because of its low molecular weight (relative to non-melt-flowable

PTFE), PTFE micropowder has no strength, and compression molded plaques for tensile or flex testing generally cannot be made from PTFE micropowder because the plaques crack or crumble when removed from the compression mold, which prevents testing for either the tensile property or the MIT Flex Life.

5 Accordingly, the micropowder is assigned zero tensile strength and an MIT Flex Life of zero cycles. In contrast, PTFE is flexible, rather than brittle, as indicated for example by an MIT flex life [ASTM D-2176-97a(2007)], using an 8 mil (0.21 mm) thick compression molded film] of at least 1000 cycles, preferably at least 2000 cycles. As a result, PTFE micropowder finds use as
 10 a blend component with other polymers such as PTFE itself and/or copolymers of TFE with other monomers such as those described below.

In other embodiments, a fluoromonomer suitable for use herein, either by itself to prepare a homopolymer or in copolymerization with other comonomers such as TFE, can be represented by the structure of the
 15 following Formula I:



I

wherein R^1 and R^2 are each independently selected from H, F, and Cl;
 20 R^3 is H, F, or a $\text{C}_1\sim\text{C}_{12}$, or $\text{C}_1\sim\text{C}_8$, or $\text{C}_1\sim\text{C}_6$, or $\text{C}_1\sim\text{C}_4$ straight-chain or branched, or a $\text{C}_3\sim\text{C}_{12}$, or $\text{C}_3\sim\text{C}_8$, or $\text{C}_3\sim\text{C}_6$ cyclic, substituted or unsubstituted, alkyl radical; R^4 is a $\text{C}_1\sim\text{C}_{12}$, or $\text{C}_1\sim\text{C}_8$, or $\text{C}_1\sim\text{C}_6$, or $\text{C}_1\sim\text{C}_4$ straight-chain or branched, or a $\text{C}_3\sim\text{C}_{12}$, or $\text{C}_3\sim\text{C}_8$, or $\text{C}_3\sim\text{C}_6$ cyclic, substituted or unsubstituted, alkylene radical; A is H, F, or a functional group; a is 0 or 1; and j and k are
 25 each independently 0 to 10; provided that, when a, j and k are all 0, at least one of R^1 , R^2 , R^3 , and A is not F.

An unsubstituted alkyl or alkylene radical as described above contains no atoms other than carbon and hydrogen. In a substituted hydrocarbyl radical, one or more halogens selected from Cl and F can be optionally substituted for one or more hydrogens; and/or one or more heteroatoms
5 selected from O, N, S and P can optionally be substituted for any one or more of the in-chain (*i.e.* non-terminal) or in-ring carbon atoms, provided that each heteroatom is separated from the next closest heteroatom by at least one and preferably two carbon atoms, and that no carbon atom is bonded to more than one heteroatom. In other embodiments, at least 20%, or at least 40%, or at
10 least 60%, or at least 80% of the replaceable hydrogen atoms are replaced by fluorine atoms. Preferably a Formula I fluoromonomer is perfluorinated, *i.e.* all replaceable hydrogen atoms are replaced by fluorine atoms.

In a Formula I compound, a linear R^3 radical can, for example, be a C_b radical where b is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 and the radical can
15 contain from 1 up to $2b+1$ fluorine atoms. For example, a C_4 radical can contain from 1 to 9 fluorine atoms. A linear R^3 radical is perfluorinated with $2b+1$ fluorine atoms, but a branched or cyclic radical will be perfluorinated with fewer than $2b+1$ fluorine atoms. In a Formula I compound, a linear R^4 radical can, for example, be a C_c radical where c is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or
20 12 and the radical can contain from 1 to $2c$ fluorine atoms. For example, a C_6 radical can contain from 1 to 12 fluorine atoms. A linear R^4 radical is perfluorinated with $2c$ fluorine atoms, but a branched or cyclic radical will be perfluorinated with fewer than $2c$ fluorine atoms.

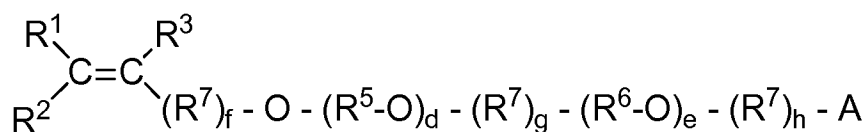
Examples of a $C_1\sim C_{12}$ straight-chain or branched, substituted or
25 unsubstituted, alkyl or alkylene radical suitable for use herein can include or be derived from a methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-octyl, trimethylpentyl, allyl and propargyl radical. Examples of a $C_3\sim C_{12}$ cyclic aliphatic, substituted or unsubstituted, alkyl or alkylene radical suitable for use herein can include or be derived from an
30 alicyclic functional group containing in its structure, as a skeleton,

cyclohexane, cyclooctane, norbornane, norbornene, perhydro-anthracene, adamantane, or tricyclo-[5.2.1.0^{2,6}]- decane groups.

Functional groups suitable for use herein as the A substituent in Formula I include ester, alcohol, acid (including carbon-, sulfur-, and phosphorus-based acid) groups, and the salts and halides of such groups; and cyanate, carbamate, and nitrile groups. Specific functional groups that can be used include $-\text{SO}_2\text{F}$, $-\text{CN}$, $-\text{COOH}$, and $-\text{CH}_2-\text{Z}$ wherein $-\text{Z}$ is $-\text{OH}$, $-\text{OCN}$, $-\text{O}-(\text{CO})-\text{NH}_2$, or $-\text{OP}(\text{O})(\text{OH})_2$.

Formula I fluoromonomers that can be homopolymerized include vinyl fluoride (VF), to prepare polyvinyl fluoride (PVF), and vinylidene fluoride (VF_2) to prepare polyvinylidene fluoride (PVDF), and chlorotrifluoroethylene to prepare polychlorotrifluoroethylene. Examples of Formula I fluoromonomers suitable for copolymerization include those in a group such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, chlorotrifluoroethylene (CTFE), trifluoroethylene, hexafluoroisobutylene, vinyl fluoride (VF), vinylidene fluoride (VF_2), and perfluoroolefins such as hexafluoropropylene (HFP), and perfluoroalkyl ethylenes such as perfluoro(butyl) ethylene (PFBE). A preferred monomer for copolymerization with any of the above named comonomers is tetrafluoroethylene (TFE).

In yet other embodiments, a fluoromonomer suitable for use herein, by itself to prepare a homopolymer or in copolymerization with TFE and/or any of the other comonomers described above, can be represented by the structure of the following Formula II:



II

25

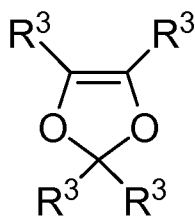
wherein R^1 through R^3 and A are each as set forth above with respect to Formula I; d and e are each independently 0 to 10; f, g and h are each independently 0 or 1; and R^5 through R^7 are the same radicals as described above with respect to R^4 in Formula I except that when d and e are both non-zero and g is zero, R^5 and R^6 are different R^4 radicals.

Formula II compounds introduce ether functionality into fluoropolymers suitable for use herein, and include fluorovinyl ethers such as those represented by the following formula: $CF_2=CF-(O-CF_2CFR^{11})_h-O-CF_2CFR^{12}SO_2F$, wherein R^{11} and R^{12} are each independently selected from F, Cl or a perfluorinated alkyl group having 1 to 10 carbon atoms, and $h = 0, 1$ or 2. Examples of polymers of this type that are disclosed in U.S. Patent No. 3,282,875 include $CF_2=CF-O-CF_2CF(CF_3)-O-CF_2CF_2SO_2F$ and perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl fluoride), and examples that are disclosed in U.S. Patent Nos. 4,358,545 and 4,940,525 include $CF_2=CF-O-CF_2CF_2SO_2F$. Another example of a Formula II compound is $CF_2=CF-O-CF_2-CF(CF_3)-O-CF_2CF_2CO_2CH_3$, the methyl ester of perfluoro(4,7-dioxa-5-methyl-8-nonenecarboxylic acid), as disclosed in U.S. Patent No. 4,552,631. Similar fluorovinyl ethers with functionality of nitrile, cyanate, carbamate, and phosphonic acid are disclosed in U.S. Patent Nos. 5,637,748, 6,300,445 and 6,177,196. Methods for making fluoroethers suitable for use herein are set forth in the U.S. patents listed above in this paragraph, and each of the U.S. patents listed above in this paragraph is by this reference incorporated in its entirety as a part hereof for all purposes.

Particular Formula II compounds suitable for use herein as a comonomer include fluorovinyl ethers such as perfluoro(allyl vinyl ether) and perfluoro(butenyl vinyl ether). Preferred fluorovinyl ethers include perfluoro(alkyl vinyl ethers) (PAVE), where the alkyl group contains 1 to 5 carbon atoms, with perfluoro(ethyl vinyl ether) (PEVE) and perfluoro(propyl vinyl ether) (PPVE), and perfluoro(methyl vinyl ether) (PMVE) being preferred. The structures of these preferred fluorovinyl ethers are respectively depicted

by FIGS. 1A-1C.

In yet other embodiments, a fluoromonomer suitable for use herein, by itself to prepare a homopolymer or in copolymerization with TFE and/or any of the other comonomers described above, can be represented by the structure
5 of the following Formula III:

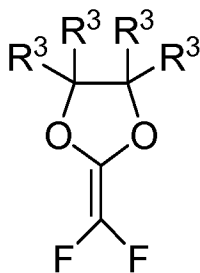


III

wherein each R³ is independently as described above in relation to Formula I.

10 Suitable Formula III monomers include perfluoro-2,2-dimethyl-1,3-dioxole (PDD).

In yet other embodiments, a fluoromonomer suitable for use herein, by itself to prepare a homopolymer or in copolymerization with TFE and/or any of the other comonomers described above, can be represented by the structure
15 of the following Formula IV:



IV

wherein each R^3 is independently as described above in relation to Formula I. Suitable Formula IV monomers include perfluoro-2-methylene-4-methyl-1,3-dioxolane (PMD).

In various embodiments, fluoropolymer copolymers suitable for use
5 herein can be prepared from any two, three, four or five of these monomers: TFE and a Formula I, II, III and IV monomer. The following are thus representative combinations that are available: TFE/Formula I; TFE/Formula II; TFE/Formula III; TFE/Formula IV; TFE/Formula I/Formula II; TFE/Formula I/Formula III; TFE/Formula I/Formula IV; Formula I/Formula II;
10 Formula I/Formula III; and Formula I/Formula IV. Provided that at least two of the five kinds of monomers are used, a unit derived from each monomer can be present in the final copolymer in an amount of at least about 1 wt.%, or at least about 5 wt.%, or at least about 10 wt.%, or at least about 15 wt.%, or at least about 20 wt.%, and yet no more than about 99 wt.%, or no more than about 95 wt.%, or no more than about 90 wt.%, or no more than about 85
15 wt.%, or no more than about 80 wt.% (based on the weight of the final copolymer); with the balance being made up of one, two, three or all of the other five kinds of monomers.

A fluoropolymer as used herein can also be a mixture of two or more of
20 the homo- and/or copolymers described above, which is usually achieved by dry blending. A fluoropolymer as used herein can also, however, be a polymer alloy prepared from two or more of the homo- and/or copolymers described above, which can be achieved by melt kneading the polymer together such that there is mutual dissolution of the polymer, chemical bonding
25 between the polymers, or dispersion of domains of one of the polymers in a matrix of the other.

Tetrafluoroethylene polymers suitable for use herein can be produced by aqueous polymerization (as described in U.S. Pat. No. 3,635, 926) or polymerization in a perhalogenated solvent (U.S. Pat. No. 3,642,742) or hybrid
30 processes involving both aqueous and perhalogenated phases (U.S. Pat. No.

4,499,249). Free radical polymerization initiators and chain transfer agents are used in these polymerizations and have been widely discussed in the literature. For example, persulfate initiators and alkane chain transfer agents are described for aqueous polymerization of TFE/PAVE copolymers.

- 5 Fluorinated peroxide initiators and alcohols, halogenated alkanes, and fluorinated alcohols are described for nonaqueous or aqueous/nonaqueous hybrid polymerizations.

Various fluoropolymers suitable for use herein include those that are thermoplastic, which are fluoropolymers that, at room temperature, are below
10 their glass transition temperature (if amorphous), or below their melting point (if semi-crystalline), and that become soft when heated and become rigid again when cooled without the occurrence of any appreciable chemical change. A semi-crystalline thermoplastic fluoropolymer can have a heat of fusion of at least about 1 J/g, or at least about 4 J/g, or at least about 8 J/g,
15 when measured by Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/min (according to ASTM D 3418-08). Various fluoropolymers suitable for use herein can additionally or alternatively be characterized as melt-processible, and melt-processible fluoropolymers can also be melt-fabricable. A melt-processible fluoropolymer can be processed in the molten state, *i.e.*
20 fabricated from the melt using conventional processing equipment such as extruders and injection molding machines, into shaped articles such as films, fibers and tubes. A melt-fabricable fluoropolymer can be used to produce fabricated articles that exhibit sufficient strength and toughness to be useful for their intended purpose despite having been processed in the molten state.
25 This useful strength is often indicated by a lack of brittleness in the fabricated article, and/or an MIT Flex Life of at least about 1000 cycles, or at least about 2000 cycles (measured as described above), for the fluoropolymer itself.

Examples of thermoplastic, melt-processible and/or melt-fabricable fluoropolymers include copolymers of tetrafluoroethylene (TFE) and at least
30 one fluorinated copolymerizable monomer (comonomer) present in the

polymer in sufficient amount to reduce the melting point of the copolymer below that of PTFE, e.g. to a melting temperature no greater than 315°C. Such a TFE copolymer typically incorporates an amount of comonomer into the copolymer in order to provide a copolymer which has a melt flow rate (MFR) of at least about 1, or at least about 5, or at least about 10, or at least about 20, or at least about 30, and yet no more than about 100, or no more than about 90, or no more than about 80, or no more than about 70, or no more than about 60, as measured according to ASTM D-1238-10 using a weight on the molten polymer and melt temperature which is standard for the specific copolymer. Preferably, the melt viscosity is at least about 10^2 Pa•s, more preferably, will range from about 10^2 Pa•s to about 10^6 Pa•s, most preferably about 10^3 to about 10^5 Pa•s. Melt viscosity in Pa•s is 531,700/MFR in g/10 min.

In general, thermoplastic, melt-processible and/or melt-fabricable fluoropolymers as used herein include copolymers that contain at least about 40 mol%, or at least about 45 mol%, or at least about 50 mol%, or at least about 55 mol%, or at least about 60 mol%, and yet no more than about 99 mol%, or no more than about 90 mol%, or no more than about 85 mol%, or no more than about 80 mol%, or no more than about 75 mol% TFE; and at least about 1 mol%, or at least about 5 mol%, or at least about 10 mol%, or at least about 15 mol%, or at least about 20 mol%, and yet no more than about 60 mol%, or no more than about 55 mol%, or no more than about 50 mol%, or no more than about 45 mol%, or no more than about 40 mol% of at least one other monomer. Suitable comonomers to polymerize with TFE to form melt-processible fluoropolymers include a Formula I, II, III and/or IV compound; and, in particular, a perfluoroolefin having 3 to 8 carbon atoms [such as hexafluoropropylene (HFP)], and/or perfluoro(alkyl vinyl ethers) (PAVE) in which the linear or branched alkyl group contains 1 to 5 carbon atoms. Preferred PAVE monomers are those in which the alkyl group contains 1, 2, 3 or 4 carbon atoms, and the copolymer can be made using several PAVE

monomers. Preferred TFE copolymers include FEP (TFE/HFP copolymer), PFA (TFE/PAVE copolymer), TFE/HFP/PAVE wherein PAVE is PEVE and/or PPVE, MFA (TFE/PMVE/PAVE wherein the alkyl group of PAVE has at least two carbon atoms) and THV (TFE/HFP/VF₂). Additional melt-processible
5 fluoropolymers are the copolymers of ethylene (E) or propylene (P) with TFE or chlorinated TFE (CTFE), notably ETFE, ECTFE and PCTFE. Also useful in the same manner are film-forming polymers of polyvinylidene fluoride (PVDF) and copolymers of vinylidene fluoride as well as polyvinyl fluoride (PVF) and copolymers of vinyl fluoride.

10 In a further aspect of the invention, composite powder material produced as described above is used to form a fluoropolymer composite body. In one embodiment, in which the fluoropolymer is not melt processible, the composite powder material is compression molded and sintered to form the composite body. The sintering operation can be carried out under
15 compression or as a free sintering, i.e., without continued application of a compressive force.

Alternative embodiments provide fluoropolymer composite bodies formed by melt processing the composite powder material. In some implementations, the melt processing comprises a multistage process, in
20 which an intermediate is first produced in the form of powder, granules, pellets, or the like, and thereafter remelted and formed into an article of manufacture having a desired final shape. In an implementation, the intermediate is formed by a melt compounding or blending operation that comprises transformation of a thermoplastic resin from a solid pellet, granule
25 or powder into a molten state by the application of thermal or mechanical energy. Requisite filler materials, such as composite powder material bearing fluoropolymers and particulate fillers prepared as described herein, may be introduced during the compounding or mixing process, before, during, or after the polymer matrix has been melted or softened. The compounding
30 equipment then provides sufficient mechanical energy to provide sufficient

stress to disperse the ingredients in the compositions, move the polymer, and distribute the additives to form a homogeneous mixture.

Melt blending can be accomplished with batch mixers (e.g. mixers available from Haake, Brabender, Banbury, DSM Research, and other manufacturers) or with continuous compounding systems, which may employ extruders or planetary gear mixers. Suitable continuous process equipment includes co-rotating twin screw extruders, counter-rotating twin screw extruders, multi-screw extruders, single screw extruders, co-kneaders (reciprocating single screw extruders), and other equipment designed to process viscous materials. Batch and continuous processing hardware suitable for carrying out steps of the present method may impart sufficient thermal and mechanical energy to melt specific components in a blend and generate sufficient shear and/or elongational flows and stresses to break solid particles or liquid droplets and then distribute them uniformly in the major (matrix) polymer melt phase. Ideally, such systems are capable of processing viscous materials at high temperatures and pumping them efficiently to downstream forming and shaping equipment. It is desirable that the equipment also be capable of handling high pressures, abrasive wear and corrosive environments. Compounding systems used in the present method typically pump a formulation melt through a die and pelletizing system.

The intermediate may be formed into an article of manufacture having a desired shape using any applicable technique known in the art of melt-processing polymers.

Such embodiments require that the fluoropolymer particles used to form the slurry and composite powder material be composed of a melt-processible fluoropolymer.

In other implementations, material produced by the melt-blending or compounding step is immediately melt processed into a desired shape, without being cooled or formed into powder, granules, or the like. For example, the production may employ in-line compounding and injection

molding systems that combine twin-screw extrusion technology in an injection molding machine so that the matrix polymer and other ingredients experience only one melt history.

In other embodiments, materials produced by shaping operations, including melt processing and forming, compression molding or sintering, may be machined into final shapes or dimensions. In still other implementations, the surfaces of the parts may be finished by polishing or other operations.

It is also contemplated that the composite powder material be used as a carrier by which the particulate filler material is introduced into a matrix that may comprise either an additional amount of the same fluoropolymer used in the composite powder material, one or more other fluoropolymers, or both. For example, the composite powder material may be formed using the present slurry technique with a first fluoropolymer particulate material that is not melt-processible, with the intermediate thereafter blended with a second, melt-processible fluoropolymer material. In an embodiment, the proportions of the two polymers are such that the overall blend is melt-processible. Other embodiments may entail more than two blended fluoropolymers. Alternatively, the intermediate is formed with a non-melt processible fluoropolymer and thereafter combined with more of the same fluoropolymer and processed by compression molding and sintering.

In still other implementations, the slurry technique is employed to disperse particulate filler material onto melt-processible fluoropolymer particles, which are either melt-processed directly to form a composite body or used as an intermediate that is let down in a melt processing operation with additional melt-processible fluoropolymer particles without the particle additions. The additional fluoropolymer particles may be of the same or different type.

The present process may be used to prepare composite bodies that in some embodiments exhibit wear rates that may be at most $1 \times 10^{-6} \text{ mm}^3/\text{N-m}$, or at most $1 \times 10^{-7} \text{ mm}^3/\text{N-m}$, or at most $1 \times 10^{-8} \text{ mm}^3/\text{N-m}$. In an

embodiment, the present process may be used to prepare composite bodies that exhibit friction coefficients that may be less than about 0.3 or less than about 0.25.

5

EXAMPLES

The operation and effects of certain embodiments of the present invention may be more fully appreciated from a series of examples (Examples 10 1–6), as described below. The embodiments on which these examples are based are representative only, and the selection of those embodiments to illustrate aspects of the invention does not indicate that materials, components, reactants, conditions, techniques and/or configurations not described in the examples are not suitable for use herein, or that subject 15 matter not described in the examples is excluded from the scope of the appended claims and equivalents thereof. The significance of the examples is better understood by comparing the results obtained therefrom with the results obtained from certain trial runs that are designed to serve as Control Examples 1-3, which provide a basis for such comparison since they are 20 fluoropolymer based, but either do not contain particulate fillers or are processed by different methods.

Materials

Materials used in carrying out the examples include the following:

25 Isopropyl alcohol (IPA): Optima® grade ($\text{H}_2\text{O} < 0.020\%$, $0.2\ \mu\text{m}$ filtered) Fisher Scientific, Pittsburgh, PA, stored over a $4\text{\AA}$ molecular sieve;

PTFE 7C particles: Teflon® PTFE 7C granular resin, DuPont Corporation, Wilmington, DE.

PFA 340: Teflon® PFA 340: perfluoroalkoxy resin, DuPont Corporation, 30 Wilmington, DE, which is loosely compacted fluff that has not been melt-

processed.

Submicron α -alumina: Stock # 44652, Alfa Aesar, Ward Hill, MA, represented by the manufacturer as having an average particle size of 60 nm.

5 Wear Resistance Testing

 The wear resistance of various samples as specified below was characterized using an automated, computer-controlled tribometer like that depicted by Fig. 2 of US Patent No. 7,790,658 to Sawyer et al. ("the '658 patent"), which patent is incorporated herein in the entirety by reference
10 thereto. Additional description of such a tribometer is provided in an article by W. G. Sawyer et al., "A Study on the Friction and Wear of PTFE Filled with Alumina Nanoparticles," *Wear*, vol. 254, pp. 573-580 (2003). The tribometer permitted a fluoropolymer-based test sample to be placed in reciprocating, sliding contact with a counterface, with the normal loading force carefully
15 controlled and the loading and sliding forces continuously monitored and logged. The wear was monitored both by a position transducer that measured the reduction in height of the test specimen and by periodically removing and weighing the test sample.

 The tribometer was used to test samples having the form of an
20 elongated prism with a square cross-section of about 6.4×6.4 mm. Typically the prism had an initial length of about 20 mm. In each case, conventional machining techniques were used to prepare samples in this form from the various starting composite bodies. The counterface used in the present wear resistance measurements was a 304 series stainless steel plate, lapped to
25 produce a surface roughness characterized by a value of about $R(\text{rms}) = 161$ nm, with a standard deviation of 35 nm. It is to be noted that observed wear rates are known to be dependent in part on the counterface material, so that the present fluoropolymer bodies would likely exhibit different wear rates if tested against different counterfaces, e.g., having different composition or
30 surface finish.

Control Example 1

Processing of an unloaded PTFE sample.

TEFLON® PTFE 7C particles were formed into a test sample using a
5 compression molding and sintering technique consistent with the protocol of
ASTM D-4894-07. The mold used had a cavity in the shape of a right circular
cylinder with a diameter of about 2.86 cm. The mold was charged with about
12 g of the starting particulate material. The material was compressed with a
loading of about 5000 psi (34 MPa) and held at ambient temperature for 2
10 minutes to form a compact about 0.9 cm high.

The compressed-particulate compact was then removed from the mold
and free-sintered to form the test sample. First, the mold containing the
compact was placed into a 290°C oven with a nitrogen purge. The oven
temperature was immediately ramped up to 380°C at a rate of 120°C/h and
15 then held at 380°C for 30 minutes. Thereafter, the specimen was cooled to
294°C at a rate of 60°C/h and held at 294°C for 24 minutes before removing it
from the oven. A sample suitable for wear testing was obtained from the
sintered body by conventional machining techniques.

Control Example 2

Preparation of an alumina-PTFE composite body using jet milling.

A sintered α -alumina/PTFE composite body was prepared generally in
accordance with the procedures set forth in US Patent 7,790,658, which is
incorporated herein in the entirety by reference thereto. In particular, a
25 mixture of 5 wt.% alpha-alumina in TEFLON® PTFE 7C was prepared, and
passed three times through an alumina-lined Sturtevant jet mill. This mixed
material was added to a 12.6 mm diameter vessel and consolidated in a press
at 500 MPa uniaxial pressure. The resulting compressed pellet was then
sintered while under 2.5 MPa of pressure with the following temperature
30 profile: ramp to 380 °C over 3 hours, hold at 380 °C for 3 hours, ramp to

ambient temperature over 3 hours. A sample suitable for wear testing was obtained from the sintered body by conventional machining techniques.

Example 1

5 Creation of a composite powder material containing PTFE with dispersed submicron α -alumina particulate filler material.

A precursor slurry containing approximately 3.45 wt.% of the same submicron particles α -alumina as used in Control Example 2 was formed by adding 5.0 g of the particles to 140 g of IPA in a 200 mL bottle. After adding
10 the submicron particles, the bottle was sonicated using an ultrasonic horn (Branson Digital Sonicator 450 with a titanium tip, operating at about 40% amplitude (400W)). The mixture was subjected to 3 cycles of 1 min duration, with a 45 sec relaxation interval after each cycle. The result was a milky dispersion with no visible particles.

15 Quickly thereafter, 91.6 g of this slurry (to provide 3.16 g of alumina) was added to a 500 mL pear-bottom flask containing 60.0 g of the same TEFLON® PTFE 7C granular powder used to prepare the samples of Control Example 2. The amount of slurry was selected to provide an alumina level of 5.0 wt.% in the final PTFE/alumina mixture. The flask wall was rinsed with an
20 additional 100 mL of IPA to clear the flask wall. The flask was then gently swirled for a few minutes to assure mixing of the PTFE powder and the IPA/alumina slurry.

Then the PTFE powder-IPA/alumina slurry mixture was dried in the flask using a rotary evaporator. Pressure was slowly reduced and the water
25 bath heated to 55°C to evenly evaporate and remove the polar organic liquid, while carefully avoiding bumping. The slurry continued to mix as the polar organic liquid was removed. The resulting powder was further dried for four hours at 50°C under high vacuum ($4 \text{ Pa} \cong 30 \text{ milliTorr}$) for 4 hours to remove any residual water and/or IPA. The dried composite powder material was free
30 flowing.

Example 2

Preparation of an alumina-PTFE composite body.

An alumina-PTFE composite body was formed into test samples by the same compression molding and sintering technique set forth in Control Example 1, but using free-flowing composite powder material containing PTFE with dispersed submicron α -alumina particulate filler material that was prepared in accordance with Example 1 above, instead of pure PTFE powder.

Example 3

Wear resistance of an α -alumina/PTFE composite body.

The wear resistance of a sample of a sintered α -alumina/PTFE composite body prepared as set forth in Example 2 was tested and compared with that of samples prepared as set forth in Control Examples 1 and 2. The results show that the IPA slurry-prepared α -alumina/PTFE composite body of Example 2 exhibits a wear rate of $k = 7.04 \times 10^{-8} \text{ mm}^3/\text{N-m}$, which is markedly better than the relatively poor wear rate $k = 3.74 \times 10^{-4} \text{ mm}^3/\text{N-m}$ of the unloaded PTFE material of Control Example 1. The slurry-prepared body had a better wear rate than the $k = 1.3 \times 10^{-7} \text{ mm}^3/\text{N-m}$ rate of the jet-milled α -alumina/PTFE composite body of Control Example 2.

Both the jet-milled and slurry-based α -alumina/PTFE composite bodies exhibited low friction characteristics, e.g. coefficients of sliding friction of about 0.2 – 0.23, versus 0.18 for unloaded PTFE, when measured under the conditions against lapped 304 stainless steel as set forth above.

Example 4

Preparation of a PFA-submicron particle composite body using melt blending.

A laboratory-scale melt-processing technique was used to prepare a composite body of TEFLON® PFA 340 loaded with 5 wt.% submicron α -alumina particulate filler material for tribology and mechanical testing.

A sample was prepared by directly melt blending the submicron α -alumina particles and TEFLON® PFA 340 matrix material. The melt blending was carried out using an Xplore™ microcompounding system (DSM Research, Galeen, NV), which employed a 15cc capacity, co-rotating, intermeshing, conical twin-screw batch mixer with a recirculation loop and sample extraction valve. Requisite amounts of the submicron α -alumina and the PFA were hand mixed and slowly loaded into the mixer through a funnel and plunger system mounted on the top of the barrel with the screws turning. When loading was complete, the feed plunger was removed and replaced with a plug. The mixing time was marked when the plug had been secured.

The microcompounder was configured with three barrel heating zones (top-center-bottom) appointed for control and operation at up to 400 °C. Temperatures were monitored with a melt thermocouple located below the screw tips. The drive motor amperage and force on the barrels imparted by the screw pumping were monitored to indicate changes in viscosity due to the composition, temperature, chemical reactions or the state of the dispersion. Average values for temperature, force and amperage were recorded. Extrudate from the mixer was collected in a heated transfer cylinder with a movable plunger and placed into an injection molding unit.

An air-driven injection molding machine having a heated and water-cooled cylinder containing a removable two-piece mold was used for melt processing the finished composite bodies. The operation of the molding machine was controlled to permit preselection of injection parameters, including injection pressure and time, and pack hold pressure and time.

The sample was mixed and placed in the transfer cylinder as described above, and then loaded and secured in the molding machine. The air driven cylinder was activated, pushing the plunger to force the molten material into the mold cavity. After completion of the injection molding cycle, the mold was removed from the heated cavity and the halves separated, so the molded part could be removed from the mold and allowed to cool to ambient temperature.

A sample suitable for wear testing was obtained from the injection-molded body by conventional machining techniques.

5 Example 5

Preparation of a PFA-submicron particle composite body using a slurry technique.

 A second PFA-submicron α -alumina particle composite body was prepared by melt processing a composite powder material prepared using the present slurry process. In particular, the same IPA slurry process and conditions set forth in Example 1 for manufacturing PTFE/ α -alumina composite powder material were used to prepare a PFA/ α -alumina composite powder material. A mixture of submicron α -alumina powder and IPA was prepared and sonicated, and thereafter mixed with the requisite amount of TEFLON® PFA 340 fluff to form an IPA slurry. The slurry was dried in the same manner to produce a composite powder comprising 5 wt.% submicron α -alumina particles associated with TEFLON® PFA 340. The composite powder material was then processed using the same mixing and injection molding apparatus set that was employed to make the melt-blended sample of Example 4. The same processing conditions were used, resulting in an injection-molded sample visually similar to that of Example 4.

 A sample suitable for wear testing was again obtained from the injection-molded body by conventional machining techniques.

25 Control Example 3

Processing of an unloaded PFA sample.

 The same laboratory-scale melt-processing and injection-molding equipment and processing conditions used to prepare the samples of Examples 4 and 5 was used to prepare injection-molded samples of TEFLON® PFA 340 without additions for comparative tribology and

mechanical testing.

Example 6

5 Wear resistance of α -alumina/PFA composite bodies.

The wear resistance of samples of melt-processed α -alumina/PFA composite bodies prepared as set forth in Examples 4 and 5 were tested using the tribometer system described above and compared with wear resistance data for the unloaded PFA body of Control Example 3.

10 The results in Table III below were obtained for the steady-state wear rate k and coefficient of sliding friction μ of these samples.

TABLE III
Friction and Wear Data for PFA Samples

15

Example	k ($\text{mm}^3/\text{N-m}$)	μ
Control 3	3.77×10^{-4}	0.28
4	8.88×10^{-8}	0.25
5	1.28×10^{-7}	0.26

20

The results show that the present slurry technique may be used to fabricate a composite body comprising a melt-processible, TEFLON® PFA 340 fluoropolymer matrix with alumina particulate filler material that exhibits a wear rate reduced by more than three orders of magnitude from the wear rate of an unloaded TEFLON® PFA 340 material, without compromise of the low coefficient of friction of the material.

25

Having thus described the invention in rather full detail, it will be understood that such detail need not be strictly adhered to, but that additional

changes and modifications may suggest themselves to one skilled in the art. For example, additional additives known for use in fluoropolymers to aid in processing or to enhance properties may be added at various stages of producing the present composite body. It is to be understood that the present
5 manufacturing process may be implemented in various ways, using different equipment and carrying out the steps described herein in different orders. All of these changes and modifications are to be understood as falling within the scope of the invention as defined by the subjoined claims.

In addition to vendors named elsewhere herein, various materials
10 suitable for use herein may be made by processes known in the art, and/or are available commercially from suppliers such as Alfa Aesar (Ward Hill, MA), City Chemical (West Haven, CT), Fisher Scientific (Fairlawn, NJ), Nanostructured & Amorphous Materials, Inc. (Houston, TX), PACE Technologies (Tucson, AZ), Sigma-Aldrich (St. Louis, MO), or Stanford Materials (Aliso Viejo, CA)art
15 of.

Where a range of numerical values is recited or established herein, the range includes the endpoints thereof and all the individual integers and fractions within the range, and also includes each of the narrower ranges therein formed by all the various possible combinations of those endpoints and
20 internal integers and fractions to form subgroups of the larger group of values within the stated range to the same extent as if each of those narrower ranges was explicitly recited. Where a range of numerical values is stated herein as being greater than a stated value, the range is nevertheless finite and is bounded on its upper end by a value that is operable within the context of the
25 invention as described herein. Where a range of numerical values is stated herein as being less than a stated value, the range is nevertheless bounded on its lower end by a non-zero value. In addition, unless explicitly stated otherwise or indicated to the contrary by the context of usage, amounts, sizes, ranges, formulations, parameters, and other quantities and characteristics
30 recited herein, particularly when modified by the term "about", may but need

not be exact, and may also be approximate and/or larger or smaller (as desired) than stated, reflecting tolerances, conversion factors, rounding off, measurement error and the like, as well as the inclusion within a stated value of those values outside it that have, within the context of this invention,
5 functional and/or operable equivalence to the stated value.

Each of the formulae shown herein describes each and all of the separate, individual compounds or monomers that can be assembled in that formula by (1) selection from within the prescribed range for one of the variable radicals, substituents or numerical coefficients while all of the other
10 variable radicals, substituents or numerical coefficients are held constant, and (2) performing in turn the same selection from within the prescribed range for each of the other variable radicals, substituents or numerical coefficients with the others being held constant. In addition to a selection made within the prescribed range for any of the variable radicals, substituents or numerical
15 coefficients of only one of the members of the group described by the range, a plurality of compounds or monomers may be described by selecting more than one but less than all of the members of the whole group of radicals, substituents or numerical coefficients. When the selection made within the prescribed range for any of the variable radicals, substituents or numerical
20 coefficients is a subgroup containing (i) only one of the members of the whole group described by the range, or (ii) more than one but less than all of the members of the whole group, the selected member(s) are selected by omitting those member(s) of the whole group that are not selected to form the subgroup. The compound, monomer, or plurality of compounds or
25 monomers, may in such event be characterized by a definition of one or more of the variable radicals, substituents or numerical coefficients that refers to the whole group of the prescribed range for that variable but where the member(s) omitted to form the subgroup are absent from the whole group.

In this specification, unless explicitly stated otherwise or indicated to the
30 contrary by the context of usage, where an embodiment of the subject matter

hereof is stated or described as comprising, including, containing, having, being composed of or being constituted by or of certain features or elements, one or more features or elements in addition to those explicitly stated or described may be present in the embodiment. An alternative embodiment of
5 the subject matter hereof, however, may be stated or described as consisting essentially of certain features or elements, in which embodiment features or elements that would materially alter the principle of operation or the distinguishing characteristics of the embodiment are not present therein. A further alternative embodiment of the subject matter hereof may be stated or
10 described as consisting of certain features or elements, in which embodiment, or in insubstantial variations thereof, only the features or elements specifically stated or described are present.

15

CLAIMS

What is claimed is:

1. A process for forming a composite powder material comprising:
 - 5 (a) creating a particle dispersion of particulate filler material in a polar organic liquid;
 - (b) mixing the particle dispersion with fluoropolymer particles to form a precursor slurry; and
 - (c) drying the precursor slurry by removing the polar organic liquid to
10 form the composite powder material, wherein the particulate filler material is associated with a surface of the fluoropolymer particles.
2. The process of claim 1, wherein the particulate filler material comprises submicron particles.
- 15 3. The process of claim 1, wherein the polar organic liquid is one of methanol, ethanol, isopropanol, *n*-butanol, *tert*-butanol, *N,N*-dimethylacetamide, a ketone, an ester, or a mixture thereof.
- 20 4. The process of claim 1, wherein the fluoropolymer particles comprise a melt processible fluoropolymer.
5. The process of claim 4, wherein the melt processible fluoropolymer comprises at least one of PFA, FEP, PTFE micropowder, or a mixture thereof.
- 25 6. The process of claim 1, wherein the fluoropolymer particles comprise a non-melt processible fluoropolymer.
7. The process of claim 6, wherein the non-melt processible
30 fluoropolymer comprises at least one of PTFE, modified PTFE, or a mixture

thereof.

8. The process of claim 1, further comprising subjecting a mixture of the particulate filler material and the polar organic liquid to mechanical energy
5 to create the particle dispersion.

9. The process of claim 8, wherein the mechanical energy is provided by a source of ultrasonic energy.

10 10. The process of claim 8, wherein the mechanical energy is provided by a high shear mixing operation

11. The process of claim 1, wherein the drying comprises at least one of applying heat to the precursor slurry or placing the precursor slurry under a
15 vacuum.

12. A composite powder material made by the process of claim 1.

13. A process for manufacturing a fluoropolymer composite body
20 comprising:

(a) creating a composite powder material by a process comprising:
(i) creating a particle dispersion of particulate filler material in a polar organic liquid, (ii) mixing the particle dispersion with fluoropolymer particles to form a precursor slurry, and (iii) drying the precursor slurry by removing the polar
25 organic liquid to form the composite powder material, wherein the particulate filler material is associated with a surface of the fluoropolymer particles; and
(b) forming the composite powder material into the fluoropolymer composite body.

30 14. The process of claim 13, wherein the particulate filler material

comprises submicron particles.

15. The process of claim 13, wherein the forming comprises compression molding and sintering the composite powder material to form the fluoropolymer composite body.

16. The process of claim 13, wherein the forming comprises melt processing the composite powder material.

17. A fluoropolymer composite body made by the process of claim 13.

18. A process for manufacturing a fluoropolymer composite body comprising:

(a) creating a composite powder material by a process comprising:

(i) creating a particle dispersion of particulate filler material in a polar organic liquid, (ii) mixing the particle dispersion with particles of a first fluoropolymer to form a precursor slurry, and (iii) drying the precursor slurry by removing the polar organic liquid to form the composite powder material, wherein the particulate filler material is associated with the surface of the particles of the first fluoropolymer;

(b) combining particles of a second fluoropolymer with the composite powder material; and

(c) melt processing the combined composite powder material and second fluoropolymer particles to form the fluoropolymer composite body.

19. The process of claim 18, wherein the particulate filler material comprises submicron particles.

20. The process of claim 18, wherein the first fluoropolymer comprises a melt processible fluoropolymer.

21. The process of claim 18, wherein the first fluoropolymer comprises a non-melt processible fluoropolymer.

5 22. The process of claim 21, wherein the second fluoropolymer comprises a melt-processible fluoropolymer.

23. The process of claim 18, wherein the first fluoropolymer and the second fluoropolymer are of the same type.

10

24. A fluoropolymer composite body made by the process of claim 18.

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FIG. 1A

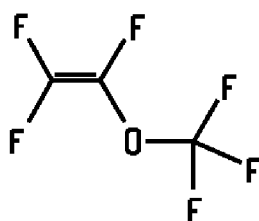


FIG. 1B

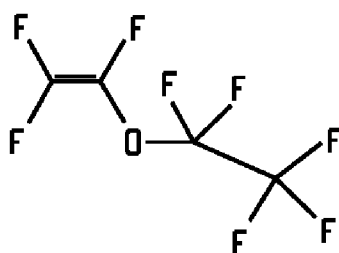
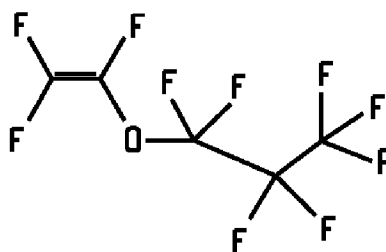


FIG. 1C



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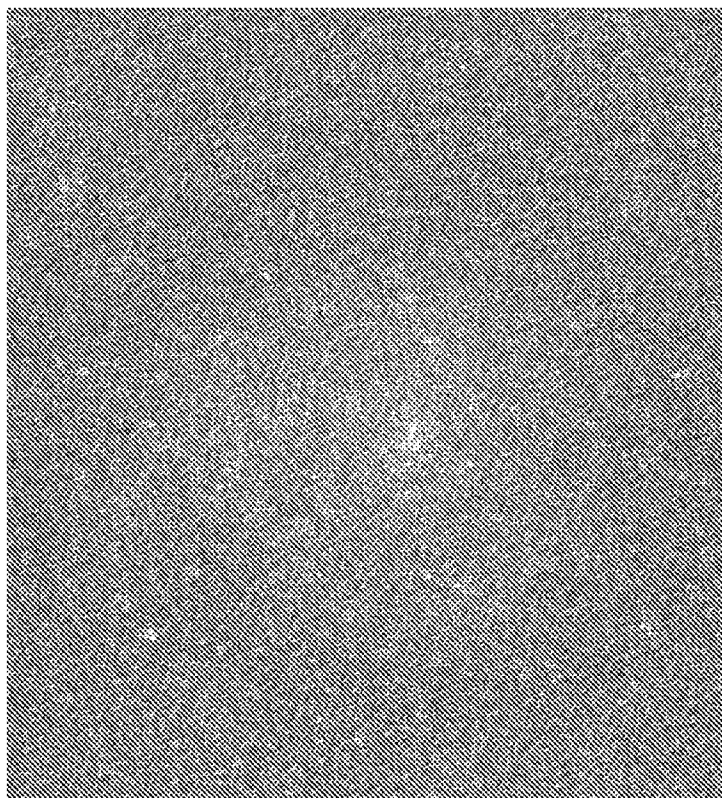


FIG. 2A

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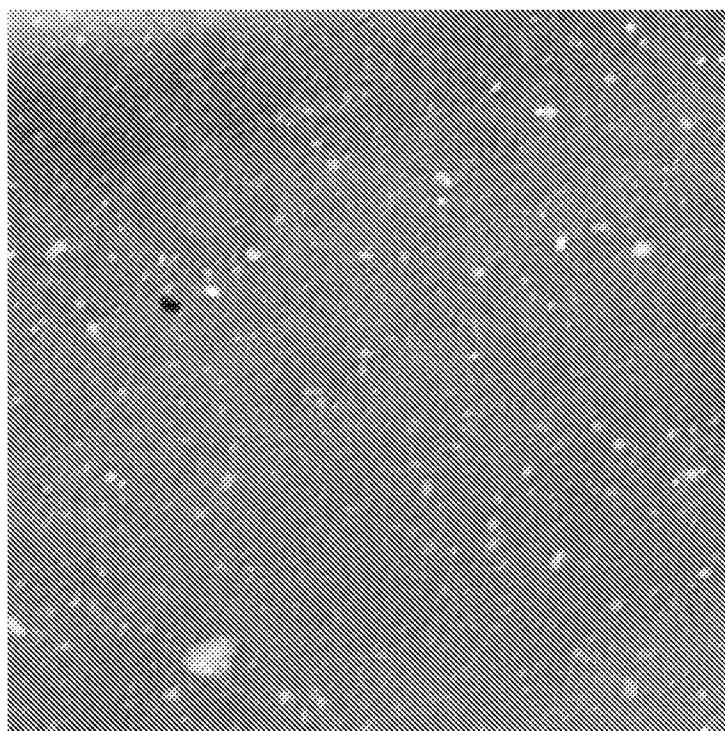


FIG. 2B

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/037840

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08F114/26 C08J3/12	C08J3/02 C08J3/205
	C08J3/09	C08J5/02 C08J5/00
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C08F C08J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 026 863 A (ISEKI SHIGERU ET AL) 31 May 1977 (1977-05-31) abstract; claims 1-14 column 4, line 12	1, 12, 13, 17
X	US 4 123 606 A (MALHOTRA SATISH C) 31 October 1978 (1978-10-31) abstract; claims 1-4	1
A	SAWYER W G ET AL: "A study on the friction and wear behavior of PTFE filled with alumina nanoparticles", WEAR, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 254, 1 January 2003 (2003-01-01), pages 573-580, XP002401587, ISSN: 0043-1648 the whole document	1-24
	-/--	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent 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 when the document is taken alone "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		
Date of the actual completion of the international search 22 August 2012		Date of mailing of the international search report 29/08/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Bergmans, Koen

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/037840

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/094764 A2 (WILD RIVER CONSULTING GROUP LL [US]; HEIKKILA KURT E [US]) 23 August 2007 (2007-08-23) the whole document -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/037840

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 4123606	A	31-10-1978	DE 2841149 A1 29-03-1979 FR 2404015 A1 20-04-1979 GB 2004896 A 11-04-1979 IT 1202776 B 09-02-1989 JP 1060049 B 20-12-1989 JP 1573276 C 20-08-1990 JP 54054156 A 28-04-1979 NL 7809580 A 23-03-1979 US 4123606 A 31-10-1978
WO 2007094764	A2	23-08-2007	BR PI0621328 A2 06-12-2011 CA 2641946 A1 23-08-2007 CN 101626885 A 13-01-2010 EP 1989047 A2 12-11-2008 JP 2009526120 A 16-07-2009 US 2009314482 A1 24-12-2009 WO 2007094764 A2 23-08-2007