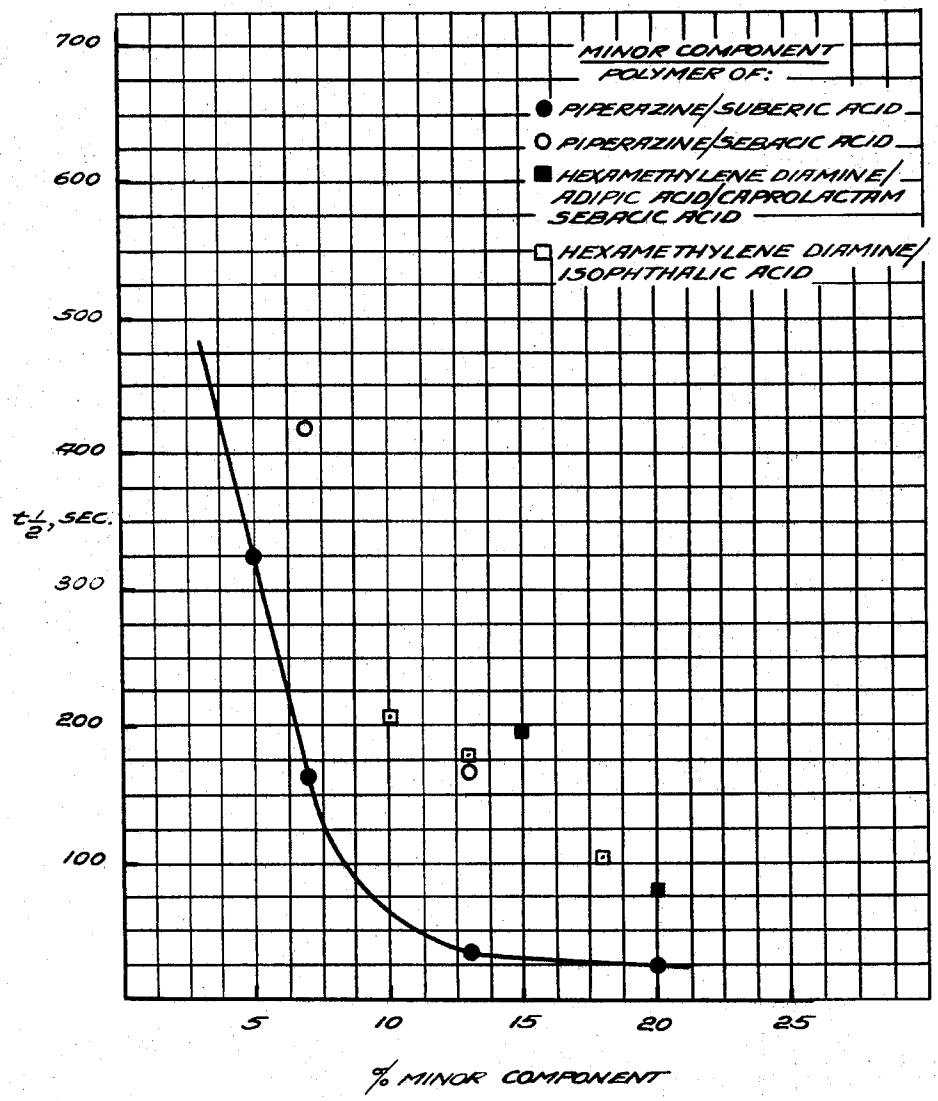
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SYNTHETIC FIBER-FORMING POLYAMIDES CONTAINING PIPERAZINE POLYAMIDES

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FILAMENT DYE RATES FOR BLENDS WITH POLY(HEXAMETHYLENE ADIPAMIDE) (~6X DRAW RATIO)



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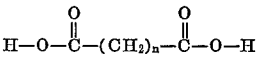
SYNTHETIC FIBER-FORMING POLYAMIDES CONTAINING PIPERAZINE POLYAMIDES

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ABSTRACT OF THE DISCLOSURE

Filaments comprising a homogeneous mixture of a synthetic, linear, fiber-forming polycarbonamide with from 5 to 40% by weight of the filament of a polycarbonamide derived from piperazine and an aliphatic dicarboxylic acid having the formula



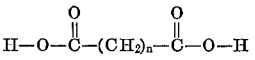
where n is a number from 3 through 6, inclusive, have been found to have improved dye rate and dyeability.

This invention concerns filaments of synthetic, linear, fiber-forming polycarbonamides having improved dyeing characteristics. More specifically, it concerns filaments from a mixture of a fiber-forming polycarbonamide with a polycarbonamide derived from piperazine.

Dyeing properties of polycarbonamide filaments, commonly known as nylon, can be improved by the use of random copolycarbonamides. Significant improvements by this route are normally realized with some sacrifice in desirable filament physical properties and a lower melting point inherent in such copolymers.

An object of this invention is to provide polycarbonamide filaments having improved dye rate and dyeability without the reduction in physical properties and melting point which results from the use of random copolymers.

This and other objects are attained in a filament comprising a homogeneous mixture of a synthetic, linear, fiber-forming polycarbonamide with from 5 to 40% by weight of the filament of a polycarbonamide derived from piperazine and an aliphatic dicarboxylic acid having the formula



where n is a number from 3 through 6, inclusive, the latter polycarbonamide having a melting point lower than the melt-spinning temperature of the fiber-forming polycarbonamide. The melt-spinning temperature as defined herein means any temperature at which the polycarbonamide homopolymer can be successfully spun into filaments.

Other objects and features of this invention will become more apparent from a consideration of the following description in conjunction with the accompanying drawing wherein a graph of $t½$ (the time necessary for the sample to pick up half the dye in the dye bath in seconds) versus percent of minor component used to enhance dye rate is shown.

By "homogeneous mixture" is meant that upon microscopic examination of the filaments there is no evidence of a second polymer phase. The polymers are compatible under molten conditions such that the piperazine based polymer dissolves in the molten fiber-forming polycarbonamide to form a homogeneous polymer melt; however, the melt is spun into filaments before sufficient time has elapsed under molten conditions to permit significant chemical interaction between said polymers. The molecular structure of the individual polymers remains substantially unchanged.

The filaments contain from about 5 to about 40% by weight of the piperazine based polymer, and preferably 7 to 25%. Below about 5%, no significant improvement in dyeability is evidenced and no significant advantage is realized above a 40% concentration level.

The piperazine based polycarbonamides are prepared by normal melt-polymerization techniques from piperazine and an acid, or mixture of acids, from the group consisting of glutaric, adipic, pimelic and suberic acids.

Because of the higher melting point of the polymer from piperazine with adipic acid, copolymers of these ingredients with another acid such as suberic acid are usually required to lower the melting point such that the resulting copolymer melts under the melt-spinning conditions employed for the fiber-forming polymer. The degree of copolymer modification required will depend upon the melting point of the fiber-forming polymer. For use with poly(hexamethylene adipamide), a melting point less than about 290° C. is required; for a higher melting polymer such as poly[bis-(4-cyclohexylene)methane dodecanediamide], a melting point less than about 330° C. is acceptable.

The subject polycarbonamides of piperazine may also be copolymerized with minor amounts of other diamines or diacids where desired.

Piperazine polymers with the higher acids, such as sebacic acid, do not give the same unexpectedly high degree of improvement in dyeability as is obtained with polymers of the subject acids. On the other hand, piperazine polymers with the lower acids, such as succinic acid, do not have a melting point suitable for this application.

The polymers may be blended prior to spinning by any conventional manner, provided they are uniformly mixed in the melt and do not remain in a molten condition long enough to permit a significant degree of chemical interaction. The polymers may be mixed as solid flake prior to melting and mixing in a screw-extruder for spinning, or they may be combined in a molten condition, for example with a screw-mixer-extruder equipped with injection means for introducing the second polymer prior to spinning.

Normal procedures can be used to reduce the tendency for chemical interaction between the polymers; such as the use of viscosity stabilizers with monofunctional amide-forming compounds to reduce the concentration of reactive end-groups, and particularly the use of polymers having a lower number of carboxyl end-groups.

Suitable fiber-forming polycarbonamides are those melt-spinnable, synthetic, linear, polycarbonamides which can be prepared by melt polymerization of aminocarboxylic acids or of aliphatic diamines and aliphatic dicarboxylic acids, or their amide-forming derivatives. Typical of such polycarbonamdes are poly(hexamethylene adipamide), poly(octamethylene oxalamide), poly(caproamide), poly(undecanoamide) and polymers containing cycloaliphatic radicals such as a polycarbonamide from bis(4-aminocyclohexyl)methane and aliphatic dicarboxylic acids containing 9 to 14 carbon atoms (e.g., sebacic and dodecanedioic acids); also polycarbonamides containing aromatic radicals such as poly(hexamethylene isophthalamide). Fiber-forming copolycarbonamides may also be used. The following examples further illustrate this invention.

EXAMPLE I

The salt of piperazine and suberic acid is prepared in the following manner: 35.4 lb. (16.07 kg.) of suberic acid is dissolved with stirring in 50,000 ml. (86.4 lb.) of ethyl alcohol at 60° C. under a nitrogen atmosphere, to

which is added a solution of 9,000 grams of anhydrous piperazine in 22,100 ml. (46.8 lb.) of warm distilled water, rapid stirring is maintained for 20 minutes and the temperature held at 60° C.; the solution is permitted to cool and stand for 3 hours under a nitrogen atmosphere; the solution is filtered and the isolated salt recrystallized by dissolving in a mixture of 36,500 ml. of ethyl alcohol and 7,500 ml. of distilled water, while boiling, adding additional water to dissolve all the salt; piperazine is added to the boiling salt solution as necessary to adjust the pH to 7.4±0.2; the boiling salt solution is decolorized with 0.8 lb. of activated carbon for 15 minutes, filtered and the filtrate cooled under nitrogen; the precipitated salt is removed by filtration, rinsed with ethyl alcohol, and dried in a vacuum oven at 70° C. using a nitrogen bleed for 24 hours.

An autoclave heated to 50° C. is charged with 5200 grams of the above salt and 27 grams of anhydrous piperazine under an inert nitrogen atmosphere. The temperature is raised to 210° C. and held for 60 minutes at 210° C. with agitation. The pressure is reduced to atmospheric and the temperature raised and held at 260° C. for 60 minutes. The pressure is then reduced gradually over a one hour period to less than 1 mm. Hg, and held, still at 260° C., for 2 hours. The resulting polymer has a relative viscosity in an 8.4% by weight solution of 90% formic acid of 19 and contains 77 carboxyl and 100 amine end-groups in microequivalents per gram of polymer. Filaments are prepared by blending 5, 7, 13 and 20% by weight of this polymer with poly(hexamethylene adipamide), having a relative viscosity of 45, using a twin-screw melter-extruder followed by a torpedo homogenizer for blending the molten polymers. The molten blend is spun into filaments in a conventional manner. The 17-filament yarns, having a spun denier of about 1224, are hot-drawn in two stages, using a heated pin at 100° C. and hot pipe, to a draw ratio of 6× giving a final drawn denier of about 204.

Dye rates of these yarns are determined by scouring yarn skeins at constant length for 5 minutes in a water bath containing 5 ml. per liter of ammonia and 0.15 gram per liter of "Alkanol" HCS, a nonionic wetting agent. The scoured yarn is agitated in a dye bath buffered to pH 6.5 which contains 1% by weight of fibers of "Capracyl" Red B, a premetallized acid dyestuff (Color Index Acid Red 182) and the time necessary for the sample to pick up half the dye in the dye bath ($t½$) is measured at 85° C.

Filament physical properties and average dye rates are shown in the following table:

	Ten./elong./mod., g.p.d./percent/g.p.d.	$t½$, sec.
Percent piperazine polymer:		
5	8.57/14.8/49.6	327 (av. of 4).
7	8.87/13.7/54.0	165 (av. of 8).
13	8.55/14.9/52.5	35 (av. of 2).
20	8.33/13.4/53.7	23 (av. of 2).

For comparison, filaments of unmodified poly(hexamethylene adipamide) prepared in a similar manner with about a 6× draw ratio give a dye rate $t½$ of >500 seconds.

The filaments containing 7% and 13% of the piperazine-suberic acid polymer have a melting point of 255° C. and 253° C., respectively.

In a similar manner filaments are prepared containing 7% and 13% by weight of a polymer of piperazine and sebacic acid. These filaments show dye rates in $t½$ of 420 and 168 seconds, respectively.

Filaments are also prepared in a similar manner by blending amounts of poly(hexamethylene isophthalamide) and also a random copolymer of poly(hexamethylene adipamide)/poly(caproamide)/poly(hexamethylene sebacamide) of about 35/38/27 percent composition respectively. The accompanying drawing clearly shows the

enhanced dye rate which the piperazine-suberic acid polymer provides over the rest of these polymer blends.

EXAMPLE II

Filaments are melt spun from a blend of 5% of a random copolymer of piperazine with suberic and adipic acids (75/25, piperazine-suberic acid/piperazine-adipic acid) in poly[bis(4 - cyclohexylene)methanedodecanediamide] having 55% of the bis(4-cyclohexylene)methane groups as the trans-trans isomer and a relative viscosity of 23 (1 gram polymer in 10 ml. of a 1:1 weight mixture of 98% formic acid and phenol). The filaments are prepared by blending polymer flake followed by melt-spinning using a screw-meter-extruder and a torpedo homogenizer for mixing prior to spinning.

Dyeability of the drawn filaments (2d.p.f.) is determined on knit tubing fabrics dyed with 1% "Celanthrene" Blue FFS (C.I. Disperse Blue 3) for one hour at the boil without carrier, measuring the dye pickup spectrophotometrically. The filaments are found to pick up 0.49% dye whereas unmodified filaments without the piperazine copolymer show a dye pickup of only 0.16%.

The filaments of this invention may be used in any stage of aggregation, e.g., plexifilament, fiber, staple, flock, yarn, tow, cord or fabric. The yarn may be separated and given different treatments wherein a differential shrinkage, bulkable yarn is produced. They may be used to produce any type of fabric, whether tufted, knitted, felted or woven. The filaments may be used alone, or may be plied or blended with other natural, synthetic or man-made fibers.

The filaments may also contain conventional additives such as suitable light stabilizers, ultraviolet absorbers, delusterants, pigments, dyes etc. These additives may be added before, during, or after spinning of the filaments. It is generally desirable to add conventional nylon antioxidants. Preferred antioxidants are sodium phenylphosphinate, sterically hindered phenolic antioxidants, manganese hypophosphite and organic copper salts in combination with inorganic and organic iodide compounds.

The filaments are especially useful where high dyeability (with acid, disperse, or vat dyestuffs) and high strength are required, such as in upholstery fabrics and safety belts or webbing.

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 limited to the specific embodiments hereof except as defined in the appended claims.

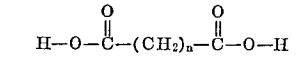
What is claimed is:

1. A composition of matter comprising a homogeneous mixture of

(1) a synthetic, linear, fiber-forming polycarbonamide and

(2) about 5 to about 40% by weight of a second different polycarbonamide

derived from piperazine and at least one of the aliphatic dicarboxylic acids having the formula



wherein n is a number from 3 through 6, inclusive, and said second polycarbonamide has a melting point lower than the melt spinning temperature of the said fiber-forming polycarbonamide.

2. Claim 1 wherein said second polycarbonamide is present as about 7–25% by weight of the said composition.

3. Claim 2 wherein said fiber-forming polycarbonamide is poly(hexamethylene adipamide) and said second polycarbonamide has a melting point less than about 290° C.

4. Claim 3 wherein said second polycarbonamide is derived from piperazine and suberic acid.

5. Claim 2 wherein said fiber-forming polycarbonamide is poly[bis(4-cyclohexylene) methane dodecanediamide] and said second polycarbonamide has a melting point less than about 330° C.

6. Claim 2 wherein said second polycarbonamide is a random copolymer of piperazine with suberic and adipic acids.

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260—78, 37, 45.7, 45.75