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(54) Mixed solvent for aramid spinning dopes.

(57) A room temperature anisotropic spinning solution and associated spinning process are disclosed for poly(p-phenylene terephthalamide) using a solvent mixture of chlorosulfuric acid and sulfuric acid of at least 100% concentration.

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Mixed Solvent for Aramid Spinning Dopes

Background of the Invention

Field of the Invention

This invention relates to spinning dopes for aramids and, more specifically, to such spinning dopes using a solvent of mixed acids. The spinning dopes of this invention utilize a combination of chlorosulfuric acid and sulfuric acid of at least 100% concentration and can be spun at room temperature.

Description of the Prior Art

United States Patent Number 3,767,756 issued October 23, 1973 discloses the use of chlorosulfonic acid, fluorosulfonic acid, concentrated sulfuric acid, and a combination of fluorosulfonic acid and concentrated sulfuric acid as solvents for aramid spinning dopes. There is discussion, in that reference, to the effect that dopes should be prepared and held during spinning at as low a temperature as possible; and dopes made using the solvent systems of that patent are spun at temperatures of at least 50 ° C. That reference utilizes sulfuric acid having concentrations as low as 98%.

Japanese Patent Publication Kokai 63-6108, published January 23, 1988, on the application of Azuma et al., discloses that spinning dopes of poly(p-phenylene terephthalamide) can be prepared by dissolving the polymer in concentrated sulfuric acid which can have any of several other materials mixed with it. Those other materials include chlorosulfuric acid, fluorosulfuric acid, dichloroacetic acid, acetic acid, phosphorus pentoxide, nitrobenzene, etc. There is, also, a general statement that the dope temperature is in the range of room temperature to 120 ° C.

United States Patent Number 3,819,587 issued June 25, 1974 disclosed, generally, that combinations of solvents can be used to make dopes of aromatic polyamides; and both chlorosulfonic acid and concentrated sulfuric acid were included in the lengthy list of such solvents.

Summary of the Invention

The present invention provides a process for spinning aramid fibers using an anisotropic dope of poly(p-phenylene terephthalamide) in a solvent mixture of chlorosulfonic acid and sulfuric acid of at least 100% concentration wherein the solvent mixture is about 20 to 70 weight percent chlorosulfonic acid based on the solvent mixture and the spinning is conducted at less than 40 ° C.

The gist of this invention and what makes it patentable resides in the discovery that anisotropic spinning dopes or solutions of poly(p-phenylene terephthalamide) are liquid at temperatures lower than 40 ° C even at concentrations of greater than 18 or as high as 21 weight percent based on the weight of the solution when the solvent consists of a mixture of 20 to 70 weight percent chlorosulfonic acid and 30 to 80 weight percent sulfuric acid of at least 100% concentration based on the weight of the solvent mixture. Such has not previously been known or reported.

Detailed Description of the Invention

Poly(p-phenylene terephthalamide) (PPD-T) is a fiber-forming polymer of excellent and renowned qualities. It is, however, difficult to dissolve and, once dissolved, difficult to work with. The solvents which have previously been used to make spinning dopes have included various extremely corrosive acids and have resulted in dopes which are solid at room temperatures. Because of the corrosive nature of the solvents and because of the fact that even small increases in the temperature of solutions using such solvents yield large increases in the degradive nature of the solvent, it has been desirable to find solvent systems for PPD-T which yield liquid spinning dopes at low temperatures.

Until the present invention, anisotropic spinning dopes of PPD-T have not been known which have been

spun at low temperatures. Dopes of the present invention can be spun at room temperature -- about 25° C.

The dopes of this invention are specifically directed toward the use of PPD-T and, for purposes of this invention, PPD-T is meant to include the homopolymer resulting from mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other aromatic diamine with the p-phenylene diamine and of small amounts of other aromatic diacid chloride with the terephthaloyl chloride. As a general rule, other aromatic diamines and other aromatic diacid chlorides can be used in amounts up to as much as about 10 mole percent of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only that the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction.

The PPD-T can be conveniently made by any of the well known polymerization processes such as those taught in U.S. Pat. Nos. 3,063,966; 3,869,429; or 4,308,374. PPD-T used in this invention has an inherent viscosity of greater than about 4 dL/g. Before preparation of spinning dope, the PPD-T and other ingredients should be carefully and completely dried, preferably to less than one-half weight percent water; the PPD-T and the solvent should be combined under dry conditions; and the dope should be stored under dry conditions. Care should be exercised to exclude atmospheric moisture.

The sulfuric acid which is used in practice of this invention should be at least 100% concentration to assure that there is no water in that acid. The sulfuric acid can be from 100% to 103% or, perhaps, as high as 105% concentration. The presence of moisture in the spinning dope is believed to cause loss of chlorine from the chlorosulfuric acid solvent component; and such loss of chlorine causes increase in melting temperature of the spinning dope.

Dopes of this invention are made by dissolving PPD-T in mixtures of chlorosulfuric acid and sulfuric acid of a concentration at least 100%. The mixture of acids is the factor which controls the acceptability of the dope as a dope of this invention. As a general rule, it has been determined that, in solutions of PPD-T in mixtures of chlorosulfuric acid and concentrated sulfuric acid, the melting point of the solutions is below about 25° C when the acid mixture is from about 20 to 65 weight percent chlorosulfuric acid; and that the melting point of such solutions is still below about 35° C when the acid mixture is as much as 70 weight percent chlorosulfuric acid.

The dopes of this invention are anisotropic. That is, microscopic regions of the dopes are birefringent and a bulk sample of such a dope depolarizes plane-polarized light because the light transmission properties of the microscopic regions of the dope vary with direction.

The above-noted melting points are substantially independent of PPD-T concentration at concentrations which result in anisotropic solutions. It has been found that solutions of PPD-T are substantially anisotropic at polymer concentrations from about 9 to about 20 weight percent based on the solution at temperatures from the melting point to at least 40° C. About 21 weight percent polymer based on the solution appears to represent the upper solubility limit for PPD-T in chlorosulfuric acid/sulfuric acid mixtures, independent of the concentration of chlorosulfuric acid in the solvent mixture.

The melting point information provided below for PPD-T dopes of this invention is based on use of PPD-T having an inherent viscosity of 4 dL/g at a concentration of 18 weight percent based on the solution.

Weight Ratio CSA/SA*	Rm. Temp. 25°C	35°C
15/85	Solid	Solid
20/80	Anis.**	Anis.
25/75	Anis.	Anis.
60/40	Anis.	Anis.
65/35	Anis.	Anis.
70/30	Solid	Anis.
80/20	Solid	Solid
90/10	Solid	Solid

*CSA = Chlorosulfuric Acid

*SA = Sulfuric Acid (100%)

**Anis. = Anisotropic dope with fiber-forming capability.

The dopes of this invention are prepared by dissolving PPD-T in the desired mixture of acids. As a general rule, the acids are combined prior to addition of the PPD-T. In combining the acids, generally, the chlorosulfuric acid is mixed into the concentrated sulfuric acid. The small amount of heat of mixing is more easily dissipated by adding the chlorosulfuric acid into the concentrated sulfuric acid rather than the other way around. After the acids have been combined, the PPD-T is added to the acids, slowly, with stirring. Solution is most easily effected if the PPD-T is in finely-divided form. The temperature of the system should be maintained as low as possible to minimize loss of chlorine from the solvent system.

The dopes, once prepared, can be used immediately or stored for future use. Even though the dopes are liquid at low temperature, if they are stored, they should be frozen and stored in solid form in an inert atmosphere such as under a dry nitrogen blanket. If the dopes are to be used immediately, they can conveniently be made continuously and fed directly to spinnerets. Continuous preparation and immediate use minimizes even the slight degradation of the PPD-T encountered in the low temperature spinning process.

Spinning the dopes of this invention is accomplished in accordance with well known spinning processes with the exception that the spinning can be conducted at very low temperatures. For example, the teachings of United States Patent No. 3,767,756 can be followed for spinning fibers from the dopes of this invention; but, due to the use of the combination of chlorosulfuric acid and sulfuric acid in this invention, the spinning can be accomplished at less than 40° C.

Test Procedures

Inherent Viscosity (IV) - Inherent viscosity is defined by

$$IV = \frac{\ln(\eta_{rel})}{c}$$

where c is concentration (0.5 grams polymer in 100 milliliters of solvent), η_{rel} is the ratio of the flow times of polymer solution and solvent as determined at 30° C in a capillary viscometer. For all inherent viscosities reported herein, the solvent is concentrated sulfuric acid (95-98%, by weight, H_2SO_4).

Linear Density - The standard for linear density herein is denier (D) expressed as weight in grams of a 9000 meter length and calculated from the measured weight of a shorter length (for example, 90

centimeters). Linear density in SI units, is dtex, and is calculated from the equation
dtex = 1.111 (D).

Tensile Properties - Break Tenacity (T), percent elongation (E), and initial modulus (M) for yarns are computed from the output of a digitized laboratory stress/strain tester according to ASTM D2101, Part 25, 1968 and as described in U.S. Patent No. 3,869,429 from Column 10, line 60 to Column 11, line 28 using a testing rate of 50% elongation per minute. Unless otherwise indicated, "tenacity" means break tenacity of yarn and "modulus" means initial modulus of yarn. Both T and M are initially determined in units of grams per (initial) denier and are converted to SI units (dN/tex) by multiplication with 0.883.

Description of the Preferred Embodiments

Example

This example demonstrates preparation and low temperature spinning of a PPD-T spinning dope using a mixture of chlorosulfuric acid and sulfuric acid of at least 100% concentration.

Chlorosulfuric acid (50 weight parts) was added, with agitation, to 100.05% sulfuric acid (50 weight parts) in a closed container purged with an inert, dry gas. After mixing the acids for a few minutes, 22 weight parts of finely-divided PPD-T of inherent viscosity 6.1 were added over the course of 3 minutes, with continued agitation. Agitation was continued for about 9 hours with no external heating. The temperature of the dope over the time of continued agitation was from 29 ° C to 33 ° C due to the heat generated by mixing. A vacuum was drawn on the dope during the last 15 minutes of agitation and for an additional 10 minutes after agitation was stopped.

The dope was spun at 25 ° C without further deareation. A first fiber sample was spun using a spinneret with 10 holes of 4 mils diameter. The throughput rate was 0.801 milliliters per minute and the spin was conducted through an air gap of 0.25 inch into an ice water coagulation bath. The yarn was collected at 32 meters per minute.

A second fiber sample was spun at the same conditions, using the same spinneret, at twice the throughput rate and at a collection rate of 70 meters per minute.

The fiber properties were as follows:

	First	Second
Denier	58	67
Tenacity (gpd)	19.6	18.9
Elongation (%)	5.3	5.4
Modulus (gpd)	286	287

Claims

1. A process for spinning aramid fibers by extruding an anisotropic solution of 9 to 21 weight percent poly(p-phenylene terephthalamide), based on the weight of the solution, from a spinneret through a layer of inert non-coagulating gas into a coagulating bath,
wherein the solvent for the solution is a mixture of 20 to 70 weight percent chlorosulfonic acid based on the weight of the solvent mixture with the remainder being sulfuric acid of at least 100% concentration and
wherein the spinning is conducted at less than 40 ° C.

2. A process for spinning aramid fibers comprising the steps of:

a) making a solution by dissolving poly(p-phenylene terephthalamide) in a solvent consisting essentially of 20 to 70 weight percent chlorosulfonic acid and 30 to 80 weight percent sulfuric acid of at least 100% concentration based on the weight of the solvent mixture such that the resulting dope includes 9 to 21 weight percent poly(p-phenylene terephthalamide), based on the weight of the solution; and

b) maintaining the temperature of the solution at less than 40 ° C while extruding it as a liquid from a spinneret through a layer of inert non-coagulating gas into a coagulating bath.

3. An anisotropic spinning solution having a melting temperature of less than 40 ° C and comprising:

a) a solvent mixture of 20 to 70 weight percent chlorosulfuric acid and 30 to 80 weight percent sulfuric acid of at least 100% concentration based on the weight of the solvent mixture; and

b) poly(p-phenylene terephthalamide) in an amount from 9 to 21 weight percent based on weight of the spinning solution.