A composition comprising a dyed polymer fiber capable of holding the color of the dye wherein the fiber comprises a polyetherimide and the dyed fiber has a colorfast score of 1/5 or higher according to ISO 105-302.
Fiber Process Schematic

Extruder

metering pump
filter
spinneret
air quench
convergence guide
finish applicator
drawing
bobbin
COLORFAST DYED POLY ETHER IMIDE ARTICLES INCLUDING FIBER

FIELD OF THE INVENTION

[0001] The present invention relates to colorfast dyed fibers comprising a polyetherimide polymer. The present invention is also directed to polyetherimide articles which are dyed and colorfast.

BACKGROUND OF THE INVENTION

[0002] Polyetherimides are a known class of polymers that have found great utility in a variety of applications because of their properties. Polyetherimides are flame resistant, have high Tg's, are ductile, generate low amounts of smoke and have good chemical resistivity. As such, PEI has found use as shaped articles, sheet materials, and coatings. Recently polyetherimide fibers have been investigated as fibers. See U.S. Pat. No. 5,670,256 to St. Clair et al. issued Sep. 23, 1997.

[0003] Polyetherimides in general, including those available from General Electric (also referred as “GE”) Plastics under the ULTEM tradename, have high viscosity at low shear rate that is still sufficient for fiber spinning of such amorphous material. PEI can be melt or solvent spun into fiber with denier ranging form 0.25 to 50. PEI in molded part has low ductility. Surprisingly, fibers of PEI have elongation at break as high as 80%. The flame performance when used 100% will meet most flame requirement for textile, furniture, bedding and aerospace industries. Surprisingly, high flame performance will be achieved when combined or blended with low flame performance materials and other high flame performance fibers (but non-melting) such as Aramids, Kevlar, Polybenzimidazole, polybenzoximidazole, Polyimide, Rayon and other fibers. The blends could contain a PEI fiber from 5 to 99% range.

[0004] Protective apparel and uniforms (clothing for firefighters, for example), furniture (flame resistant sofa's, for example), bedding (flame resistant mattresses), automotive and aerospace seating industries have been requiring high flame resistance performance from construction materials. In many instances flame resistant performance fibers are significantly more expensive than non-flame resistant fibers, thus impeding the use of more expensive fibers in these important applications. For example, the prices of flame resistant polymers such as PBO, PI, and PBI can range from $80-$200/lb at the time of the filing of this patent application. Expensive fibers such as PBO, PI, PBI, Aramid Flame retarded materials such as FR Rayon, FR cotton, NOMEX and Kevlar fibers have been used, these fibers have low resistance to ultra violet light, which weakens them and consequently shortens their useful lifetime.

[0005] Polyetherimide fiber is an amorphous fiber with excellent flame resistance (predicted), ability to melt and stick to other fiber (blocks emission of flame supporting volatiles) combined with high UV resistance when use alone (100%) or blended with other flammable or non-flammable fibers will result in flame resistant (woven or non-woven) fire resistant materials with long life expectancy.

[0006] One significant impediment to the more widespread use of polyetherimide fibers has been their subjectively unattractive yellow color. In fact, polyetherimide has been difficult, if not impossible to dye. Dr. D. Bohringer states in his article “New Filaments and Fibers of Polyetherimide”, Chemiefasern/Textilindustrie (CTI) Vol. 41/93 (March 1991) pp. T12-T16 that “due to their amorphous structure it is not possible to dye the [polyetherimide] fiber by conventional processes” (bracketed material added). In the AKZO “PEI High Performance Fiber” publication issued by the Akzo Fibres and Polymers Division of ENKA AG, polyetherimide fiber is characterized as "cannot be dyed by usual processes".

[0007] There exists a important and unmet need for dyed polyetherimide fibers across numerous industries, including but not limited to furniture, aerospace, transportation and textile.

SUMMARY OF THE INVENTION

[0008] A composition, a dyed polymer fiber capable of holding the color of the dye wherein the fiber comprises a polyetherimide and the dyed fiber has a colorfast score of 1/5 or higher according to ISO 105-302.

BRIEF DESCRIPTION OF THE FIGURES

[0009] FIG. 1 is a schematic of a method of producing the dyed PEI fiber according to the present invention. Heated Polymer is fed into a metering pump (1) and then through a filter (20) to remove unwanted debris and prevent clogging of the spinneret (3). After being filtered (2) the heated polymer is passed through a spinneret (3) to produce one or more strands of PEI fiber (4) which are air quenched (5) and processed through a convergence guide (6). A finish, if desired, can be applied via a finish applicator (7). The PEI fibers are then drawn (8), placed on a bobbin (9) and exposed to a dye.

DETAILED DESCRIPTION OF THE INVENTION


[0011] According to the present invention the term “Denier” refers to a unit of fineness of silk and some artificial fibers such as nylon equal to one gram per 9,000 meters of yarn.

[0012] The term “dyeing” denotes imparting a substantially permanent color (as defined by the ISO 105-B02 colorfastness standard of at least 1) to organic fibrous or filamentous material or other porous material by the use of substances, or preparations possessing tincorial properties and which are not dependent for their ability to become fixed to the base solely upon the presence of an adhesive of bindive vehicle or ingredient, as distinguished from the application of an insoluble pigment suspended in a bindive vehicle, e.g., paint or any colored coating composition where the coloring agent does not actually color the base.

[0013] “Dyability” refers to one or more constellation of related properties of a fiber's, in this case a polymer fibers, ability to be dyed including the rate at which the polymer can be dyed, the amount of dye that can be applied to the polymer (ie dye exhaustion), and the fastness of the dyes on the dyed polymers.

[0014] “Dye Additive” or “dye assistant” is defined to be any material added to a dye to help in dyeing and is not basically a part of the dye itself.
"Mordants" are substances of organic or inorganic origin which combine with the coloring matter and are used to fix the same in the production of the color. For the purpose of the present invention, materials as oils and sulfonated oils, soaps, fats and higher acids, are not generally considered as mordants, but as coming within the scope of "assistants" in dyeing.

For purposes of the present invention the term "polyetherimide" refers to a polymer containing monomer units which comprise both an ether and an imide group.

An ether group is well known in the art and consists of an oxygen atom single bonded to two different carbon atoms. An imide group is a nitrogen containing acid having two double bonds.

Chromophore means the chemical group that gives color to a molecule.

The term substrate is used here to refer to the base material being dyed.

The Dyed Fiber

The dyed fibers of the present invention comprise one or more polyetherimide polymers. The polyetherimide can be any polyetherimide that will hold a dye with a colorfastness according to ISO 105-302 of greater than 1 or, in alternate embodiments of the present invention, a colorfastness of greater than 2, 3, 4, and, up to, and including 5. The skilled artisan will appreciate the variety of polyetherimides that may be employed in the claimed invention.

The thickness of the dyed fiber according to the present invention is preferably between 0.1 and 50,000 d (denier), or, in another embodiment, from 0.1 to 50.0 d, or from 0.25 to 10.0 d, or still yet further from 0.25 to 1.0. Depending on the end use of the fiber, other dimensional characteristics may also be employed to describe the dyed fibers according to the present invention. For example, dyed fibers according to the present invention also include those from 0.01 dpf (denier per filament) through 50,000 dpf, or more particularly, 0.1 dpf to about 100 dpf. The dyed fiber may also be measured based on its diameter which can range from about 0.00001 mm to about 2 mm or more specifically from about 0.0001 mm to about 0.5 mm. The skilled artisan will appreciate that these ranges include different breadths depending on the use of the dyed fiber and that the present invention covers the entire range from smallest to largest possible dyed PEI fiber.

The dyed fiber may be either of a continuous filament shape or a short staple fiber shape (for example, staple yarn sizes can be 2.25/2 and 10/1 English cotton count, which equates to deniers of 4703 and 532 respectively), including those uniform or irregular in thickness in the lengthwise direction, the cross-sectional shape of which may be circular, triangular, polygonal, multi-lobal or indefinite, including a 1-shape, a T-shape, a Y-shape, a W-shape, an octagonal lobal shape, a flat shape and a dog-bone shape. The dyed fiber may be either solid or hollow.

The dyed fiber according to the present invention may be made exclusively of one polyetherimide or may comprise a blend of two or more polyetherimides. Alternatively, polyetherimide co-polymers may be used to make the dyed fibers of the present invention.

Any final dyed fiber may be included in a multifilament yarn including, in addition to, one or more fibers comprising a polyetherimide, other synthetic, organic, inorganic or natural fibers. Other fibers which may be blended with one or more polyetherimide fibers are selected from synthetic fibers selected from the group consisting of nylons, acrylic, modacrylic, PBI, polyesters, polypropylene, polyethylene, latex, PET, PI, polyesters, spandex, sulfur, vividon, NOMEX, carbon, aramid, ceramic, metal, glass, etc., and mixtures thereof. Natural fibers including but not limited to cellulose fibers, e.g., cotton, rayon, linen, poly/cotton blends, Tencel, and mixtures thereof; proteinaceous fibers, e.g., silk, wool, related mammalian fibers, and mixtures thereof; long vegetable fibers, e.g., jute, flax, ramie, coir, kapok, sisal, henequen, abaca, hemp, sunn, and mixtures thereof; and natural material in the form or fibers including asbestos, for example.

The dyed fiber may be converted to a yarn form according to any method known in the art, such as a spun yarn manufactured from a ring spinning frame or an open end spinning frame, a filament yarn having a single fiber thickness in a range from 0.001 inch to 0.35 inch (including an ultra-fine, yarn), a soft or hard twisted yarn, a mixed fiber yarn, a false-twist textured yarn (including a draw-twist textured yarn of POY) or an air jet textured yarn. In this regard, the mixed fiber yarns according to the present invention may be made through such well known processes as fiber-mixing means, such as a mixed-spinning process (including a ciro-span or a ciro-fil), an entanglement mixing process (wherein yarns having various shrinkages are mixed together), a mixed-twisting process, a composite false-twist process (including an elongation-difference-false-twist process) or a two-feed air jet texturing process.

End uses of dyed polyetherimide fiber include blending thereof with other fibers are: textiles for home furnishings-sofas, pillows, drapes, bed linens, comforters, floor covering, table linens, towels, wall coverings; textiles for safety and protection-vests, firefighter jackets, pants, shirts, underwear, socks, shoes, hats, military apparel, flight apparel, space apparel; textiles for transportation (air, rail, mass, nautical, ear, space)-interior fabrics, floor covering, wall coverings, seating, encasings for foam; textiles for performance apparel-athletic apparel, outdoor apparel, indoor apparel.

The Polyetherimide

Some examples of polyetherimides useful in the present invention include those which comprise more than 1, typically about 10 to about 1,000, or more specifically, about 10 to about 500 structural units, of the formula (12)
wherein T is —O— or a group of the formula —O—Z—O— wherein the divalent bonds of the —O— or the —O—Z—O— group are in the 3,3', 3,4', 4,3', or the 4,4' positions, and wherein Z includes, but is not limited, to divalent radicals of formula:

![Chemical Structure](image)

[0028] Representative polyetherimides are those produced under the ULTEM® trademark, including, but not limited to ULTEM 9011 resin by GE plastics, Pittsfield, Mass., in the United States of America. ULTEM type polyetherimides are described in detail in U.S. Pat. Nos. 3,647,867; 4,650,850; 4,794,157; 4,855,391; 4820,781; and 4,816,527, which are herein incorporated by reference in their entirety as though set forth in full.

[0029] In one embodiment, the polyetherimide may be a copolymer which, in addition to the etherimide units described above, further contains polyimide structural units of the formula: (13)

![Chemical Structure](image)

wherein R is as previously defined for formula (8) and M includes, but is not limited to, radicals of formulas: (14).

![Chemical Structure](image)

[0030] The polyetherimide can be prepared by various methods, including, but not limited to, the reaction of an aromatic bis(ether anhydride) of the formula (15)

![Chemical Structure](image)

with an organic diamine of the formula (16)

![Chemical Structure](image)

wherein R and T are defined in relation to formulas (8) and (12).

[0031] Examples of specific aromatic bis(ether anhydride)s and organic diamines are disclosed, for example, in U.S. Pat. Nos. 3,972,902 and 4,455,410. Illustrative examples of aromatic bis(ether anhydride)s of formula (15) include: 2,2'-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)phenyl ether dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride; 2,2-bis[(3,3'-dicarboxyphenoxy)phenyl]propane dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride; 4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfone dianhydride; and 4,4'-bis(3,3'-dicarboxyphenoxy)diphenyl sulfone dianhydride, as well as various mixtures comprising at least one of the foregoing.

[0032] The bis(ether anhydride)s can be prepared by the hydrolysis, followed by dehydration, of the reaction product of a nitro substituted phenyl dinitrile with a metal salt of a bisphenol compound (e.g., BPA) in the presence of a dipolar, aprotic solvent. An exemplary class of aromatic bis(ether anhydride)s included by formula (15) above includes, but is not limited to, compounds wherein T is of the formula (17):

![Chemical Structure](image)

and the ether linkages, for example, are in the 3,3', 3,4', 4,3', or 4,4' positions, and mixtures comprising at least one of the foregoing, and where Q is as defined above.

[0033] Any diamino compound may be employed. Examples of suitable compounds are ethylenediamine, propylenediamine, trimethylenediamine, diethylenetriamine, triethylenetetramine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 1,12-dodecanediamine, 1,18-octadecanediame, 3-methylheptamethylenediamine,
4,4-dimethylheptamethylenediamine, 4-methylnonamethylenediamine, 5-methylnonamethylenediamine, 2,5-dimethylhexamethylenediamine, 2,5-dimethylheptamethylenediamine, 2,2-dimethylproplylenediamine, N-methyl-bis(3-aminopropyl)amine, 3-methoxyhexamethylenediamine, 1,2-bis(3-aminopropoxy)methane, bis(3-aminopropyl)sulfide, 1,4-cyclohexanediamine, bis(4-aminocyclohexyl)methane, m-phenylenediamine, p-phenylenediamine, 2,4-dianisotoluene, 2,6-dianisotoluene, m-xylene diamine, p-xylene diamine, 2-methyl-4,6-diethyl-1,3-phenylene diamine, 5-methyl-4,6-diethyl-1,3-phenylene diamine, benzidine, 3,3’-dimethylbenzidine, 3,3’-dimethoxybenzidine, 1,5-diaminonapthalene, bis(4-aminophenyl)methane, bis(2-chloro-4-amino-3,5-diethylphenyl)methane, bis(4-aminophenyl)propane, 2,4-bis(6-bromo-t-butyl)toluene, bis(p-b-aminot-butyl)phenyl ether, bis(p-b-methyl-o-aminophenyl)benzene, bis(p-b-methyl-o-aminophenyl)benzene, 1,3-diamino-4-isopropylbenzene, bis(4-aminophenyl)sulfide, bis(4-aminophenyl)sulfone, bis(4-aminophenyl)ether and 1,3-bis(3-aminopropyl)tetramethyldisiloxane. Mixtures of these compounds may also be present. Desirably, the diamino compounds are aromatic diamines, especially m-phenylenediamine and mixtures comprising at least one of the foregoing.

In one embodiment, the polyetherimide resin comprises structural units according to formula 12 wherein each R is independently p-phenylene or m-phenylene or a mixture comprising at least one of the foregoing and T is a divalent radical of the formula (18)

```
R
O

CH3
```

Included among the many methods of making the polyimides, particularly polyetherimides, are those disclosed in U.S. Pat. Nos. 3,847,867; 3,850,885; 3,852,242; 3,855,178; 3,983,693; and, 4,443,591 herein incorporated in their entirety, as though set forth in full.

The reactions can be carried out employing solvents, e.g., o-dichlorobenzene, m-cresol/toluene and the like, to effect a reaction between the anhydride of formula (15) and the diamine of formula (16), at temperatures of about 100°C to about 250°C. Alternatively, the polyetherimide can be prepared by melt polymerization of aromatic bis(ether anhydride)s (15) and diamines (16) by heating a mixture of the starting materials to elevated temperatures with concurrent stirring. Generally, melt polymerizations employ temperatures of about 200°C to about 400°C. Chain stoppers and branching agents may also be employed in the reaction.

When polyetherimide/polyimide copolymers are employed, a dianhydride, such as pyromellitlic anhydride, is used in combination with the bis(ether anhydride). The polyetherimide resin can optionally be prepared from reaction of an aromatic bis(ether anhydride) with an organic diamine in which the diamine is present in the reaction mixture at less than or equal to about 0.2 molar excess. Under such conditions the polyetherimide resin may have less than or equal to about 15 microequivalents per gram (µeq/g) acid titratable groups, or, more specifically less than or equal about 10 µeq/g acid titratable groups, as shown by titration with chloroform solution with a solution of 33 weight percent (wt %) hydrobromic acid in glacial acetic acid. Acid-titratable groups are essentially due to amine end-groups in the polyetherimide resin.

One route for the synthesis of polyetherimides proceeds through a bis(4-halophthalimide) having the following structure (19):

```
O
O
N-R-N X X O
```

wherein R is as described above and X is a halogen. The bis(4-halophthalimide) wherein R is a 1,3-phenyl group (20) is particularly useful.

Bis(halophthalimide)s (19) and (20) are typically formed by the condensation of amines, e.g., 1,3-diaminobenzene with anhydrides, e.g., 4-halophthalic anhydride (21):

```
N
O
O

N
```

Polyetherimides may be synthesized by the reaction of the bis(halophthalimide) with an alkali metal salt of a bisphenol such as bisphenol A or a combination of an alkali metal salt of a bisphenol and an alkali metal salt of another dihydroxy substituted aromatic hydrocarbon in the presence or absence of phase transfer catalyst. Suitable phase transfer catalysts are disclosed in U.S. Pat. No. 5,229,482. Suitable dihydroxy substituted aromatic hydrocarbons include those having the formula (22)

```
OH-A1-A2-OH
```

wherein A1 is a divalent aromatic hydrocarbon radical. Suitable A2 radicals include m-phenylene, p-phenylene, 4,4'-biphenylene, and similar radicals.

Making the PEI fibers according to the present invention may be produced by a method that uses techniques known in the art. The skilled practitioner will understand that the art of manufacturing polymer fibers is old and that
many different methods may be employed to manufacture fibers for dyeing according to the present invention.

[0042] One basic procedure which may need to be performed depending upon the PEI used, for instance, is the dyeing, or water content reduction and/or removal, of the polymer which will go through a spinning process to remove that water content which interferes with the spinning process. Typical conditions for drying the polymer are well within the knowledge of the skilled artisan and can be, for example, heating to 150 °C for 4 hours. Drying may be done right at the start of the spinning process before the polymer chip enters the extruder to be molten.

[0043] As a first step the particular PEI to be used in the present invention is heated to a temperature sufficient to allow the polymer to be further processed through, for example, filters and spinnerets. Depending upon the properties of the individual PEI to be made into fibers, including the melting temperature, the glass transition temperature, melt flow rate or viscosity, molecular weight distribution and intrinsic viscosity, the PEI to be used can be heated to a wide variety of different temperatures to achieve a particular type of fiber, processing parameters, or fiber property. The skilled artisan will appreciate that these temperature properties are routinely published by the manufacturer of any PEI and are widely available to the public. After heating the PEI can be fed into a metering pump to dose the polymer melt to the spinneret, i.e. cm3/min, as one of the defining parameters for the fiber thickness or denier. The skilled artisan will appreciate that other factors, such as the wind-up speed, i.e. how far given amount of polymer melt is stretched into the fiber will also be one of the defining parameters for fiber thickness). The polymer melt may also be passed through a filter to remove unwanted debris, gels, black specs, oligomers, etc. and prevent clogging of the spinneret. For ULTEM 1010, the melt temperature is ideally close to 400 °C.

[0044] The heated polymer can then be processed through a spinneret according to techniques well known in the art. The spinneret can have any number of holes depending on the volume, denier, commercial requirement or end properties of the fiber to be produced. For example, the spinneret can have from 1 to 500 mm filaments to 1,000 holes, or in another embodiment from 32 to 256 holes. In yet another embodiment, the number of holes can be from 32 to 128. The spinneret holes can be of any diameter that will produce a desired denier fiber. Diameters can range from 0.01 mm up to 3 cm, or range from 0.1 mm up to 1 cm, or more specifically can range from 0.3 mm up to 5 mm. In many circumstances, the diameter of the spinneret hole will be directly relatable to the denier of the fiber to be produced. For example, a spinneret hole diameter of 0.45 mm to 0.6 mm will produce a fiber from 2-4 denier using ULTEM 1010, a commercially available PEI from GE Plastics, Pittsfield, Mass., USA. A spinneret hole of from 0.8 mm to about 1.0 mm will produce a fiber of ULTEM 1010 having a denier of about 10.

[0045] The intermediate fibers produced by the spinneret can be quenched, including by air quenching, or not, depending on the end use properties, processing conditions, commercial considerations, etc. that the skilled artisan producing the fibers desires. For Ultem 1010, the lower the melt flow of the material, the lower the temperature of the quench to spin fine denier fibers.

[0046] The intermediate fibers can then be passed through a conversion guide. At the conversion guide the individual filaments from each hole in the spinneret can be brought together once solidified into a bundle of filaments or yarn. Spin finish may also be applied at this point.

[0047] A finish, if desired, can be applied via a finish applicator. As the skilled artisan will appreciate the finish can be a suspension of oils and other additives such as anti-stat, anti-bacterial etc. which can be added to the fiber for further processing. In the described process the fiber or yarn can end up on a spool. This yarn can then either be dyed in a subsequent process on the spool, or converted into a fabric which can then be dyed. Finish can be washed off the yarn or fabric before the dyeing process in a step called scouring.

[0048] The PEI fibers can then be drawn. The drawing process can occur during spinning and involves the fiber or yarn being stretched or drawn between two sets of rolls (sometimes called Godets) moving at different speeds. The skilled artisan understands that by drawing a yarn the balance of tenacity and elongation to break properties can be affected. For example, higher draw can provide a stronger yarn, but with reduced elongation to break. Drawing can either be done cold, or hot via heated rolls. Drawing can also be done off-line, i.e. in a second step.

[0049] Before or after drawing the yarn is normally wound onto a bobbin. Some in-line (i.e. during the spinning process) “processing” can still be done such as, for example, intermingling the yarn with air, which entangles the individual filaments further, or relaxing to reduce yarn shrinkage upon heating in subsequent processes. Subsequently, the fiber may be further processed, for example, by making a yarn of more than one fiber, or packaged such as for example, placing the fiber on a bobbin. Some staple yarn processes wind the filaments onto a cutting drum and cut into different staple lengths during the melt spinning process.

Color Dyeing the Fiber

[0050] Dyed fibers according to the present invention may be dyed any color of the spectrum. These colors include, but are not limited to, black, white, red, orange, yellow, green, blue, indigo and violet. The skilled artisan will appreciate that depending on the specific polyetherimide, polyetherimide blend and/or polyetherimide co-polymer which a fiber is produced from will have an important effect on what dyes can be effectively used. Classes of dye useful in the claimed invention include: animal dyes, vegetable dyes, mordant dye (dyes that require a mordant), acid dyes (dye in which the chromophore is part of a negative ion), aniline dyes (any of the many dyes made from aniline), azo dyes (any dye containing one or more azo groups), basic dyes (dyed in which the chromophore are part of a positive ion), cyanine dye (any class of dyes containing a —CH= group linking two nitrogen containing heterocyclic rings), disperse dyes (water insoluble, neutral dyes applied to the substrate from a fine aqueous suspension, which were originally developed for use in dying of cellulose acetate and polyester materials), oxidation dyes (produce color by oxidation on the substrate of compounds such as anilamino, hydroxyaryl), or similar compounds to produce, e.g. aniline black or diphenyl black), reactive dyes (reacts chemically with a substrate having reactive —H atoms thereon, e.g., ester or ether formation with cellulose), solvent dye (soluble in an organic solvent and is commonly introduced in the form of a solution in an organic solvent), sulfur dyes (contain sulfur linkages within their molecules which are produced by sulfuration, i.e.,
heating of organic compounds with sulfur or alkali polysulfides) and vat dyes (applied to the substrate in reduced, soluble form and then oxidize to the original insoluble pigment. Common vat dyes are quinononic dyes and particularly common are anthraquinones and indigos) to name a few.

[0051] As a general, but non-limiting rule, those dyes useful in dyeing polyester can be used to dye polyetherimides. Non-limiting examples of dyes which can be used to dye one or more polyetherimide fibers of the present invention: Genacryl Red 4B (basic violet), C.I. Disperse Red 367, C.I. Disperse Red 357, Genacryl Blue 3G (basic blue), Diarix.RTM.Blue 27, Diarix.RTM. Blue FBL-E, Diarix.RTM. Blue SB-G, Diarix.RTM. Navy S2-G, Genacryl Blue SB, (basic blue 5), Genacryl Orange G (basic orange), Genacryl Orange R (basic orange), Genacryl Pink 3G (basic red), Genacryl Pink G (basic red), Genacryl Yellow 4G (basic yellow), Genacryl Brilliant Yellow 10GF (basic yellow), Genacryl Yellow GGL (basic yellow), Genacryl Yellow RRL (basic yellow), C.I. Disperse Yellow-54, C.I. Disperse Yellow-64, C.I. Disperse Yellow-82, C.I. Disperse Yellow-88, Genacryl Brilliant Pink FFB (basic red), Genacryl Blue BGLA (basic blue), Genacryl Blue RLG (basic blue), Genacryl Violet RL (basic violet), Genacryl Black GM, Genacryl Black OM, Genacryl Brilliant Red B (Basic Red), Victoria Green S Ext. Cone (basic green), Sevron Yellow L (basic yellow), Genacryl Yellow 5GF (basic yellow), Astraon Orange G (basic orange), Rhodamine B (basic violet), Sevron Yellow R (basic yellow), Sevron Brilliant Red 4G (basic red), Sevron Blue B (basic blue), Sevron Blue 2G (basic blue). Other suitable dyes include Dianex.RTM disperse dyes available from DyStar.

[0052] Amounts of adjacent ingredients effective to impart, or improve a desirable fiber property such as, brightness of color, strength, cleanliness, flame retardance, colorfastness, or dyability. For example, one or more ingredients from the following classes of ingredients may be added to the fiber: perfume, odor control agent, antimicrobial active and/or preservative, surfactant, optical brightener, antioxidant, chelating agent includingaminocarboxylate chelating agent, antistatic agent, dye transfer inhibiting agent, fabric softening active, and/or static control agent.

[0053] The skilled artisan will appreciate the at least three thousand year tradition of dying on the planet, and will appreciate the number and variety of dying procedures. Any dying procedure which will yield a dyed polyetherimide fiber having a colorfast score of 1/5 or higher according to ISO 105-302.

[0054] Pigment can also be added to the fiber through “solution dying” whereby the pigment is added before or after the undyed polymer is melted to produce the polymer melt in the melt spinning process to yield a solution dyed yarn.

[0055] A typical dying procedure for PEI fibers according to the present invention would be: 1) pretreatment of fiber with a solution of detergent for example; 2) drop the wash solution and further pre-treat fiber with acetic acid and a leveling agent (to even out final dye color) at appropriate temperature and for appropriate time; 3) a dye is added to the bath and allowed to contact the fibers for a time and at a temperature sufficient to attain the color shade desired; the temperature is raised at a particular rate and for an appropriate time depending upon shade formulation; 4) after dyeing is complete, cooling at an appropriate rate; and 5) a rinse step; and, 6) drying.

[0056] The present invention also relates to an article of manufacture comprising fabric care compositions at usage concentrations to facilitate treatment of fabric surfaces with said fabric care compositions containing a fabric color care active and other optional ingredients at a level that is effective, said composition is applied to fabric in a positive step, e.g., dipping, soaking, padding process, or by a roller, followed by a drying step to maximize the application and retention of the active to the surface of the fibers. More preferably, the article of manufacture comprises concentrated fabric care compositions to be diluted to usage concentrations in use.

[0057] The important physical properties for textile fibers include tenacity, shrinkage, dyeability and dye permanence. The dyed PEI fibers of the present invention meet acceptable levels of each of these properties for incorporation into a wide variety of end uses, including textiles.

[0058] Preferably, the articles of manufacture are in association with a set of instructions that direct the consumer how to use the composition to treat fabrics correctly, to obtain the desirable fabric care results, viz, color renewal, and preferably, other additional fabric care benefits, such as wrinkle removal, wrinkle resistance, fiber strengthening/anti-wear, pill prevention, anti-shrinkage, soiling prevention and/or reduction, and/or fabric shape retention, including, e.g., the manner and/or amount of composition to used, and the preferred ways of checking for completeness of application, stretching and/or smoothing of the fabrics. Ironing and/or smoothing can help distribute the active over the surface and partially compensate for incomplete distribution. As used herein, the phrase “in association with” means the instructions that are either directly printed on the container itself or presented in a different manner including, but not limited to, a brochure, print advertisement, electronic advertisement, and/or verbal communication, so as to communicate the set of instructions to a consumer of the article of manufacture. It is important that the instructions be simple and clear. The use of pictures and/or icons within the instructions may be desirable.

EXAMPLES

[0059] Without further elaboration, it is believed that the skilled artisan can, using the description herein, make and use the present invention. The following examples are included to provide additional guidance to those skilled in the art of practicing the claimed invention. These examples are provided as representative of the work and contribute to the teaching of the present invention. Accordingly, these examples are not intended to limit the scope of the present invention in any way. Unless otherwise specified below, all parts are by weight.

[0060] In the following examples the following terms may be used:

[0061] “Final dpf denier per filament in the final yarn, i.e. thickness of each individual filament as wound up on the bobbin.”
“R&L Melt pumps rate”—right and left meter pumps rate: these dose the polymer melt via a certain rpm, dosing a given volume of melt for each revolution of the pump. Rate refers to rpm.

“Temperatures Zone 1, 2 and 3”—Extruder zone temperatures along the barrel.

“Temperature Head”—Temperature of the pack, i.e. where the spinnerets are positioned.

“Temperature Head/Melt” (this would be the temperature of the spinneret and therefore the polymer melt finally).

“Temperature Quench”—in order to cool filaments and solidify or “quench” them, cooled air is blown at the filaments, or quench air. This refers to the air temp.

### TABLE 1

<table>
<thead>
<tr>
<th>Processing Data</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Material</td>
<td>Ultem 1040</td>
<td>Ultem 1040</td>
<td>Ultem 1040</td>
<td>Ultem 1040</td>
</tr>
<tr>
<td>Color</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Lot</td>
<td>U2KWB</td>
<td>U2KWB</td>
<td>U2KWB</td>
<td>U2KWB</td>
</tr>
<tr>
<td>Dpf</td>
<td>10</td>
<td>6</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>2. Spinning head dia.</td>
<td>1.0/0.8</td>
<td>0.8</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>3. Holes/spinneret</td>
<td>72</td>
<td>40</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Number of spinneret</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Total # of Filaments</td>
<td>144</td>
<td>80</td>
<td>128</td>
<td>128</td>
</tr>
<tr>
<td>R&amp;L Melt Pumps rpm</td>
<td>10.5</td>
<td>3.397</td>
<td>3.845</td>
<td>1.822</td>
</tr>
<tr>
<td>Extruder Zone 1 °C.</td>
<td>362</td>
<td>362</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>Zone 2 °C.</td>
<td>348</td>
<td>348</td>
<td>348</td>
<td>348</td>
</tr>
<tr>
<td>Zone 3 °C.</td>
<td>358</td>
<td>358</td>
<td>362</td>
<td>362</td>
</tr>
<tr>
<td>Head T °C.</td>
<td>364</td>
<td>364</td>
<td>374</td>
<td>374</td>
</tr>
<tr>
<td>Melt T °C.</td>
<td>363</td>
<td>363</td>
<td>368.8</td>
<td>368.8</td>
</tr>
<tr>
<td>4. Quench T °C.</td>
<td>24.6</td>
<td>24.6</td>
<td>23.9</td>
<td>16.1</td>
</tr>
<tr>
<td>Quench rpm</td>
<td>259</td>
<td>222.9</td>
<td>222.9</td>
<td>222.9</td>
</tr>
<tr>
<td>Room T °C.</td>
<td>22.1</td>
<td>22.1</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Roll T °C.</td>
<td>125</td>
<td>125</td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>Godets Roll 1 rpm</td>
<td>33.9</td>
<td>33.9</td>
<td>33.9</td>
<td>33.9</td>
</tr>
<tr>
<td>2 rpm</td>
<td>34</td>
<td>34</td>
<td>33.85</td>
<td>33.85</td>
</tr>
<tr>
<td>3 rpm</td>
<td>34.1</td>
<td>34.1</td>
<td>33.93</td>
<td>33.93</td>
</tr>
<tr>
<td>4 rpm</td>
<td>34.2</td>
<td>34.2</td>
<td>34.2</td>
<td>34.2</td>
</tr>
<tr>
<td>5. Finish</td>
<td>Lural 912</td>
<td>Lural 912</td>
<td>Lural 912</td>
<td>Lural 912</td>
</tr>
</tbody>
</table>

A dyed polyetherimide fiber is created by heating 10 kilograms of the material listed in row 1 of Table 1. The heated polymer is fed into a metering pump and then a filter to remove unwanted debris and prevent clogging of the spinneret. The spinneret has the number of holes specified in row 3 of Table 1 and wherein each hole has a diameter specified in Row 2 of table 1. PEI fiber exits from the spinneret and is cooled through air quenching at the temperature set forth in row 4 of Table 1. After quenching a finish of LUROL 912, commercially available from Goulston Technologies, Inc., of Monroe, N.C. is applied to the PEI fiber and the fiber is drawn and spun onto a bobbin for dying.

Examples 5-9

“Roll 1, 2, 3 and 4”—Rolls or godets on the spinning machine taking up the yarn and drawing it by running at different speeds.

“Pack Pressure” (psi)—pressure melt is exerting on the pack/spinnerets.

“Speeds for Rolls 1, 2, 3 and 4”—speed in meters/min is the unit of measure. This is achieved by turning the roll at a certain rpm and given its diameter gives the wind-up speed. The Hz refers to the inverter unit that drives the electric motor of the godet and is a set point that results in a certain roll speed. Rolls are for take up of the yarn, and subsequent drawing or relaxing via different roll speeds. All to affect the yarn properties (mainly tenacity, elongation to break and shrinkage) to a desired value.

A dyed polyetherimide fiber is created by heating 10 kilograms of the material listed in row 1 of Table 2. The heated polymer is feed into a metering pump and then a filter to remove unwanted debris and prevent clogging of the spinneret. The spinneret has the number of holes specified in row 3 of Table 2 and wherein each hole has a diameter specified in Row 2 of table 2. PEI fiber exits from the spinneret and is cooled through air quenching at the temperature set forth in row 4 of Table 2. After quenching a finish of LUROL 912, commercially available from Goulston Technologies, Inc., of Monroe, N.C. is applied to the PEI fiber and the fiber is drawn and spun onto a bobbin for dying.
### Table 2

<table>
<thead>
<tr>
<th>Processing Data</th>
<th>Example 5</th>
<th>Example 6</th>
<th>Example 7</th>
<th>Example 8</th>
<th>Example 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot</td>
<td>UL268Q</td>
<td>UL268Q</td>
<td>UL268Q</td>
<td>UL268Q</td>
<td>UL268Q</td>
</tr>
<tr>
<td>Drying</td>
<td>155°C (4 hrs)</td>
<td>155°C (4 hrs)</td>
<td>155°C (4 hrs)</td>
<td>155°C (4 hrs)</td>
<td>155°C (4 hrs)</td>
</tr>
<tr>
<td>2. Spinnoret Hole Diameter</td>
<td>0.8/1.0 mm</td>
<td>0.8/1.0 mm</td>
<td>0.45 mm</td>
<td>0.45 mm</td>
<td>0.6 mm</td>
</tr>
<tr>
<td>3. Spinnoret number of holes</td>
<td>148</td>
<td>148</td>
<td>128</td>
<td>128</td>
<td>128</td>
</tr>
<tr>
<td>Final df</td>
<td>10</td>
<td>10</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Roll 1 (RPM)</td>
<td>29.4</td>
<td>29.4</td>
<td>10.33</td>
<td>10.33</td>
<td>5.512</td>
</tr>
<tr>
<td>Roll 2 (RPM)</td>
<td>320</td>
<td>320</td>
<td>330</td>
<td>330</td>
<td>330</td>
</tr>
<tr>
<td>Roll 3 (RPM)</td>
<td>360</td>
<td>360</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Roll 4 (RPM)</td>
<td>370</td>
<td>370</td>
<td>380</td>
<td>380</td>
<td>370</td>
</tr>
<tr>
<td>Roll 5 (RPM)</td>
<td>382</td>
<td>382</td>
<td>391</td>
<td>391</td>
<td>388</td>
</tr>
<tr>
<td>Roll 6 (RPM)</td>
<td>26.4</td>
<td>26.8</td>
<td>27.5</td>
<td>27.2</td>
<td>25.7</td>
</tr>
<tr>
<td>Roll 7 (RPM)</td>
<td>22.4</td>
<td>22.4</td>
<td>26</td>
<td>26.5</td>
<td>24.3</td>
</tr>
<tr>
<td>Roll 8 (RPM)</td>
<td>113</td>
<td>113</td>
<td>113</td>
<td>113</td>
<td>113</td>
</tr>
<tr>
<td>Roll 9 (RPM)</td>
<td>102</td>
<td>102</td>
<td>102</td>
<td>102</td>
<td>118</td>
</tr>
<tr>
<td>Roll 10 (RPM)</td>
<td>60</td>
<td>60</td>
<td>71</td>
<td>71</td>
<td>77</td>
</tr>
<tr>
<td>Roll 11 (RPM)</td>
<td>60</td>
<td>60</td>
<td>65</td>
<td>65</td>
<td>70</td>
</tr>
<tr>
<td>Pack Pressure (psi)</td>
<td>728</td>
<td>704</td>
<td>663</td>
<td>1297</td>
<td>875</td>
</tr>
<tr>
<td>Roll 12 (RPM)</td>
<td>7912</td>
<td>7912</td>
<td>7912</td>
<td>7912</td>
<td>7912</td>
</tr>
<tr>
<td>Roll 13 (RPM)</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Roll 14 (RPM)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Speeds</td>
<td>3,997*</td>
<td>3,997*</td>
<td>3,997*</td>
<td>3,997*</td>
<td>3,997*</td>
</tr>
</tbody>
</table>

Examples 10-18

Color Dyeing of PEI Fiber

A cone of fiber produced according to examples 1-9 is prescoured in a 0.5% solution of Pentex AS at a temperature of between 100 and 120°F, for 10 minutes. The same cone is then washed with distilled water and then exposed to a solution containing Albe Rag FFA, anti-foaming agent, 0.5 gs/lit, Tinegali NT, carrier, 0.5 gs/lit, Inagla DA, dispersing agent, 0.5 gs/lit, Unividane OD stops oligomers from forming, 0.25/11, Intravex, sequestering agent, 0.25 gs/lit, and Ammonium Sulphate, PH control, 1 gs/lit. This solution is circulated for 5 minutes at 140°F. An amount of Disperse Blue 027 dye sufficient to make a solution containing 1.50% of the weight of the fiber in dye.

The yarn is then cooled and goes through several washes to lower the PH level to about 4.5 using a reductive clear solution of Sodium Hydrosulphite at 3 gs/lit and Soda ash at 4 gs/lit having a PH of about 7.5. (How will a solution having a PH of 7.5 be able to lower the PH of the solution to 4.5?)

Examples 19-27

Dyeing of PEI Fiber

The same procedure as used for examples 10-18, with the exception that the fiber is dyed using a solution containing 3.0% by weight of the fiber of the Dye Disperse Yellow 114 (most from Ciba Chemical).

Colorfastness of Fiber manufactured and dyed according to examples 1-36 is determined according to ISO 105-302 and all fibers receive a score of between 1 and 5.

All aforementioned patents, patent applications and other publications are herein specifically incorporated by reference in their entirety, as though set forth in full.

While the invention has been described with reference to an exemplary embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

1. A composition comprising a dyed polymer fiber capable of holding the color of the dye wherein the fiber comprises a polyetherimide and the dyed fiber has a colorfast score of 1/5 or higher according to ISO 105-302.
2. A dyed fiber according to claim 1 wherein the fiber has a colorfast score of 2/5 or higher.
3. A dyed fiber according to claim 1 wherein the fiber has a colorfast score of 3/5 or higher.
4. A dyed fiber according to claim 1 wherein the fiber has a colorfast score of 4/5 or higher.
5. A dyed fiber according to claim 1 wherein the fiber has a colorfast score of 5/5 or higher.

6. A dyed fiber according to claim 1 wherein the dyed color of the fiber is selected from the group consisting of black, white, red, orange, yellow, green, blue, indigo and violet, and combinations thereof.

7. A dyed fiber according to claim 1, wherein the dyed fiber further comprises one or more ingredients selected from the group consisting of perfumes, odor control agents, antimicrobial actives and/or preservatives, surfactants, optical brighteners, antioxidants, chelating agents, antistatic agents, dye transfer inhibiting agents, fabric softening actives, static control agents, and combinations thereof.

8. A dyed fiber according to claim 1, wherein the dyed fiber further comprises one or more dyes, or dye component selected from the group consisting of: animal dyes, vegetable dyes, mordant dyes, acid dyes, aniline dyes, azo dyes, basic dyes, cyanine dye, disperse dyes, oxidation dyes, reactive dyes, solvent dye, sulfur dyes and vat dyes, and combinations thereof.

9. A composition comprising a dyed polymer fiber capable of holding the color of the dye wherein the fiber comprises a polyetherimide and the dyed fiber has a colorfast score of 1/5 or higher according to ISO 105-302 and wherein the polyetherimide comprises between about 1 and about 1,000, structural units, of the formula:

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{R} \\
\end{align*}
\]

wherein

\[T = \text{—O—} \quad \text{or a group of the formula —O-Z-O—; and,}
\]

Z is selected from the group consisting of divalent radicals of formula:

\[
\begin{align*}
\text{—C(O)—} \\
\text{—SO_2—} \\
\text{—C(O)H} \\
\text{and} \\
\text{—SO_2H}
\end{align*}
\]

Q is selected from the group consisting of —O—, —S—, —C(O)—, —SO_2—, CYH_2—, and halogenated derivatives thereof, including perfluoroalkylene groups; and,

y being an integer from 1 to 5.

10. A composition comprising a dyed polymer fiber capable of holding the color of the dye wherein the fiber according to claim 9 wherein the divalent bonds of the —O— or the —O-Z-O— group are in the 3,3', 3,4', 4,3', or the 4,4' positions.

11. A method of making a dyed polyetherimide compositions comprising the steps of:

a) supplying a PEI composition selected from the group consisting of fibers and shaped articles of manufacture;

b) exposing said PEI composition to a dye.

12. A composition comprising a dyed polymer fiber capable of holding the color of the dye according to claim 1 wherein the fiber has a denier of between about 0.1 and about 50,000.

13. A composition comprising a dyed polymer fiber capable of holding the color of the dye according to claims 1 wherein the fiber has a denier of between about 0.1 to about 10,000.

14. A composition comprising a dyed polymer fiber capable of holding the color of the dye according to claim 1 wherein the fiber has a denier of between about 0.25 to about 50.

15. A composition comprising a dyed polymer fiber capable of holding the color of the dye according to claim 1 wherein the fiber has a denier of between about 0.25 to about 10.

16. A composition comprising a dyed polymer fiber capable of holding the color of the dye according to claims 1 or 5 wherein the fiber has diameter which can range from about 0.00001 mm to about 2 mm.

17. A composition comprising a dyed polymer fiber capable of holding the color of the dye according to claims 1 or 5 wherein the fiber has diameter which can range from about 0.00001 mm to about 0.5 mm.

* * * * *