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PREVENTION OF FILAMENT TWINNING IN DRY SPINNING

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ABSTRACT OF THE DISCLOSURE

Solutions of synthetic polymers containing liquid polysiloxanes are dry spun to produce filaments. The polysiloxanes by reducing the tendency of the filaments to twin, i.e., prematurely coalesce, in the spinning cell permit closer hole spacing in the spinneret and consequently higher productivity.

This invention relates to the dry spinning of synthetic filaments. In particular, it relates to the addition of certain silicones to spinning solutions in order to prevent twinning of the extruded filaments.

One method of increasing productivity in dry-spinning cells is to spin more filaments per cell. This may be accomplished by decreasing the distance between the orifices in the spinneret so that a great number of orifices are used within the cell. As the distance between the orifices is decreased, however, it is found that some of the filaments prematurely combine or "twin" in the cell. "Twinning" is defined as the premature combination of two or more filaments near the face of the spinneret. This effect is not to be confused with "coalescence," which is the deliberate combination of filaments to form a coalesced multifilament bundle.

Twinning of dry-spun filaments is undesirable, because it causes an unintentionally high filament denier, which in turn inhibits solvent removal and results in poor physical properties and sticking of spun yarn on packages. Although a heat treatment of the yarn may overcome some of these difficulties, a product having high denier variation along the length of the yarn is not avoided. The problem of twinning may be avoided, when encountered, by increasing the hole spacing in the spinneret, but this restricts the number of holes which can be used in a spinning cell and thus lowers productivity.

This invention provides a method of using a greater number of spinneret holes without adverse effects during spinning, thereby improving the productivity in the dry spinning of yarns. This invention also provides a method for improving the quality and uniformity of dry-spun yarn.

The advantages of the invention are attained in the dry spinning of filaments of a synthetic polymer from a solution containing said polymer dissolved in a solvent by discharging the solution into a spinning cell from a spinneret containing a plurality of orifices, simultaneously passing a stream of heated gas into the spinning cell to remove solvent, and collecting the filaments so obtained; the improvement, for reducing the tendency of the filaments to twin in the spinning cell, which comprises providing in said solution at least 0.05% by weight, based on said polymer, of a liquid polysiloxane having a viscosity from 1.5 centistokes to 60,000 centistokes at 25° C. and having a boiling point of at least 190° C. at atmospheric pressure. The invention is particularly applicable to the dry spinning of essentially linear synthetic organic polymers of filament-forming molecular weight, especially to spandex polymers, acrylonitrile polymers, and polycarbonamides.

In a preferred embodiment, the invention relates to the dry spinning of spandex polymer by the steps of:

(a) Preparing a spinning solution containing a filament-forming spandex polymer and a liquid polysiloxane having a viscosity from 1.5 centistokes to 60,000 centistokes at 25° C. and having a boiling point of at least 190° C. at atmospheric pressure, said polysiloxane being present at a concentration of at least 0.05% by weight based on said polymer,

(b) Extruding the solution into a spinning cell from a spinneret containing a plurality of orifices arranged in close proximity,

(c) Simultaneously passing a stream of heated gas into the spinning cell in the direction of travel of the filaments in order to remove solvents therefrom,

(d) Removing the gas at a position along the direction of travel of the filaments remote from the spinneret, and

(e) Recovering from the cell filaments having a high degree of denier uniformity.

The spandex polymers useful in this invention are the segmented polyurethanes which are well known in the art and are generally prepared from hydroxyl-terminated prepolymers, such as hydroxyl-terminated polyethers and polyesters of low molecular weight, or mixtures thereof. Reaction of the prepolymer with a stoichiometric excess of diisocyanate produces an isocyanate-terminated material which may then be chain-extended with a compound containing active hydrogen, for example, water, hydrazine, organic diamines, glycols, amino alcohols, etc. Many segmented polyurethanes of this type are described in several patents. Among these are U.S. Patents 2,929,800, 2,929,801, 2,929,802, 2,929,804 2,957,852, 2,962,470, 2,999,839, 3,009,901, 3,071,557 and 3,097,192.

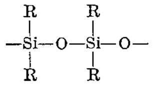
The acrylonitrile polymers useful in this invention are homopolymers of acrylonitrile and copolymers thereof containing at least 85% of acrylonitrile units. Suitable comonomers are, for example, methyl acrylate, methyl methacrylate, vinyl acetate, methyl vinyl ketone, styrenesulfonic acid and its water-soluble salts. Such acrylonitrile polymers are described in U.S. Patents 2,837,501 and 2,486,241.

Although polycarbonamide filaments are generally obtained by the process of melt spinning, polycarbonamide polymers may be dry spun from solution. In the dry spinning of polycarbonamide filaments, twinning is not usually encountered as a problem. Nevertheless, the process of this invention when applied to spinning solutions of polycarbonamide polymers, especially the wholly aromatic polycarbonamides, provides an increased rate of solvent removal from the extruded filaments and is therefore valuable in increasing productivity. Such polycarbonamide polymers are described in U.S. Patent 3,068,188.

Although the polymers with which this invention may be used are considerably diverse, they have in common the property of solubility in certain solvents, in particular, the dialkylamides of the lower fatty acids. These solvents include N,N-dimethylformamide, N,N,-dimethylacetamide, N,N-diethylpropionamide, etc. Other inert solvents such as tetramethylene sulfone, N-methylpyrrolidone, and dimethyl sulfoxide, may also be used. In some cases, the presence of small amounts of an inorganic halide, as for example described in U.S. Patent 3,068,188, are necessary to obtain adequate solubility.

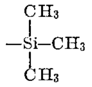
The silicone agents which are useful in the practice of this invention are the polysiloxanes having viscosities between 1.5 centistokes and 60,000 centistokes at 25° C. and having boiling points of at least 190° C. at atmospheric pressure.

A preferred class of polysiloxanes consists essentially of recurring units of the structure



$$-\underset{R}{\overset{R}{\mathrm{Si}}}-O-\underset{R}{\overset{R}{\mathrm{Si}}}-O-$$

wherein R represents hydrocarbon radicals, such as methyl, ethyl, butyl, and phenyl or lower alkoxy radicals such as methoxy and butoxy. The radicals R may be the same or different. The polysiloxanes are generally terminated with a



$$-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-CH_3$$

group, although part of all of the methyl groups may be substituted by other alkyl groups, such as ethyl and propyl, by an aryl group, such as phenyl or by an alkoxy group, such as methoxy. The terminal groups in the polydimethylsiloxanes are —$Si(CH_3)_3$ groups.

Another suitable polysiloxane is a block copolymer having the above general formula except that the R and the terminal groups may be substituted with up to 85% by weight of units derived from alkylene oxides of 1 to 4 carbons, e.g., ethylene oxide.

As is well known, the polysiloxanes are formed by hydrolysis and condendsation of the organochlorosilanes, for example, dimethyldichlorosilane. By this procedure the well known linear polysiloxanes having methyl, ethyl, and/or phenyl substituents are obtained. A more detailed description of the preparation and properties of these materials may be found in Chapter 7 of the book entitled "Synthetic Lubricants," by R. C. Gunderson and A. W. Hart (1962). The preparation of polysiloxanes containing up to 85% by weight of units derived from ethylene oxide or substituted ethylene oxides is taught by Bailey and O'Connor in U.S. Patent 2,834,748.

It is not necessary that the silicones useful in this invention be substantially linear. A polysiloxane existing in the form of cyclic chains may be used. An example of such a material is the liquid, trifunctional polyamylsiloxane prepared by the hydrolysis and condensation of n-amyltrichlorosilane. The hydrolysis is carried out in a medium comprised of isopropyl ether and water. Several washing steps are carried out, and the hydrolyzate is neutralized by refluxing with a mixture of sodium bicarbonate and water. The ether and water are removed, and the hydrolysis product is dissolved in toluene and refluxed with sodium hydroxide to effect a further condensation-equilibration reaction. During this reaction, residual water is removed as an azeotrope with toluene. The product is then filtered and is obtained as a liquid having a viscosity in the range of 8,000 to 20,000 centistokes. This trifunctional polyamylsiloxane is quite different from the conventional, trifunctional siloxane resins in that care is taken to reduce residual chloride and hydroxyl contents to a minimum.

Examples of specific polysiloxanes which are useful in the practice of this invention are polydimethylsiloxane having a molecular weight of 2,000 polydimethylsiloxane having a molecular weight of 1,000, polydimethylsiloxane having a molecular weight of 75,000–80,000, and block copolymers in which the silicone block is a polydimethylsiloxane and the organic block is a polyether derived from an alkylene oxide. All the above materials are commercially available. In addition, polysiloxanes in which there is a multiplicity of alkoxy groups such as hexa-2-ethylbutoxydisiloxane is useful in the practice of this invention. The useful concentrations for the polysiloxanes in the practice of this invention range from 0.05% to about 15% by weight based on the polymer solids. The upper limit is not critical and is dictated mainly by factors of economy. Preferably, the polysiloxanes are used in the range of concentrations from about 0.1% to about 6% by weight. The preferred polysiloxanes for this invention are polydimethylsiloxanes having viscosities of 2 to 1,000 centistokes at 25° C. For use in spandex, these will advantageously have viscosities in the range of 8–25 and will be used at concentrations of about 0.3%.

In the practice of this invention, the polysiloxane may be added by any convenient method to the spinning solution of polymer prior to extrusion. The method chosen should, of course, ensure that the polysiloxane is evenly distributed throughout the spinning solution. It may be stirred directly into the spinning solution, or it may be incorporated in a finish which is added to the solution before spinning, i.e., the finish is cospun. Alternatively, the polysiloxane may be first mixed with stabilizers, pigments, or other additives and then added to the spinning solution. Still another method for incorporatnig the polysiloxane occurs in the reclamation of waste yarn containing a polysiloxane-based finish. Thus, the dissolving of waste yarn in a spinning solution constitutes a satisfactory means for adding the polysiloxane, if sufficient finish is present on the waste yarn to provide the amount of polysiloxane that is required.

As pointed out hereinabove, this invention permits higher productivity in the spinning cell because it allows the spinneret holes to be placed more closely together without the occurrence of twinned filaments. In a preferred embodiment of the invention the dry spinning method is thus carried out with a spacing between orifices that would, in the absence of any added polysiloxane, be insufficient to prevent any substantial amount of filament twinning.

As will be further apparent from a consideration of Example I hereinafter, it is possible to establish for a given spinning system a mathematical relationship between the quantity of added polysiloxane and the spacing between orifices. While any single relationship so established will be largely specific for a given polymer spun under certain process conditions, nevertheless it will be of significant value for a commercial operation since it is then possible to establish the most efficient spacing between orifices with assurance that twinning will be consistently avoided.

This invention will be further illustrated, but is not intended to be limited, by the following examples in which parts and percentages are by weight unless otherwise specified.

EXAMPLE I

Polytetramethylene ether glycol of molecular weight about 2,000 and p,p'-methylenediphenyl diisocyanate are mixed in the ratio of 2 mols of diisocyanate per mol of polyether glycol and are reacted to yield an isocyanate-terminated polyether. To 132 parts of the isocyanate-terminated polyether is then added 158 parts of N,N-dimethylacetamide to form a mixture of 45.5% solids. Then a mixture of 80 parts of dimethylacetamide, 6.8 parts of m-xylylenediamine and 0.47 part of diethylamine is added with mixing. The polymer solution so obtained contains approximately 36% solids and has a viscosity of about 2,400 poises at 40° C.

To the viscous polymer solution is added titanium dioxide and 4,4'-butylidenebis(6-t-butyl-m-cresol) such that the final mixture contains 4.5% and 1%, respectively, of each additive based on the spandex solids. The foregoing mixture is heated to a temperature of 75° C. and spun into a dry-spinning cell heated to 235° C. through which Kemp gas, essentially a mixture of about 87%

nitrogen and 13% carbon dioxide, heated to 340° C. is passed cocurrently. The spinneret contains 172 orifices of 0.23 mm. in diameter (0.009 inch), the spacing between centers of which varies from 4.7 millimeters to 5.6 millimeters. After a steady state in the spinning cell as achieved, it is seen by observation through a sight-glass in the cell wall in the vicinity of the spinneret that about 30% of the 172 filaments are twinned. Four yarns, each having a denier of about 420, are wound up.

Without interruption of the spinning, there is now fed to the spinneret an additional portion of the same spinning solution except that 3% of a finish, based on spandex solids, is added to the solution before spinning. The finish comprises 10% polyamylsiloxane described hereinabove and 90% polydimethylsiloxane with the mixture having a viscosity of 23 centistokes. On spinning of the new solution under the same conditions as before, no twinned filaments are observed.

When spinning filaments from the above, a correlation can be established between the spacing between orifices and the concentration of siloxane. Thus even throughout a wide range of conditions in the spinning of this composition, twinning may be avoided if the spinneret holes are spaced by a distance no less than that given by the following relationship:

$$h=1.23/S^{0.24}$$

wherein h is the distance in millimeters between spinneret holes (center to center) and S is the concentration of polysiloxane in percent by weight based on the polymer being spun. Again for this particular system, the concentration of polysiloxane is preferably within the range from about 0.1% to about 6% by weight, and the preferred minimum distance between spinneret holes is given by the expression

$$1.45/S^{0.24}$$

EXAMPLE II

To the spinning solution described in the second paragraph of Example I is added 0.3% by weight (based on spandex solids) of polydimethylsiloxane having a molecular weight of 2,000. The mixture is slowly agitated for three hours to ensure thorough mixing and is then introduced to the spinning cell under the conditions specified in Example I. The severe twinning noticed in the first part of Example I disappears.

Similarly, polydimethylsiloxane having a molecular weight of 2,000 is added to the dispersion of titanium dioxide and 4,4′-butylidenebis(6-t-butyl-m-cresol) at a concentration of 0.3% and introduced with this dispersion into the polymer solution. Similar results, i.e., absence of twinned filaments, are obtained.

EXAMPLE III

To the viscous polymer solution described in the first paragraph of Example I are added a slurry of titanium dioxide in dimethylacetamide, a solution of poly(N,N-diethyl-β-aminoethyl methacrylate) in dimethylacetamide and a solution of 4,4′-butylidenebis(6-t-butyl-m-cresol) in dimethylacetamide, such that the final mixture contains 5%, 5%, and 1%, respectively, of each additive based on the spandex solids. The polymer solution containing approximately 35% solids is spun in a dry-spinning cell under the conditions specified in Example I. It is observed that approximately 20% of the total filaments are twinned.

When 0.5% by weight (based an spandex solids) of polydimethylsiloxane having 2,000 molecular weight is added to the spinning solution, all twinning disappears.

EXAMPLE IV

A spinning solution of spandex polymer is prepared as described in Example I except that in place of the m-xylylenediamine of that example there is used an equivalent amount of hydrazine hydrate. The final polymer solution contains about 35% of spandex solids. The spinning solution is spun through a spinneret containing 80 holes each 0.11 millimeter (0.0034 inch) in diameter, spaced 2.6 millimeters (0.102 inch) apart on a circle 66 millimeters (2.6 inches) in diameter. The filaments are coalesced to a single multifilament thread at a point about 1.5 meters from the exit of the cell by means of a jet twister, according to the process described in Smith U.S. 3,094,374. After a steady state in the spinning cell has been attained, observation of the filaments in the vicinity of the spinneret shows that about 30% of the filaments are twinned.

A similar solution containing 3% of polydimethylsiloxane of 2,000 molecular weight is spun through the cell under the same conditions. No twinning of the filaments is observed.

EXAMPLE V

A solution containing about 32% by weight of an acrylic polymer which contains 03.6% polymerized units of acrylonitrile, 6.0% polymerized units of methyl acrylate, and 0.4% polymerized units of sodium styrene sulfonate is spun into a dry-spinning cell through a spinneret containing 80 holes in two segments of 40 holes each. The holes are 0.2 millimeter (0.008 inch) in diameter, spaced 1.5 millimeters (0.060 inch) apart on a circle 43 millimeters (1⅝ inches) in diameter. The temperature of of the spinning solution is 130° C. The cell is heated to 200° C. and the cocurrent aspiration gas is heated to 335° C. After a steady state in the spinning cell is attained, visual inspection of 12 filaments in the region below the spinneret shows that about 10 of the 12 filaments are twinned.

On substitution of a spinning solution containing 3% by weight (based on the acrylic polymer solids) of polydimethylsiloxane having a molecular weight of 2,000 only 2 of the 12 filaments are twinned.

EXAMPLE VI

Polydimethylsiloxane having a molecular weight of 2,000 is added to a solution of 19.8% poly(m-phenylene isophthalamide) in dimethylacetamide containing 45% calcium chloride based on the polyamide, such that the mixture contains 1.7% by weight of polysiloxane based on the polyamide. The polyamide, having an inherent viscosity of 1.56, is prepared substantially as described in Example XIV of U.S. Patent 3,063,966. The mixture is spun under standard conditions in a dry-spinning cell through a spinneret the orifices of which are spaced one millimeter apart. No twinning of filaments is observed. There is a substantial reduction of solvent content in the yarn leaving the cell exit, as compared with yarn containing no polysiloxane. Also, in the case of yarn containing the polysiloxane there is a decrease in the number of hollow or soft-centered filaments.

EXAMPLE VII

Example I is repeated with similar results using a spinning solution temperature of 65° C. The polysiloxane employed, in this case 0.3% by weight based on the spandex polymer, was a polydimethylsiloxane having a viscosity of 10 centistokes.

EXAMPLE VIII

To the viscous polymer solution described in the first paragraph of Example I are added a slurry of titanium dioxide in dimethylacetamide, and solutions of poly (N,N-diethyl-β-aminoethyl methacrylate), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)-benzene and 2-(2′-hydroxy-5-t-butylphenyl) - 5 - chlorobenzotriazole in dimethylacetamide, such that the final mixture contains 5%, 3%, 1% and 0.5% of each additive based on the spandex solids. The polymer solution containing approximately 37% solids is spun in a dry-spinning cell under the conditions specified in Example I. It is observed that approximately 11% of the total filament are twinned.

When 0.3% by weight (based on spandex solids) of polydimethylsiloxane having a 25° C. viscosity of 2 centistokes is added to the spinning solution, all twinning disappears.

EXAMPLE IX

When 1% by weight (based on spandex solids) of polydimethylsiloxane having a 25° C. viscosity of 30,000 centistokes is added to the spinning solution described in Example VIII, all twinning disappears.

EXAMPLE X

To the polymer solution described in the first paragraph of Example I is added 1.0% by weight (based on spandex solids) of a polybutoxy polysiloxane. The mixture is slowly agitated for three hours to ensure thorough mixing and is then introduced to the spinning cell under the conditions specified in Example I. The severe twinning which occurs without the additive disappears.

The polybutoxy polysiloxane employed in this example has a molecular weight of 802, a boiling point in excess of 200° C. at 1 mm. Hg., and a viscosity at 37.8° C. of 16.5 centistokes.

EXAMPLE XI

To the polymer solution described in the first paragraph of Example I is added 0.9% by weight (based on spandex solids) of a block copolymer of polydimethylsiloxane and polyethylene oxide which has a viscosity of 1100 centistokes at 25° C. The mixture is slowly agitated for three hours to ensure adequate mixing and is then spun as specified in Example I. The severe twinning which had occurred without the additive disappears.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

1. In the dry spinning of filaments of a synthetic polymer from a solution containing said polymer dissolved in a solvent by discharging the solution into a spinning cell from a spinneret containing a plurality of orifices, simultaneously passing a stream of heated gas into the spinning cell to remove solvent, and collecting the filaments so obtained, the spacing of orifices in the spinneret being insufficient to prevent filament twinning; the improvement, for reducing the tendency of the filaments to twin in the spinning cell, which comprises providing in said solution at least 0.05% by weight, based on said polymer, of a liquid polysiloxane having a viscosity from 1.5 centistokes to 60,000 centistokes at 25° C. and having a boiling point of at least 190° C. at atmospheric pressure.

2. Method according to claim **1** wherein the polymer is selected from the group consisting of spandex polymers, acrylonitrile polymers, and polycarbonamides.

3. Method according to claim **1** wherein the polysiloxane is a polydimethylsiloxane.

4. Method according to claim **1** wherein the polysiloxane is present in amounts up to 15% by weight based on said polymer.

5. Dry spinning method comprising the steps of:

(a) preparing a spinning solution containing a filament-forming spandex polymer and a liquid polysiloxane having a viscosity from 1.5 centistokes to 60,000 centistokes at 25° C. and having a boiling point of at least 190° C. at atmospheric pressure, said polysiloxane being present at a concentration of at least 0.05% by weight based on said polymer,

(b) extruding the solution into a spinning cell from a spinneret containing a plurality of orifices arranged in close proximity, the spacing between said orifices being insufficient to prevent filament twinning in the absence of said polysiloxane,

(c) simultaneously passing a stream of heated gas into the spinning cell in the direction of travel of the filaments in order to remove solvent therefrom,

(d) removing the gas at a position along the direction of travel of the filaments remote from the spinneret, and

(e) recovering from the cell filaments having a high degree of denier uniformity.

6. Method according to claim **5** wherein the spacing between said orifices in millimeters is at least $1.23/S^{0.24}$ wherein S is said concentration of said polysiloxane in percent by weight based on said polymer.

7. Method according to claim **5** wherein said polysiloxane is a polydimethylsiloxane.

8. Method according to claim **5** wherein said spandex polymer is a polyetherpolyurethane.

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