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FILAMENTS OF IMPROVED DYE-RECEPTIVITY

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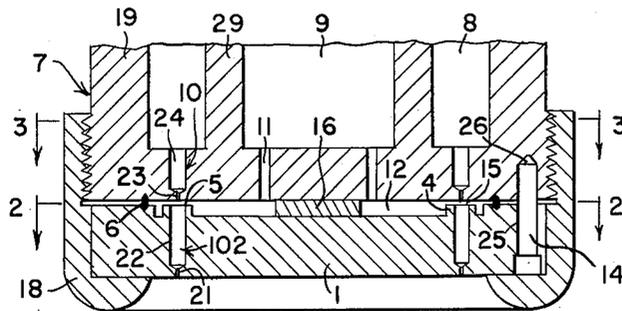


Fig. 1

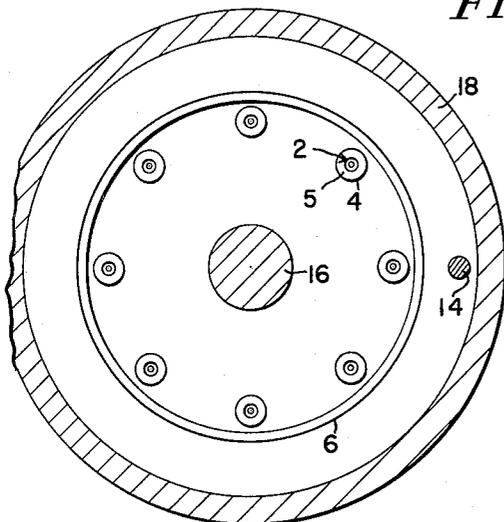


Fig. 2

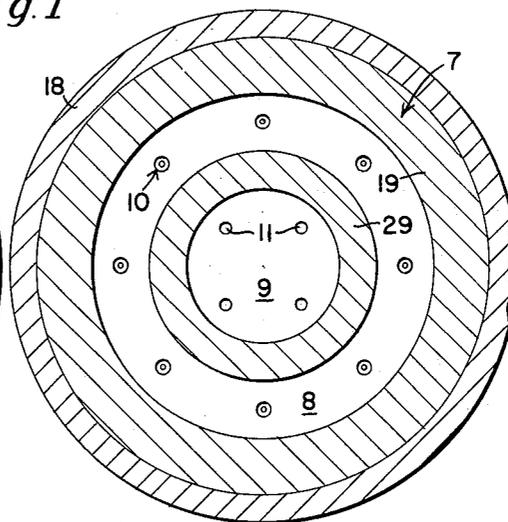


Fig. 3

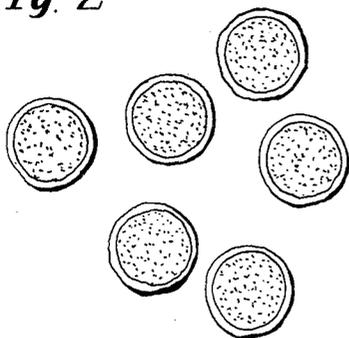


Fig. 4

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1

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This invention relates to extrusion of fiber-forming compositions, concerning especially formation of readily dyeable nylon filaments.

Many synthetic fiber-forming polymers are known, among which the polyamides have achieved considerable commercial importance. Unfortunately, textile materials constituted of polyamides generally are difficult to dye to deep fast colors. Furthermore, modification of polyamide compositions to improve their dyeability has proved a handicap to filament formation, and after-treatment of unmodified polyamide filaments for better dyeing has presented problems of control and economy.

A primary object of the present invention is provision of nylon filaments of improved dyeability. An object is provision of multicomponent filaments containing readily dyeable polyamide composition. Other objects, together with means and methods for attaining the various objects, will be apparent from the following description and the accompanying diagrams.

FIGURE 1 is an axial longitudinal section of a spinneret assembly designed according to this invention for extrusion of multicomponent filaments. FIGURE 2 is a transverse cross section of the apparatus of FIGURE 1 taken at 2—2 thereof and showing the plan of the front or bottom spinneret plate. FIGURE 3 is a transverse cross section taken at 3—3 of FIGURE 1 to show the plan of the top or back plate thereof. FIGURE 4 is a transverse cross section of a filamentary product of the apparatus of FIGURE 1.

In general, the objects of the present invention are accomplished by simultaneous extrusion of more than one polymeric substance, including one that is characterized by amine end-groups, as a core, and one that is essentially free of amine end-groups, as a surrounding sheath. This is done by extruding the polymers, of which at least one has fiber-forming characteristics, simultaneously, after having surrounded a stream of the polymer having amine end-groups with a fluid layer of the polymer relatively free of amine end-groups. The invention comprehends particularly a polyamide filamentary structure characterized by dyeability with acid dyes and formed by simultaneous extrusion of a first polyamide having acid-receptive amine end-groups and constituting the core of the structure and a second polyamide essentially lacking such amine end-groups and constituting a surrounding sheath.

Polyamides having an intrinsic viscosity of at least about 0.4 can be converted into self-supporting filaments by extrusion of the molten polymer through fine orifices ("melt-spinning"), tenacity and other properties of the product being enhanced subsequently by cold-drawing it to increased length. Sometimes an excess of one or the other of the polymerizing reactants is employed in the polymerization of diamines and dicarboxylic acids or their amide-forming derivatives, or some other "viscosity stabilizer" is used with these reactants or in the polymerization of aminocarboxylic acids, with the objective of terminating growth of the polymer molecules. Residual unreacted amine and carboxyl end-groups are determinable by microtitration methods, as described by Waltz and Taylor in "Analytical Chemistry" 19, 448 (1947); neutral (e.g., alkyl) and end-group content can be calculated from the amount of stabilizer (e.g., acetic acid) reacted with the polymer or its polymerizable components. According to G. B. Taylor, who discusses relationships of end-groups,

2

relative viscosity, intrinsic viscosity, and number-average molecular weight of polyhexamethylene adipamide in J. Am. Chem. Soc. 69, 635 (1947), use of equal amounts of diamine and dicarboxylic acid (as their salt) and an acidic viscosity stabilizer always produces polymer with a finite quantity of amine end-groups (e.g., from 14 to 40 equivalents, per 10⁶ grams for polymer having relative viscosity of from 12 to 46). For the present purpose, polymer having fewer than about 50 amine equivalents per 10⁶ grams of polymer is considered essentially free of amine end-groups because at that content melt-spinning of the polymer is commercially feasible, despite degradation (attributable to amine content) that occurs upon exposure of the polymer to the atmosphere. Spinning of polymer containing more than this amount has not been commercial, and a content of 10² equivalents of amine end-groups per 10⁶ grams of polymer is termed high in degradable amine. Although the usual terminal amine group is primary, secondary and tertiary amine groups are included also. Filaments of high average amine end-group content are dyeable to deep fast colors with acid dyes.

Devices for making sheath-core filaments are known; a recently developed preferred form of apparatus for use in practicing this invention is illustrated in the diagrams. FIGURE 1 shows in axial section a spinneret assembly useful for this purpose. Front or bottom plate 1 with orifices 2 is recessed at the back about plateau-like protrusions 4. Back or top plate 7 is sealed against and spaced from the front plate by gasket 6 and shim 16, the former being ring-shaped and located near the periphery of the opposing faces of the two plates and the latter being disc-shaped and located concentric with the two plates. Relatively unconstricted region 12 between the two plates is interrupted at intervals by constricted regions 15 between the opposing face of the back plate and plateaus 5 of the protrusions from the front plate. The back plate is partitioned on top by outer wall 19 and inner wall 29 into annular chamber 8 and central chamber 9. The annular chamber communicates with the constricted regions between the two plates through counter-bored apertures 10, and the central chamber communicates with the intervening relatively unconstricted region through holes 11. The two plates are retained in place by cap 18 threaded onto the end of the back plate. The upper part of the housing (not shown) receives suitable piping or other supply means for separate connection to the two chambers, which may constitute distribution or filtering spaces as desired. Pin 14 through cylindrical openings (opening 25 in the front plate and opening 26 in the back plate) near one edge of the plates ensures concentricity of the two plates.

FIGURE 2 shows the plan of the front plate. Appearing in this view are eight plateaus, each concentric with an extrusion orifice and uniformly spaced about a circle inside the outer gasket. As shown in this view and in FIGURE 1, each orifice consists of capillary 21 at the exit end and larger counterbore 22 extending to the capillary from the plateau. Also visible, supported in a shallow annular groove, is gasket 6, the opposing face of the back plate being similarly grooved to ensure a good seal between the two plates. The apertures in the top plate opposite the orifices of the bottom plate are similarly constructed, each being composed of terminal capillary 23 and introductory counterbore 24. FIGURE 3 shows the appearance of the back plate sectioned as indicated on FIGURE 1. Visible are the concentric outer and inner walls, the capillaries and counterbores of eight apertures spaced uniformly on a circle between the two walls, and four openings located within the central chamber defined by the inner wall.

Operation of the described apparatus in the practice of

this invention is readily understood. Separate polymers characterized by relative freedom from amine end-groups and high content of degradable amine end-groups are supplied to the inner and outer chambers, respectively, of the back plate; the former flows through the openings into the relatively unstricted space between back and front plates, through the relatively constricted regions between the plateaus and the opposing plate face, and through the extrusion orifices while the latter passes first through the apertures in the back plate and directly into and through the aligned orifices in the front plate. Upon emerging from the spinneret orifices, the core-forming component is protected from the atmosphere by a uniform cover of the sheath-forming component. For practical purposes this eliminates troublesome bending, flicking, and dripping of the extruded filamentary stream normally encountered in the spinning of filaments composed of polymers having high amine end-group content, as well as precautions (e.g., inclusion of antioxidants, wiping of spinneret face) undertaken to prevent deviations in the extruded stream owing to oxidation of amine.

The practice of this invention is described below in illustrative detail, using a spinneret assembly patterned after that shown in the diagrams and discussed above and having 34 apertures, spaced uniformly on an inch radius, for injecting core-forming component into a like number of orifices, through which that component passes surrounded by sheath-forming component. All parts and percentages are expressed by weight unless otherwise indicated.

EXAMPLE I

A polyamide is formed by reacting 10,523 grams of hexamethylenediammonium adipate (40.1 moles), 93.7 grams of hexamethylene diamine (0.808 mole), and 0 gram of acetic acid (0 mole), under the conditions taught by Carothers in Patent 2,130,948, September 20, 1938. A solution of 5.5 grams of the polymer in 50 ml. of 90% formic acid has a relative viscosity of 31.4 at 25° C. and contains 26 and 135 equivalents of carboxyl and amine end-groups, respectively per 10⁶ grams of polymer. This polymer is spun as the core of a two-component fiber simultaneously with a polyhexamethylene adipamide of 41 relative viscosity having 43 and 74 equivalents of amine and carboxyl end-groups, respectively, per 10⁶ grams of polymer as the sheath component. The pump speeds for the two components are adjusted to give a sheath-core weight ratio of 30/70. The polymers are spun at 285° C. and the resultant yarn wound up at 1206 yards per minute. Good spinning ensues for a period of five hours, at which time the spin is discontinued, with no spinneret drips having occurred. (When the high-amine component polyamide was spun as a single-component fiber under similar conditions, spinneret drips occurred at an average frequency of one in 3.5 hours.) The yarn is drawn 3.22× over a cold pin to give a final yarn with a total denier of 95. The yarn has a tenacity of 4.7 grams per denier and an elongation at break of 24.3%. The yarn is of uniform denier and shows uniform concentric sheath/core relationships from filament to filament.

Tubings knit from the two-component yarn prepared as above and from a single-component yarn prepared under similar conditions but using only the low-amine polyhexamethylene adipamide used for the sheath above were dyed separately at the boil for one hour (ratio of bath: tubing of 50:1) in an acid dye bath having the following composition: 0.5% 1-amino-4-anilino-2-anthraquinone sodium sulfonate, 3% acetic acid, and 2% sodium lauryl sulfate. From saturation dyeings the high-amine two-component tubing picked up 3.4 weight percent of dye as contrasted with 1.8 percent dye takeup by the tubing made of the one-component, low-amine yarn. When both tubings were dyed to the same shade and then submitted to repeated launderings, the tubing made of the two-component yarn retained 91% of the dye in contrast

to the low-amine yarn tubing which retained only 78% of the dye.

EXAMPLE II

Polyhexamethylene adipamide with a relative viscosity of 31 and containing 43 and 70 equivalents each of amine and carboxyl end-groups, respectively, per 10⁶ grams of polymer is mixed with 1.9% of its weight of titanium dioxide and melt-spun into yarn at 800 yards per minute, a spinning speed previously known to give minimum frequency of spinneret drips. The observed spinneret drip frequency averages only one in twenty hours. The yarn is cold-drawn to give a final delustered yarn (hereinafter designated as "control 1") with total denier of 70.

A polyhexamethylene adipamide is made by reacting hexamethylenediammonium adipate with hexamethylene diamine equivalent to 1.14 mol percent of the salt and with acetic acid equivalent to 0.182 mol percent of the salt as above. The final polyamide has a relative viscosity of 36 and contains 110 and 44 equivalents of amine and carboxyl end-groups, respectively, per 10⁶ grams of polymer. This polymer is mixed with 1.9% of its weight of titanium dioxide and 0.56% of its weight of the sodium salt of phenyl phosphinic acid (as disclosed by Gray in Patent 2,510,777), in order to reduce the atmospheric degradation of the polymers at the spinning temperature and spun at 800 yards per minute. The frequency of spinneret drips is one per six hours in spite of the added stabilizer. The yarn is cold-drawn to give a delustered yarn (hereinafter designated as "control 2") with a total denier of 72.

Another high-amine polyamide is made by reacting hexamethylenediammonium adipate with 1.94 mol percent of hexamethylene diamine under conditions as given above. The resulting polymer has a relative viscosity of 41 and contains 146 and 22 equivalents of amine and carboxyl end-groups, respectively, per 10⁶ grams of polymer. This polymer is mixed with 2.4% of its weight of titanium dioxide and spun as the core of a two-component yarn; and a polymer as used for control 1, but without titanium oxide is used for the sheath of the yarn. The spinning pumps for the two-component melts are adjusted to give a ratio of sheath/core of 15/85. The polymers spin well and no spinneret drips occur in 44 hours, at which time the run is stopped. The filaments are drawn over a cold pin to give a delustered yarn with a total denier of 71, total TiO₂ content of 1.9%, and an over-all amine content of 122×10⁻⁶ equivalents per gram. Representative transverse cross sections of these filaments appear in FIGURE 4, the dyeing of the core being represented by stippling.

It is surprising not only that the sheath-core yarn exemplified here spun much better than the single-component high-amine yarn (more than 44 hours versus 6 hours for the same drip frequency) even though it contained more amine groups but also that the two-component yarns with a bright sheath, i.e., with no delusterant present, spun much better than control 1, which contained pigment but less than 0.3 as many amine groups as the core of the two-component fiber (more than 44 hours per drip as compared to 20 hours).

The three yarns had physical properties given in Table I below.

Table I

Yarn	Tenacity (g.p.d.)	Elongation (percent)
Control 1.....	5.0	29
Control 2.....	5.2	30
Sheath-Core.....	4.2	24

The abrasive qualities of the three yarns were measured by the time required by the yarn to cut through a small standard copper wire under controlled conditions of tension and speed with results as shown in Table II.

5
Table II

Yarn:	Cutting time in seconds
Control 1 -----	385
Control 2 -----	500
Sheath-core -----	67,000

Knit tubings were made of the three yarns and dyed competitively in the dye bath of Example I. Control 1 gave the lightest shades, control 2 gave an intermediate shade and the sheath-core yarn gave the darkest blue shades. Similar results were obtained for 2, 5, and 15-minute dyeing. Fabrics were also woven of the three yarns and dyed separately under equivalent conditions in the dye bath of Example I to similar shades. The fabric woven of the sheath-core yarn with the high-amine core showed the greatest wash-fastness, with control 2 being intermediate between it and control 1. Similarly, the dyed fabric woven of the sheath-core yarn showed the greatest light-fastness as determined by 20 hours' exposure in a fadeometer instrument, with control 2 being intermediate. Similar dyeing results were obtained with the acid dye C.I. 430. Three fabrics woven to the same specifications were considered to be equivalent in covering power, as determined by ultraviolet light-transmission measurements. This is surprising because the sheath-core yarn had an undelustered sheath. Thus, by use of a sheath-core structure a delustered yarn was made that had the relatively non-abrasive characteristics of a lustrous yarn.

Although this invention has been illustrated with polyhexamethylene adipamide because of its recognized commercial importance, it is applicable also to other polyamides, including copolymers, whether prepared by the reaction of diamines and dibasic acids, and their derivatives, amino acids, or other compounds (e.g., caprolactam, which yields a polyamide under proper reaction conditions). The invention is applicable similarly to other fiber-forming polymers that may contain amine groups, including polyureas derived, for example, from a diisocyanate and a diamine, as shown by Rinke et al. in Patent 2,511,544; polyurethanes; polythioureas; polythioamides; polysulfonamides, as taught by Jones et al. in Patent 2,667,468; polyimides; and poly-4-amino-1-2-4-triazoles as taught by Fisher et al. in Patent 2,512,629. Copolyesteramides also can be used. The amine content of the core polymer may arise from a blend of a polymer containing amine groups and another polymer with few or no amine groups as, for example, a blend of a polyamide and a polyester, such as polyethyleneterephthalate.

Although this invention has its greatest application to polymers containing primary amine groups, it is of value with polymers containing secondary and tertiary amine groups. Thus, an N-amino-alkyl morpholine can be used as a viscosity stabilizer in the preparation of polyamides, as taught by Watson in Patent 2,585,199, in order to obtain polymers with tertiary amine end-groups having increased dyeability with acid dyes. Other means of forming amine end-groups by polymerization or after-treatment of a polymer will be obvious to those skilled in the art.

In general, this invention is of value when spinning polyamides containing from about 4 to 400 equivalents of amine group per 10^6 grams of polymer. The invention affords a process for the commercial spinning of any polymers containing any finite concentration of amine groups. In order to obtain a satisfactory deep-dyeing (with acid

dyes) product, the over-all amine concentration in the two-component filament should be between 80 and 400 equivalents per 10^6 grams of polymer and preferably between 100 and 200. This can be obtained by balancing the amine content of the core and sheath and their relative thickness. The products of this invention can be dyed with that class of dyes containing acid groups known as acid or direct dyes, including those with the following color index numbers: 176, 161, 1088, 365, 589, 594, and 583.

Although this invention has been illustrated by the co-spinning of two different polyamides, the sheath and core of a filament need not be composed of the same type of polymer. For example, a polyester sheath can be spun over polyamide core having a high content of amine end-groups. In this manner the acid-dyeing characteristics of one polymer can be combined with the surface properties of a second polymer.

This invention is of value in that it provides two-component filaments that can be dyed to deep, uniform shades that are wash- and light-fast. Although this invention has been illustrated with filaments containing the sheath and core components in a concentric relation, any eccentric arrangement can be used and, furthermore, the shape can be as desired, e.g., cruciform, ribbon, Y-shape, as well as circular. Regardless of shape, the dyed products display greater fastness to laundering and light than single-component filaments dyed to the same shade. The products are eminently suitable for all manner of textile applications.

The claimed invention:

1. A filament of improved dye receptivity and retention comprising a sheath-core filament having comprising as a core a polymeric substance containing at least 10^2 equivalents of amine end-groups per 10^6 grams of polymer and as a sheath a polymeric substance having fewer than about 50 amine equivalents per 10^6 grams of polymer.

2. A filament of improved dye receptivity and retention comprising a sheath-core filament having as a core a fiber-forming polyamide containing at least 10^2 equivalents of amine end groups per 10^6 grams of polymer, and as a sheath a fiber-forming polyamide having fewer than about 50 amine equivalents per 10^6 grams of polymer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,989,798

June 27, 1961

Douglas G. Bannerman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 33, strike out "comprising", second occurrence.

Signed and sealed this 16th day of January 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents