A laminate article can include a substrate and a layer of a heterogeneous mixture of a non-fluorinated polymer compound and a fluorinated polymer compound. The laminate article can include a gradual concentration gradient along an axis perpendicular to the substrate. The gradual concentration gradient can include the change of the amount of the non-fluorinated polymer and the fluorinated polymer compound relative to the axis perpendicular to the substrate. The layer can further include at least one filler. The laminate can be applied as a bearing material.
POLYMER COATING ON SUBSTRATES USING THERMAL SPRAY TECHNIQUES

TECHNICAL FIELD

The disclosure relates to a laminates comprising a substrate, a transition layer comprising a non-fluorinated thermoplastic applied directly thereto and a fluorinated polymer, which can serve as a sliding layer applied to the transition layer.

BACKGROUND ART

Laminates which comprise a layer structure having a metallic support material, an intermediate layer and a sliding layer applied thereto have been known for a long time in a variety of forms from the prior art and are used in a wide variety of technical fields, for example in the field of automotive engineering.

For slide bearings, especially conventional DU® bearing material, a sliding layer composed of a PTFE compound material is in turn applied to the intermediate layer. In this slide bearing material, the intermediate layer, which has the function of establishing firm adhesion of the sliding layer to the support material, is just a bronze layer sintered from bronze particles. However, this process is problematic for a variety of reasons, including performance limitations of the laminate product and failure in ensuring the combination between PTFE and the support material. As such, there is a continued need for improved laminates for applications such as slide bearings.

Therefore, it would be advantageous if a laminate could be produced that has strong adhesion to the metal support and the sliding layer.

SUMMARY OF THE INVENTION

In a first aspect, a laminate article includes a substrate and a layer. The layer can include a heterogeneous mixture of a non-fluorinated polymer compound and a fluorinated polymer compound. The laminate article can include a gradual concentration gradient along an axis perpendicular to the substrate. The gradual concentration gradient can include the change of the amount of the non-fluorinated polymer and the fluorinated polymer compound relative to the axis perpendicular to the substrate.
In a second aspect, a laminate article can include a substrate and a porous non-fluorinated polymer layer overlying the substrate. The laminate can further include a fluorinated polymer compound layer. The fluorinated polymer compound layer can overlie and penetrate the porous non-fluorinated layer.

In a third aspect, bearing article can include a metal substrate and a discontinuous layer of a non-fluorinated polymer overlying the metal substrate. The bearing article can further include a layer of a fluorinated polymer compound. The fluorinated polymer compound layer can overlie and penetrate the discontinuous layer.

In a fourth aspect, a bearing material can include a metal substrate having a roughened surface. The bearing material can further include a porous PEEK layer. The bearing material can further include a continuous PTFE composition layer. The continuous PTFE composition layer can overlie and penetrate the porous PEEK layer.

In a fifth aspect, a method of manufacturing a bearing article can include providing a substrate having a major surface and roughening the major surface of the substrate. The method can further include applying a layer of a non-fluorinated polymer onto the major surface. The method can further include coating the non-fluorinated polymer layer with a fluoropolymer composition to form a laminate. The method can further include pressing the laminate to form the bearing article.

BRIEF DESCRIPTION OF THE DRAWINGS

The present disclosure may be better understood, and its numerous features and advantages made apparent to those skilled in the art by referencing the accompanying drawings.

FIG. 1 shows an exemplary laminate in sectional view; and

FIG. 2 shows a process for forming a laminate.

FIG. 3 shows results of tribological tests for laminate samples

The use of the same reference symbols in different drawings indicates similar or identical items.
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

In one embodiment, a laminate article includes a substrate. The laminate can further include a layer comprising a heterogeneous mixture. The heterogeneous mixture can further include a non-fluorinated polymer compound. Moreover, the heterogeneous mixture can include a fluorinated polymer compound. The laminate article can include a gradual concentration gradient along an axis perpendicular to the substrate. The gradual concentration gradient includes a change of an amount of the non-fluorinated polymer and the fluorinated polymer compound relative to the axis perpendicular to the substrate.

FIG. 1 shows an exemplary laminate in sectional view. Layer 102 depicts a fluorinated polymer compound, such as PTFE, overlying non-fluorinated polymer layer material 106, which in this example is PEEK. The non-fluorinated polymer compound of layer 102 and the fluorinated compound can penetrate layer 106, thereby forming mixed regions 104. Layer 106 overlies substrate 108.

Addressing the substrate 108 of the laminate, in embodiments, the substrate can include a metal substrate or metal alloy substrate. The metal substrate can include a metal or a metal alloy. In one particular embodiment, the metal substrate can include aluminium. In another particular embodiment, the metal alloy substrate can include steel, bronze, or brass. In embodiments, the metal support includes steel, cold-rolled steel material No. 1.0338, cold-rolled steel material No. 1.0347, matt zinc-plated steel, stainless steel material No. 1.4512, stainless steel material No. 1.4720, stainless steel material No. 1.4310, aluminum, alloys, or any combinations thereof.

Further addressing the substrate 108, the substrate can have a surface roughness of at least about 0.5 microns, such as at least about 1 micron, at least about 5 microns, at least about 10 microns, or at least about 100 microns. In another embodiment, the substrate can have a surface roughness of not greater than about 500 microns, such as not greater than about 200 microns, not greater than about 100 microns, not greater than about 80 microns, or even not greater than about 40 microns. Moreover, it will be appreciated that the total surface roughness of substrate 108 can be within a range between any of the minimum and maximum values noted above.

In yet another embodiment, the substrate 108 can be pretreated to have a desired surface roughness. In one instance, substrate 108 can include a surface feature. For example,
for metal or metal alloy substrates, the major surface can include a structured plate, a ribbed sheet, a woven fabric, a mesh, or metal foam. In a particular embodiment, the metal or metal alloy substrate has a honeycomb surface feature. In yet other embodiments, the surface of a metal substrate can be treated by electrolytic zinc-plating to roughen, upgrade, or coat the surface. In other embodiments, the major surface of the metal support can be increased by mechanical structuring. The structuring can include brush-finishing, sand-blasting, etching, perforating, pickling, punching, pressing, curling, deep drawing, decambering, incremental sheet forming, ironing, laser cutting, rolling, hammering, embossing, undercutting, and any combinations thereof.

Addressing layer 106 formed by the non-fluorinated polymer compound, in embodiments, the non-fluorinated polymer compound forms a porous or discontinuous non-fluorinated polymer layer overlying the substrate 108. The non-fluorinated polymer layer can have a porosity, defined as the ratio of void volume over total volume of non-fluorinated polymer and determined after applying the non-fluorinated polymer as layer 106 to the substrate 108 and before any further processing.

The porosity may be in the form of open porosity defining an interconnected network of channels extending throughout the layer 106. Alternatively, the layer 106 may include a content of closed porosity described and characterized by discrete and individual pores separated from each other. In at least one embodiment, layer 106 can include a mix of open porosity and closed porosity.

The amount of porosity within the layer can comprise a majority content, such as greater than 50 vol% for the total volume of layer 106. In still other instances, layer 106 may include a minority content of porosity, which can represent less than 50 vol% of the total volume of the layer. Furthermore, the body may contain a majority content of closed porosity. Still, in other instances, the bonded abrasive body may contain a majority content of open porosity.

In certain instances, the porosity may be not greater than about 70 vol% for the total volume of layer 106. In yet other instances, layer 106 may be formed such that the amount of porosity is not greater than about 60 vol%, such as not greater than about 50 vol%, not greater than about 40 vol%, not greater than about 30 vol%, not greater than about 25 vol%, not greater than about 20 vol%, not greater than about 15 vol%, not greater than about 10 vol%...
vol%, not greater than about 5 vol%, or even not greater than about 2 vol% In at least one non-limiting embodiment, layer 106 may contain an amount of porosity of at least about 1 vol%, such as at least about 5 vol%, at least about 10 vol%, at least about 20 vol%, at least about 30 vol%, or even at least about 40 vol%. Moreover, it will be appreciated that the total amount of porosity within layer 106 can be within a range between any of the minimum and maximum percentages noted above.

Still referring to layer 106, in other embodiments, the non-fluorinated polymer compound forms a discontinuous layer. A discontinuous layer provides the basis for a concentration gradient. A concentration gradient in a cross-section of a laminate is the difference of the amount of one ingredient between two adjacent unit cells. A gradual concentration gradient is established when the amount of ingredient decreases or increases subsequently in three adjacent unit cells, wherein the three unit cells are aligned along an axis.

As shown in FIG. 1, unit cells 110, 112, and 114 are aligned along an axis that is perpendicular to substrate 108. The unit cells have the edge length a. The edge length a can vary and can be a fraction of the average thickness of layer 106. For example, edge length a can be a third, a fourth, a fifth, or even a sixth of the average thickness of layer 106. In other embodiments, edge length can be at least about 2 microns, such as at least about 4 microns, or even about 8 microns. In other embodiments, edge length a can be not greater than about 20 microns, such as not greater than about 15 microns, or even not greater than about 10 microns. In other embodiments, edge length a is selected in such a way that three adjacent unit cells along an axis perpendicular to substrate 108 cover at least about 0.7, such as at least about 0.8, or even at least about 0.9 of the average thickness of layer 106. In other embodiments, edge length a is selected such that three adjacent unit cells along an axis perpendicular to substrate 108 cover not greater than about 0.99, such as not greater than about 0.98, or even not greater than about 0.95 of the average thickness of layer 106.

For a gradual concentration gradient, unit cells 110, 112, and 114 contain different amounts of the non-fluorinated polymer compound, wherein the amount is decreasing along the axis perpendicular to substrate 108. In one embodiment, for a gradual concentration gradient, the amount of non-fluorinated polymer in unit cell 114 is less than in unit cell 112 and the amount of non-fluorinated polymer in unit cell 112 is less than in unit cell 110. The
amount of non-fluorinated polymer compound can be determined by integrating the area occupied by layer 106 over total unit cell area a².

In another embodiment, layer 106 can occupy a majority, such as at least about 50%, such as at least about 70%, or even at least about 90% and not greater than about 99.9%, such as not greater than about 98%, or not greater than about 95% of unit cell area a² in unit cell 110. In another embodiment, layer 106 can occupy at least about 30%, such as at least about 40%, or even at least about 50% and not greater than about 90%, such as not greater than about 80%, or even not greater than about 70% of unit cell area a² in unit cell 112. In another embodiment, layer 106 can occupy a minority, such as at least about 1%, such as at least about 2%, or even at least about 5% and not greater than about 50%, such as not greater than about 40%, or even not greater than about 30% of unit cell area a² in unit cell 114.

Further addressing layer 106 and the material comprising that layer, the non-fluorinated polymer compound can include a poly-ether-ether-ketone (PEEK), an ultra-high-molecular-weight polyethylene (UHMWPE), a polyimide (PI), a polyamide (PA), a polyamideimide (PAI), a polyphenylsulfide (PPS), a polyhydroxybutyrate (PHB), and any combination thereof. In one particular embodiment, the non-fluorinated polymer compound consists essentially of a poly-ether-ether-ketone (PEEK).

Moving to element 102 in FIG. 1 which comprises the fluorinated polymer compound, the fluorinated polymer compound can include polytetrafluoroethylene (PTFE), a perfluoroalkoxy polymer (PEA), fluorinated ethylene-propylene (FEP), polyvinylfluoride (PVF), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), a polyethylenetetrafluoroethylene (ETFE), a polyethylenechlorotrifluoroethylene (ECTFE), and any combination thereof. In one particular embodiment, the fluorinated polymer compound consists essentially of polytetrafluoroethylene (PTFE).

The combined thickness of layers 106 and 102 (including mixed zones 104) can be at least about 2 microns, such as at least about 5 microns, at least about 10 microns, at least about 20 microns, at least about 40 microns, at least about 80 microns, or even at least about 120 microns. In another embodiment, the combined thickness of layers can be not greater than about 1 mm, such as not greater than about 800 microns, not greater than about 500 microns, not greater than about 300 microns, not greater than about 200 microns, or not greater than about 150 microns. Moreover, it will be appreciated that the combined thickness
of layers 106 and 102 can be within a range between any of the minimum and maximum percentages noted above.

Addressing the average thickness of layer 106. In instances, the thickness of the non-fluorinated polymer compound layer 106 can be at least about 1 micron, such as at least about 2 microns, at least about 5 microns, at least about 10 microns, at least about 20 microns, at least about 30 microns, at least about 50 microns, at least about 70 microns, or at least about 100 microns. In other instances, the porous non-fluorinated polymer layer 106 can have a thickness of not greater than about 800 microns, such as not greater than about 500 microns, such as not greater than about 300 microns, not greater than about 200 microns, not greater than about 180 microns, not greater than about 150 microns, or not greater than about 120 microns. Moreover, it will be appreciated that the average thickness of layer 106 can be within a range between any of the minimum and maximum percentages noted above.

Addressing the average thickness of layer 102, the fluorinated polymer compound layer can have a thickness of at least about 2 microns, such as at least about 5 microns, at least about 10 microns, at least about 20 microns, at least about 30 microns, at least about 50 microns, at least about 70 microns, or at least about 90 microns. In other instances, the fluorinated polymer compound layer 102 can have a thickness of not greater than about 800 microns, such as not greater than about 500 microns, not greater than 300 microns, not greater than about 200 microns, not greater than about 180 microns, not greater than about 150 microns, or not greater than about 120 microns. Moreover, it will be appreciated that the average thickness of layer 102 can be within a range between any of the minimum and maximum percentages noted above.

Addressing the weight amounts of the various layer materials, in embodiments, the non-fluorinated polymer compound can include at least about 5 wt%, such as at least about 10 wt%, at least about 20 wt%, or at least about 30 wt% of the combined weight of layers 102 and 106 (including mixed zones 104). In other embodiments, the non-fluorinated polymer compound can include not greater than about 80 wt%, such as not greater than about 60 wt%, or not greater than about 40 wt% of the combined weight of layers 102 and 106 (including mixed zones 104).

In yet other embodiments, the amounts of the layer materials included in layer 102 and 106 can be addressed by volumetric amounts. In embodiments, the non-fluorinated
polymer comprises at least about 5 vol%, such as at least about 10 vol%, at least about 20 vol%, at least about 30 vol%, or at least about 40 vol% of the total volume of the layers 102 and 106, which includes mixed zones 104 and any closed porosity (not shown in FIG. 1). In other embodiments, the non-fluorinated polymer comprises not greater than about 90 vol%, such as not greater than about 80 vol%, not greater than about 60 vol%, not greater than about 40 vol%, or not greater than about 30 vol% of the total volume of the non-fluorinated polymer layer and the fluorinated layer.

In instances, the non-fluorinated compound or the fluorinated layer can include at least one filler. The filler can include fibers, glass fibers, carbon fibers, aramids, inorganic materials, ceramic materials, carbon, glass, graphite, aluminum oxide, molybdenum sulfide, bronze, silicon carbide, woven fabric, powder, sphere, thermoplastic material, polyimide (PI), polyamidimide (PAI), polyphenylene sulfide (PPS), polyethersulfone (PES), polyphenylene sulfone (PPS02), liquid crystal polymers (LCP), polyetherketone (PEK), polyether ether ketones (PEEK), aromatic polyesters (Ekonol), mineral materials, wollastonite, barium sulfate, or any combinations thereof.

The filler can be present in different amounts in each polymer compound. In embodiments, the amount of filler can be at least about 1 vol%, such as at least about 2 vol%, at least about 5 vol%, at least about 10 vol%, at least about 20 vol%, or even at least about 30 vol% of the total volume of the polymer compound. In other embodiments, the filler can be present at not greater than about 90 vol%, such as not greater than about 75 vol%, not greater than about 60 vol%, not greater than about 50 vol%, or not greater than about 40 vol% of the total volume of the polymer compound. Moreover, it will be appreciated that the amount of the at least one filler can be within a range between any of the minimum and maximum volume percentages noted above.

In yet further embodiments, the polymer compounds can include an additive. The additives can include softeners, lubricants, plasticizers, dispersants, UV absorbers, or any other agent necessary to improve the applicability of the laminate article. In embodiments, the additives can include fluoropolymers.

In embodiments, the laminate includes bearing articles. In a particular embodiment, the laminate includes slide bearings. Bearings can be prepared in a vast number of very
different shapes and sizes. The smallest bearing, also called a pico bearing, is only a few µm in height compared to bearings for other applications that could be up to 500 mm.

Bearings can include plane bearings, annular bearings, bushings, balljoint bearings (half spheres), plain bearings, axial bearings, thrust bearings, linear bearings, bearing shells, bearing cups and combinations thereof.

In one embodiment, laminates as described herein are maintenance free. The term "maintenance-free" describes laminates that do not need to be greased as was the case for bearings in early car doors. Yet, the life time of maintenance-free bearings exceeds the average life time of the product these bearings are incorporated or the life time of conventional bearings applied for the same purpose.

In one particular embodiment, a bearing article includes a PEEK layer, wherein the PEEK layer is porous. The porosity, which is the ratio of void volume over total volume of the PEEK layer, can be at least about 0.05, such as at least about 0.1, or at least about 0.2. The porosity can be no greater than about 0.8, such as no greater than about 0.7, or not greater than about 0.5.

In one embodiment, the bearing article includes a PTFE composition layer with a thickness of at least about 10 microns, such as at least about 20 microns, at least about 30 microns, at least about 50 microns, or at least about 70 microns. In another embodiment, the bearing article includes a PTFE composition layer with a thickness of not greater than about 500 microns, such as not greater than about 400 microns, not greater than about 300 microns, not greater than about 200 microns, not greater than about 180 microns, or not greater than about 150 microns.

In one embodiment, the bearing article includes a PEEK in an amount of at least about 10 vol%, such as at least about 20 vol%, at least about 40 vol%, or at least about 50 vol% of the combined polymer layers, i.e. the combination of the PEEK layer and the PTFE composition layer. In another embodiment, the bearing article includes a PEEK layer in an amount of not greater than about 80 vol%, such as not greater than about 70 vol%, not greater than about 60 vol%, or not greater than about 50 vol% of the combined layers, i.e. the combination of the PEEK layer and the PTFE composition layer.
In yet another embodiment, the bearing article has PTFE composition layer which further includes a filler. The filler can include fibers, glass fibers, carbon fibers, aramids, inorganic materials, ceramic materials, carbon, glass, graphite, aluminum oxide, molybdenum sulfide, bronze, silicon carbide, woven fabric, powder, sphere, thermoplastic material, polyimide (PI), polyamidimide (PAI), polyphenylene sulfide (PPS), polyethersulofone (PES), polyphenylene sulfone (PPS02), liquid crystal polymers (LCP), polyetherketone (PEK), polyether ether ketones (PEEK), aromatic polyesters (Ekonol), mineral materials, wollastonite, barium sulfate, or any combinations thereof.

In one embodiment, a method of forming a bearing article can include providing a substrate having a major surface. The method can further include roughening the major surface of the substrate. The method can further include applying a layer of a non-fluorinated polymer onto the major surface. The method can also include coating the non-fluorinated polymer layer with a fluoropolymer composition to form a laminate. Furthermore, the method can include pressing the laminate to form the bearing article.

FIG. 2 shows an exemplary process for forming a laminate. A metal substrate 202 including a roughened surface is thermally (205) sprayed with a non-fluorinated powder 204. The spraying is conducted through device 206 capable of thermal spraying. Thermal spraying creates a porous layer 214 of the non-fluorinated polymer. The porous layer 214 can be sprayed to any desired thickness. The amount of non-fluorinated polymer applied can be made dependent from properties such as desired adhesion strength to the metal backing or other properties, e.g., electrical insulation, which may require a thicker layer. After the thermal spraying of the non-fluorinated polymer layer, the layer is smoothened by skimming board 208. Next, a fluorinated polymer compound powder 212 from applicator 210 is applied onto the porous layer 214. The fluorinated polymer compound can include any of the fluorinated polymer compounds described herein or a mixture of a fluoropolymer with another polymer, filler, surface agent, softening agent, plasticizer, or any other beneficial agent.

The fluorinated polymer compound layer can be applied to any desired thickness depending from its application purpose. The fluoropolymer compound layer can be sprayed, brushed, paint coated, or applied by any conventional process onto the porous layer 214. For example, as shown in FIG. 2 the fluoropolymer can be sprayed. In embodiments, the non-fluorinated polymer compound and the fluorinated polymer compound can be sprayed
subsequently as shown in FIG. 2, concurrent (not shown in FIG. 2) or partially concurrent (not shown in FIG. 2). With respect to the partial concurrent spraying, there is a phase when the non-fluorinated polymer compound is sprayed, a phase when the non-fluorinated polymer compound and the fluorinated polymer compound is applied concurrently, and a phase when the fluorinated polymer compound is applied.

Upon application of the fluoropolymer compound powder, the assembly undergoes pressure and/or heat treatment. As shown in FIG. 2, the assembly can be pressed through rolls 216. In another embodiment, rolls 216 can also be heated, thereby calendering the assembly. Heat 220 can be applied with heater 218. Optionally, after heat treatment, the assembly can be pressed or calendered by rolls 220 to form compound layer 224. In other embodiments and not shown in FIG. 2, the assembly can undergo cold rolling followed by polymer or plastic sintering.

Addressing the non-fluorinated polymer powder, the non-fluorinated polymer can include a poly-ether-ether-ketone (PEEK), an ultra-high-molecular-weight polyethylene (UHMWPE), a polyimide (PI), a polyamide (PA), a polyamideimde (PAI), a polyphenylsulfide (PPS), a polyhydroxybutyrate (PHB), and any combination thereof. In one embodiment, the non-fluorinated polymer consists essentially of poly-ether-ether-ketone (PEEK).

The non-fluorinated powder can have an average particle size of at least about 1 micron, such as at least about 2 microns, at least about 5 microns, or even about 10 microns. In another embodiment, the non-fluorinated powder can have an average particle size of not greater than about 100 microns, such as not greater than about 80 microns, not greater than about 60 microns, or even not greater than about 40 microns.

In another embodiment, the method can include spraying the substrate with a non-fluorinated polymer powder to form the layer 214 to a thickness of not greater than about 800 microns, such as not greater than about 500 microns, not greater than about 400 microns, not greater than about 300 microns, not greater than about 200 microns, not greater than about 180 microns, or not greater than about 150 microns. In one embodiment, the method includes spraying the metal substrate with a non-fluorinated polymer powder to form layer 214 to a thickness of at least about 5 microns, such as at least about 10 microns, at least about 20 microns, at least about 30 microns, at least about 50 microns, or at least about 70 microns. In
embodiments, the method includes applying the non-fluorinated polymer by thermal spraying or by flame spraying the non-fluorinated polymer.

Addressing the fluorinated polymer powder, the fluorinated polymer compound can include a polytetrafluoroethylene (PTFE), a perfluoroalkoxy polymer (PFA), fluorinated ethylene-propylene (FEP), polyvinylfluoride (PVF), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), a polyethylenetetrafluoroethylene (ETFE), a polyethylenechlorotrifluoroethylene (ECTFE), or any combination thereof. In one embodiment, the fluorinated polymer compound consists essentially of polytetrafluoroethylene.

The fluorinated polymer powder can have an average particle size of at least about 1 micron, such as at least about 2 microns, at least about 5 microns, or even about 10 microns. In another embodiment, the non-fluorinated powder can have an average particle size of not greater than about 100 microns, such as not greater than about 80 microns, not greater than about 60 microns, or even not greater than about 40 microns.

The fluorinated polymer powder can be applied as dispersion or in dry form. The method includes coating the fluorinated polymer powder by spray coating or paint coating.

In another embodiment, the method can further include heat rolling the laminate layer. In another embodiment, the method can include heat pressing or calendaring the laminate.

In one embodiment, the non-fluorinated layer and the fluorinated layer have a combined thickness of at least about 20 microns, such as at least about 40 microns, at least about 80 microns, or at least about 100 microns. In another embodiment, the combined thickness is not greater than about 1 millimeter, such as not greater than about 500 microns, or at not greater than about 300 microns.

Examples

High performance non-fluorinated polymers, such as PEEK have favorable properties such as chemical resistance, electric insulation, self-lubrication, or durability against stress. Fluorinated polymers such as PTFE have favorable properties such as chemical resistance, heat resistance, and low friction.
Example 1

An aluminum metal backing was sandblasted at 3 bar to a surface roughness $R_a$ of 3 microns to 4 microns. PEEK with an average particle size of about 20 microns was thermally sprayed onto sandblasted aluminum substrate. Thermal spraying was conducted with an ABB robot 4400. PEEK was flame sprayed using a Castodyn 8000 torch with a M40 nozzle. The spraying distance was between 100 and 300 mm, and the nozzle scanning speed was regulated between 150 and 400 mm/s. The scanning steps were regulated between 1 and 5 mm. Between 1 and 5 passes were run over the substrate. After that a PTFE compound was applied with a paint spray gun. The PTFE compound was sprayed from a distance between 100 and 300 mm, with a spray speed between 150 and 400 mm/s, and for 1 to 5 passes. Afterwards, the assembly was sintered at 340 °C for 10 minutes and 430 °C for 5 minutes.

Tribological testing was conducted using a CSM ball-on-disk tribometer using a load of 5N at a speed of 70 cm/s, a ball having a radius of 12 mm. The tests were run over a distance of 2000m. The results for three samples are summarized in FIG. 3.

Tribological testing results show that COF (Coefficient of Friction) all samples of PEEK/PTFE coatings show substantially constant COF values over the complete duration of the testing. The end values for COF were between 0.125 and 0.175. Although not illustrated in FIG. 3, the end of test COF values for all PEEK/PTFE coatings were lower than the end of test COF values for single PEEK layers (no PTFE coating) or for single PTFE layers (no PEEK layer).

Note that not all of the activities described above in the general description or the examples are required, that a portion of a specific activity may not be required, and that one or more further activities may be performed in addition to those described. Still further, the order in which activities are listed are not necessarily the order in which they are performed.

In the foregoing specification, the concepts have been described with reference to specific embodiments. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the invention as set forth in the claims below. Accordingly, the specification and figures are to be regarded in an illustrative rather than a restrictive sense, and all such modifications are intended to be included within the scope of invention.
As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of features is not necessarily limited only to those features but may include other features not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive-or and not to an exclusive-or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

The term "averaged," when referring to a value, is intended to mean an average, a geometric mean, or a median value.

Benefits, other advantages, and solutions to problems have been described above with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or all the claims.

After reading the specification, skilled artisans will appreciate that certain features are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. Further, references to values stated in ranges include each and every value within that range.
CLAIMS:

1. A laminate article, comprising
   a substrate;
   a layer comprising a heterogeneous mixture of a non-fluorinated polymer compound
   and a fluorinated polymer compound;
   wherein the laminate article includes a gradual concentration gradient along an axis
   perpendicular to the substrate, wherein the gradual concentration gradient includes a change
   of an amount of the non-fluorinated polymer and the fluorinated polymer compound relative
   to the axis perpendicular to the substrate.

2. The laminate according to claim 1, wherein the non-fluorinated polymer compound is
   selected from a poly-ether-ether-ketone (PEEK), an ultra-high-molecular-weight
   polyethylene (UHMWPE), a polyimide (PI), a polyamide (PA), a polyamideimde (PAI), a
   polyphenylsulfide (PPS), a polyhydroxybutyrate (PHB), and any combination thereof.

3. The laminate according to claim 1, wherein the non-fluorinated polymer compound
   consists essentially of a poly-ether-ether-ketone.

4. The laminate according to claim 1, 2, or 3, wherein the fluorinated polymer compound
   is selected from polytetrafluoroethylene (PTFE), a perfluoroalkoxy polymer (PFA), fluorinated
   ethylene-propylene (FEP), polyvinylfluoride (PVF), polyvinylidene fluoride (PVDF),
   polychlorotrifluoroethylene (PCTFE), a polyethylenetetrafluoroethylene (ETFE), a
   polyethylenechlorotrifluoroethylene (ECTFE), or any combination thereof.

5. The laminate according to claim 1, 2, or 3, wherein the fluorinated polymer compound
   consists essentially of polytetrafluoroethylene.

6. The laminate according to any one of claims 1 through 5, wherein the layer has a thickness
   of at least about 5 microns, such as at least about 10 microns, or at least about 20 microns.

7. The laminate according to claim 6, wherein the layer has a thickness of not greater than
   about 1 mm, such as not greater than about 500 microns, or not greater than about 300
   microns.
8. The laminate according to any one of claims 1 through 7, wherein the non-fluorinated polymer comprises at least about 10 wt%, such as at least about 20 wt%, or at least about 30 wt% of the layer.

9. The laminate according to claim 8, wherein the non-fluorinated polymer comprises not greater than about 80 wt%, such as not greater than about 60 wt%, or not greater than about 40 wt% of the layer.

10. The laminate according to any one of claims 1 through 9, wherein the layer further includes a filler.

11. The laminate according to claim 10, wherein the filler is selected from fibers, glass fibers, carbon fibers, aramids, inorganic materials, ceramic materials, carbon, glass, graphite, aluminum oxide, molybdenum sulfide, bronze, silicon carbide, woven fabric, powder, sphere, thermoplastic material, polyimide (PI), polyamidimide (PAI), polyphenylene sulfide (PPS), polyethersulfone (PES), polyphenylene sulfone (PPS02), liquid crystal polymers (LCP), polyetherketone (PEK), polyether ether ketones (PEEK), aromatic polyesters (Ekonol), mineral materials, wollastonite, barium sulfate, or any combinations thereof.

12. The laminate according to any one of claims 1 through 11, wherein the substrate includes a metal substrate or a metal alloy substrate.

13. The laminate according to claim 12, wherein the metal substrate has a surface roughness of at least about 1 micron, at least about 5 microns, at least about 10 microns, or at least about 100 microns.

14. The laminate according to claim 13, wherein the surface roughness is not greater than about 200 microns, such as not greater than about 100 microns, or not greater than about 80 microns.

15. The laminate according to any one of claims 1 through 14, wherein the non-fluorinated polymer further includes a softener or plasticizer.

16. The laminate according to claim 15, wherein the softener or the plasticizer includes a fluoropolymer.
17. A laminate article, comprising
   a substrate;
   a porous non-fluorinated polymer layer overlying the substrate; and
   a fluorinated polymer compound layer overlying and penetrating the porous non-
   fluorinated layer.

18. The laminate according to claim 17, wherein the non-fluorinated polymer is selected
   from a poly-ether-ether-ketone (PEEK), an ultra-high-molecular-weight polyethylene
   (UHMWPE), a polyimide (PI), a polyamide (PA), a polyamideimide (PAI), a
   polyphenylsulfide (PPS), a polyhydroxybutyrate (PHB), and any combination thereof.

19. The laminate according to claim 17, wherein the non-fluorinated polymer consists
   essentially of a poly-ether-ether-ketone.

20. The laminate according to claim 17, 18, or 19, wherein the fluorinated polymer
    compound is selected from polytetrafluoroethylene (PTFE), a perfluoroalkoxy polymer
    (PEA), fluorinated ethylene-propylene (FEP), polyvinylfluoride (PVF), polyvinylidene
    fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), a polyethylene-tetrafluoroethylene
    (ETFE), a polyethylenechlorotrifluoroethylene (ECTFE), or any combination thereof.

21. The laminate according to claim 17, 18, or 19, wherein the fluorinated polymer
    compound consists essentially of polytetrafluoroethylene.

22. The laminate according to any one of claims 17 through 21, wherein the porous non-
    fluorinated polymer layer has a thickness of at least about 10 microns, such as at least about
    30 microns, or at least about 70 microns.

23. The laminate according to claim 22, wherein the porous non-fluorinated polymer layer
    has a thickness of not greater than about 500 microns, such as not greater than 300 microns,
    not greater than about 180 microns, or not greater than about 150 microns.

24. The laminate according to any one of claims 17 through 23, wherein the fluorinated
    polymer compound layer has a thickness of at least about 10 microns, such as at least about
    30 microns, or at least about 70 microns.
25. The laminate according to claim 24, wherein the fluorinated polymer compound layer has a thickness of not greater than about 500 microns, such as not greater than 300 microns, not greater than about 180 microns, or not greater than about 150 microns.

26. The laminate according to any one of claims 17 through 25, wherein the non-fluorinated polymer comprises at least about 10 vol%, such as at least about 20 vol%, or at least about 30 vol% of the combined polymer layers.

27. The laminate according to claim 26, wherein the non-fluorinated polymer comprises not greater than about 80 vol%, such as not greater than about 60 vol%, or not greater than about 40 vol% of a combination including the non-fluorinated polymer layer and the fluorinated layer.

28. The laminate according to any one of claims 17 through 27, wherein the layer further includes a filler.

29. The laminate according to claim 28, wherein the filler is selected from fibers, glass fibers, carbon fibers, aramids, inorganic materials, ceramic materials, carbon, glass, graphite, aluminum oxide, molybdenum sulfide, bronze, silicon carbide, woven fabric, powder, sphere, thermoplastic material, polyimide (PI), polyamidimide (PAI), polyphenylene sulfide (PPS), polyethersulofone (PES), polyphenylene sulfone (PPS02), liquid crystal polymers (LCP), polyetherketone (PEK), polyether ether ketones (PEEK), aromatic polyesters (Ekonol), mineral materials, wollastonite, barium sulfate, or any combinations thereof.

30. The laminate according to any one of claims 17 through 29, wherein the substrate includes a metal substrate or a metal alloy substrate.

31. The laminate according to claim 30, wherein the metal substrate has a surface roughness of at least of at least about 1 micron, at least about 5 microns, at least about 10 microns, or at least about 100 microns.

32. The laminate according to claim 31, wherein the surface roughness is not greater than about 200 microns, such as not greater than about 100 microns, or not greater than about 80 microns.

33. A bearing article, comprising
   a metal substrate;
a discontinuous layer of a non-fluorinated polymer overlying the metal substrate;
a continuous layer of a fluorinated polymer compound overlying and penetrating the discontinuous layer.

34. The bearing article according to claim 33, wherein the non-fluorinated polymer is selected from a poly-ether-ether-ketone (PEEK), an ultra-high-molecular-weight polyethylene (UHMWPE), a polyimide (PI), a polyamide (PA), a polyamideimde (PAI), a polyphenylsulfide (PPS), a polyhydroxybutyrate (PHB), and any combination thereof.

35. The bearing article according to claim 33, wherein the non-fluorinated polymer consists essentially of poly-ether-ether-ketone.

36. The bearing article according to claim 33, 34, or 35, wherein the fluorinated polymer compound is selected from polytetrafluoroethylene (PTFE), a perfluoroalkoxy polymer (PEA), fluorinated ethylene-propylene (FEP), polyvinylfluoride (PVF), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), a polyethylene-tetrafluoroethylene (ETFE), a polyethylenechlorotrifluoroethylene (ECTFE), or any combination thereof.

37. The bearing article according to claim 33, 34, or 35, wherein the fluorinated polymer compound is polytetrafluoroethylene.

38. The bearing article according to any one of claims 33 through 37, wherein the discontinuous layer has a thickness of at least about 5 microns, such as at least about 10 microns, or at least about 20 microns.

39. The bearing article according to claim 38, wherein the discontinuous layer has a thickness of not greater than about 500 microns, such as not greater than about 300 microns, not greater than about 180 microns, or not greater than about 150 microns.

40. The bearing article according to any one of claims 33 through 39, wherein the continuous polymer layer has a thickness of at least about 10 microns, such as at least about 30 microns, or at least about 70 microns.

41. The bearing article according to claim 40, wherein the continuous polymer layer has a thickness of not greater than about 500 microns, such as not greater than about 300 microns, not greater than about 180 microns, or not greater than about 150 microns.
42. The bearing article according to any one of claims 33 through 41, wherein the discontinuous layer comprises at least about 10 vol%, such as at least about 20 vol%, or at least about 30 vol% of the combined layers.

43. The bearing article according to claim 42, wherein the discontinuous comprises not greater than about 80 vol%, such as not greater than about 60 vol%, or not greater than about 40 vol% of the combined layers.

44. The bearing article according to any one of claims 33 through 43, wherein the layer further includes a filler.

45. The bearing article according to claim 44, wherein the filler is selected from fibers, glass fibers, carbon fibers, aramids, inorganic materials, ceramic materials, carbon, glass, graphite, aluminum oxide, molybdenum sulfide, bronze, silicon carbide, woven fabric, powder, sphere, thermoplastic material, polyimide (PI), polyamidimide (PAI), polyphenylene sulfide (PPS), polyethersulfone (PES), polyphenylene sulfone (PPS02), liquid crystal polymers (LCP), polyetherketone (PEK), polyether ether ketones (PEEK), aromatic polyesters (Ekonol), mineral materials, wollastonite, barium sulfate, or any combinations thereof.

46. The bearing article according to any one of claims 33 through 45, wherein the metal substrate has a surface roughness of at least of at least about 1 micron, at least about 5 microns, at least about 10 microns, or at least about 100 microns.

47. The bearing article according to claim 46, wherein the surface roughness is not greater than about 200 microns, such as not greater than about 100 microns, or not greater than about 80 microns.

48. A bearing material comprising:

   a metal substrate having a roughened surface;

   a porous PEEK layer;

   a continuous PTFE composition layer overlying and penetrating the porous PEEK layer.

49. The bearing article according to claim 48, wherein the porous PEEK layer has a porosity of at least about 0.1, such as at least about 0.2, or even at least about 0.4.
50. The bearing article according to claim 49, wherein the porosity of not greater than about 0.7, such as not greater than about 0.6, or even not greater than about 0.5.

51. The bearing article according to any of claims 48 through 40, wherein the porous PEEK layer has a thickness of at least about 30 microns, such as at least about 50 microns, or at least about 70 microns.

52. The bearing article according to claim 51, wherein the porous PEEK layer has a thickness of not greater than about 200 microns, such as not greater than 180 microns, or not greater than about 150 microns.

53. The bearing article according to any one of claims 48 through 52, wherein the continuous PTFE composition layer has a thickness of at least about 10 microns, such as at least about 30 microns, or at least about 70 microns.

54. The bearing article according to claim 53, wherein the continuous PTFE composition layer has a thickness of not greater than about 150 microns, such as not greater than 130 microns, or not greater than about 100 microns.

55. The bearing article according to any one of claims 48 through 54, wherein the porous PEEK layer comprises at least about 20 vol%, such as at least about 40 vol%, or at least about 50 vol% of the combined layers.

56. The bearing article according to claim 55, wherein the porous PEEK layer comprises not greater than about 80 vol%, such as not greater than about 60 vol%, or not greater than about 50 vol% of the combined layers.

57. The bearing article according to any one of claims 48 through 56, wherein the continuous PTFE layer further includes a filler.

58. The bearing article according to claim 57, wherein the filler is selected from fibers, glass fibers, carbon fibers, aramids, inorganic materials, ceramic materials, carbon, glass, graphite, aluminum oxide, molybdenum sulfide, bronze, silicon carbide, woven fabric, powder, sphere, thermoplastic material, polyimide (PI), polyamidimide (PAI), polyphenylene sulfide (PPS), polyethersulfone (PES), polyphenylene sulfone (PPS02), liquid crystal polymers (LCP), polyetherketone (PEK), polyether ether ketones (PEEK), aromatic polyesters (Ekonol), mineral materials, wollastonite, barium sulfate, or any combinations thereof.
59. The bearing article according to any one of claims 48 through 58, wherein the metal substrate has a surface roughness of at least of at least about 1 micron, at least about 5 microns, at least about 10 microns, or at least about 100 microns.

60. The bearing article according to claim 59, wherein the surface roughness is not greater than about 200 microns, such as not greater than about 100 microns, or not greater than about 80 microns.

61. A method of manufacturing a bearing article, the method comprising:
   providing a substrate having a major surface;
   roughening the major surface of the substrate;
   applying a layer of a non-fluorinated polymer onto the major surface;
   coating the non-fluorinated polymer layer with a fluoropolymer composition to form a laminate; and
   pressing the laminate to form the bearing article.

62. The method according to claim 61, wherein the non-fluorinated polymer is selected from a poly-ether-ether-ketone (PEEK), an ultra-high-molecular-weight polyethylene (UHMWPE), a polyimide (PI), a polyamide (PA), a polyamideimde (PAI), a polyphenylsulfide (PPS), a polyhydroxybutyrate (PHB), and any combination thereof.

63. The method according to claim 61, wherein the non-fluorinated polymer consists essentially of a poly-ether-ether-ketone.

64. The method according to claim 61, 62, or 63, wherein the fluorinated polymer compound is selected from polytetrafluoroethylene (PTFE), a perfluoroalkoxy polymer (PEA), fluorinated ethylene-propylene (FEP), polyvinylfluoride (PVF), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), a polyethylenetetrafluoroethylene (ETFE), a polyethylenechlorotrifluoroethylene (ECTFE), or any combination thereof.

65. The bearing article according to claim 61, 62, or 63, wherein the fluorinated polymer compound consists essentially of a polytetrafluoroethylene.

66. The method according to any one of claims 61 through 65, wherein applying the non-fluorinated polymer includes thermal spraying or flame spraying the non-fluorinated polymer.
67. The method according to any one of claims 61 through 66, wherein the coating includes paint coating or spray coating.

68. The method according to any one of claims 61 through 67, wherein the pressing includes heat pressing or calendaring.
$F = 5 \text{ N}; \; v = 70 \text{ cm/sec}; \; r = 12 \text{ mm}; \; d = 2000 \text{ m}$

**FIG. 3**
INTERNATIONAL SEARCH REPORT  

A. CLASSIFICATION OF SUBJECT MATTER  

B32B 27/06(2006.01)i, B32B 15/08(2006.01)i, B32B 5/18(2006.01)i, F16C 33/24(2006.01)i  

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)
B32B 27/06; B05D 1/36; B05D 1/08; B32B 15/08; C08G 18/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic database consulted during the international search (name of database and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: fluorinated polymer, PEEK (poly ether ether ketone), PTFE (polytetrafluoroethylene), thermal spray

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 2003-0049485 (RUPBACHER et al.) 13 March 2003</td>
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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 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  
11 April 2013 (11.04.2013)

Date of mailing of the international search report  
12 April 2013 (12.04.2013)

Name and mailing address of the ISA/KR  
Korean Intellectual Property Office  
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea  
Facsimile No. 82-42-472-7140

Authorized officer  
CHANG, Bong Ho

T\*.\*, Jo. 82-42-481-3353

Form PCT/ISA/210 (second sheet) (July 2009)
### Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 7,9,11,13,14,16,23,25,27,29,31,32,39,41,43,45,47,54,56,58,60
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   Claims 7,9,11,13,14,16,23,25,27,29,31,32,39,41,43,45,47,54,56,58,60 refer to unsearchable claims which do not comply with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 6,8,10,12,15,22,24,26,28,30,38,40,42,44,46,53,55,57,59,66-68
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

☐ The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

☒ The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2))  (July 2009)
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<td>CN 101437905 A</td>
<td>20.05.2009</td>
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<tr>
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<td></td>
<td>EP 1976945 A1</td>
<td>08.10.2008</td>
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<td>09.11.2010</td>
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<td>WO 2007-089620 A1</td>
<td>09.08.2007</td>
</tr>
<tr>
<td>EP 0988898 A2</td>
<td>29.03.2000</td>
<td>AR 021821 A1</td>
<td>07.08.2002</td>
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<td>CA 2283022 A1</td>
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<td>14.06.2000</td>
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<td>EP 0988898 A3</td>
<td>02.05.2001</td>
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<td>28.01.2005</td>
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<td>01.02.2009</td>
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<td>US 7875563 B2</td>
<td>25.01.2011</td>
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