

Dec. 28, 1965

R. H. KNOSPE

3,225,534

DIFFERENTIAL SHRINKAGE YARN

Filed Feb. 25, 1964

2 Sheets-Sheet 1

FIG. 1

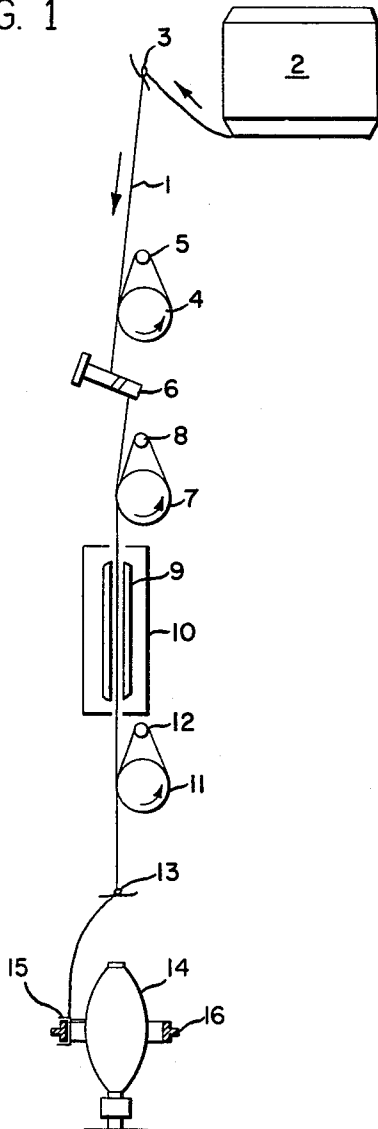
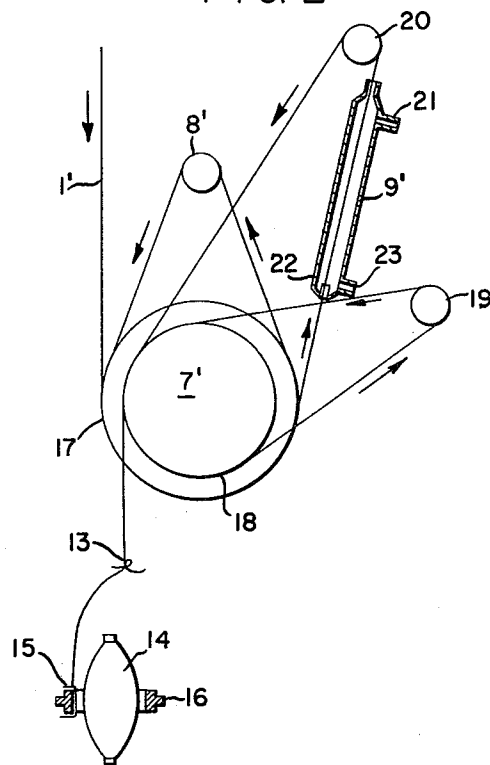


FIG. 2



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FIG. 3

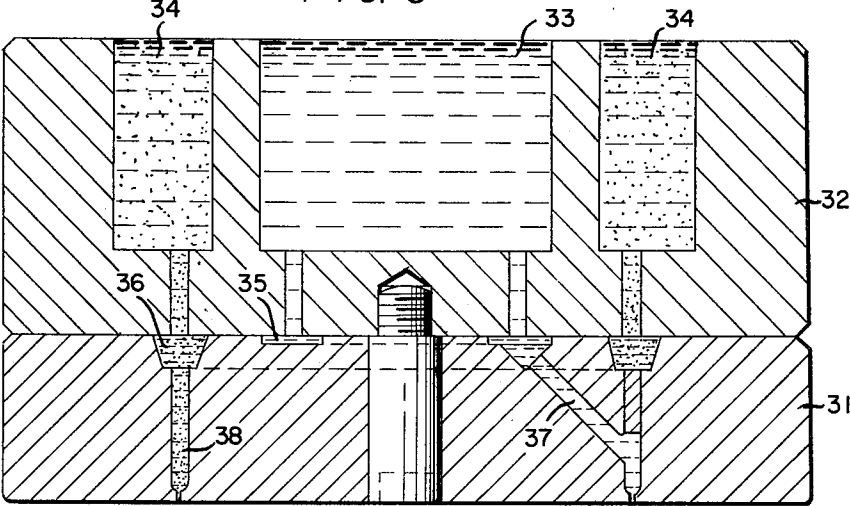
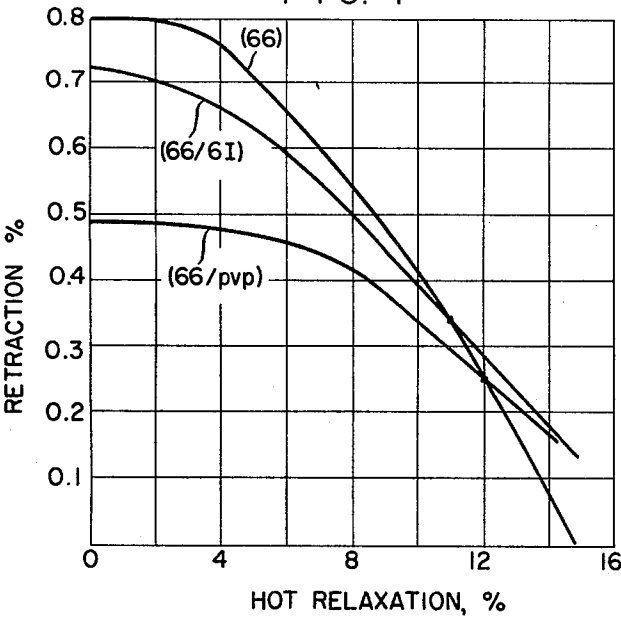


FIG. 4



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DIFFERENTIAL SHRINKAGE YARN

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15 Claims. (Cl. 57—140)

This application is a continuation-in-part of my co-
pending application Serial No. 99,883, filed March 31,
1961, now abandoned.

This invention relates generally to textile fibers and,
more particularly, to the production of continuous fila-
ment yarns made from thermoplastic synthetic polymers.

In relatively recent years, the introduction of synthetic
yarns, such as those from polyamides and polyesters, has
led to fabrics having high strength, improved resistance
to wear and, most important, improved launderability and
wrinkle resistance. However, fabrics made from these
yarns, particularly the continuous filament yarns, are im-
perfect in some respects. For example, fabrics of filamen-
tary polyamide yarns tend to have a slick, cold hand and
are deficient in cover and luster in many end uses. Thus,
in spite of their superior functional properties, fabrics
produced from these yarns do not have the desirable
aesthetic qualities of silk fabrics such as a warm, dry
hand and good luster.

Improvements in aesthetics have been attained with
mixed shrinkage yarns. When the resulting fabric is
scoured in hot or boiling water the lower shrinkage fila-
ments tend to crimp or loop thus giving the fabric greater
bulk and cover as well as improved hand. Mixed shrink-
age yarns are most readily achieved by combining fila-
ments from different polymeric compositions. However,
when available yarns of this type are unwound from the
package for processing into fabric, the filaments retract
slightly and there is a difference in retraction between the
high and low shrinkage filaments. As a result, the low
shrinkage filaments form loops which cause great diffi-
culties in yarn handling and during the preparation of
fabrics. In addition, these mixed shrinkage yarns fre-
quently lead to undesirable separation ("cracking") of
the filament bundles in the fabric. Although mixed
shrinkage yarns may in some instances be achieved with-
out varying the polymer composition, such yarns not
only tend to suffer from the defects noted above but also
require special processing conditions (e.g., differential den-
ier and/or stretching) which are not always desirable
or practical.

The most important object of the present invention is
to provide yarns from thermoplastic synthetic polymer
compositions which yield fabrics having improved aesthetic
qualities. It is a corollary objective to provide yarns of
thermoplastic synthetic polymer compositions which pro-
duce fabrics having a warm dry hand as well as im-
proved luster and bulk. A more specific objective is the
provision of yarns which are easily processed into fabrics.

The above objects are accomplished in a yarn con-
sisting of a plurality of highly oriented filaments prepared
from at least two different but related thermoplastic syn-
thetic polymer compositions, the filaments from the dif-
ferent polymer compositions being intermingled and char-
acterized by having substantially the same initial moduli,
the same stress decay behavior at room temperature when
stressed slightly and held at constant length, and a differ-
ence in shrinkage when subjected to boiling water.

Further objectives will become apparent in the follow-
ing specification wherein reference is made to the accom-
panying drawings in which:

FIGURE 1 is a schematic illustration of apparatus for
carrying out the process of the present invention;

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FIG. 2 is a detailed schematic of an alternate apparat-
us embodiment which may be employed in the relaxing
step;

FIG. 3 is a vertical sectional view through a spinneret
which is suitable for use when the process is coupled;
and

FIG. 4 is a graph of the curves resulting when the re-
traction and relaxation data for the exemplified polymers
are plotted.

Preferably, the different polymer compositions should
each contain at least 70% by weight of monomer units
of the same class as contained in major proportion in the
other composition and up to 30% by weight of monomer
units of a different class, one of the compositions con-
taining at least 5% (based on the total weight of polymer
in the composition) more of the monomer from the said
different class. In addition, the temperatures (T_g) of
maximum work loss for filaments spun from the different
polymer compositions preferably differ by no more than
30° C. and their initial moduli should be approximately
equal.

The process comprises the steps of intermingling a plu-
rality of filaments from two different thermoplastic syn-
thetic polymer compositions, drawing the filaments to
produce highly oriented structures and hot relaxing the
drawn filaments under conditions which substantially
equalize the room temperature stress decay characteristics.
The compositions should be such that the drawn filaments,
before hot relaxation, exhibit a difference in shrinkage of
at least 1% when subjected to boiling water and a differ-
ence in room temperature stress decay properties.

In one process embodiment (Example I), the inter-
mingled filaments are drawn to produce highly oriented
structures, simultaneously heated and relaxed after draw-
ing to cause the filaments to retract in length, the per-
centage of retraction resulting from hot relaxation being
in the range of 5 to 15% and being substantially equal
to the percentage relaxation at the point of coincidence
of the relaxation-retraction curves (FIG. 4) for the dif-
ferent filaments.

In another embodiment (Example V), the filaments
are subjected to a constant length annealing treatment
followed by relaxation of the heated filaments, the per-
centage of retraction due to the hot relaxation being in
the range of 2-10%, depending on the annealing tem-
perature, i.e., hot relaxation conditions are such as to
insure substantial equalization of instantaneous retrac-
tions.

The intermingling step may be carried out at any con-
venient stage in the process but is preferably accomplished
by extruding the different polymers from adjacent orifices
of the same spinneret (FIG. 3). Alternately, the filaments
may be intermingled by first gathering them in a bundle
and thereafter passing the filament bundle through a
zone of fluid turbulence.

The process may be carried out as illustrated schemat-
ically in FIG. 1 of the drawing. The yarn 1 consisting of
filaments from at least two different thermoplastic syn-
thetic polymers is withdrawn from a supply source 2,
passed through guide 3 and then passed in multiple wraps
around driven feed roll 4 and associated separator roll
5. From feed roll 4, the undrawn yarn 1 passes in
several wraps about snubbing pin 6, as taught by Bab-
cock in U.S. 2,289,232. The yarn is drawn in frictional
contact with pin 6 under the urging of draw roll 7 and
its associated separator roll 8. Draw roll 7 has a higher
peripheral speed than feed roll 4 whereby the yarn is
elongated to several times its original length. From draw
roll 7, the yarn passes through heating means 9, with
jacket 10, to relaxing roll 11 and its separator roll 12.
The relaxation permitted the yarn is controlled by ad-
justing the relative peripheral speeds of rolls 7, 11. The

application of heat to the yarn is adjusted to give sufficient contraction of the yarn to insure the slight tension necessary to keep the yarn running smoothly on the rollers. The hot relaxed yarn next passes through guide 13 and is wound on a suitable package 14 by the traveler 15 on a ring twister 16.

FIG. 2 shows a preferred apparatus embodiment for accomplishing the relaxing step. In this arrangement, draw roll 7' is of stepped construction, having a portion of larger diameter indicated at 17 and a portion 18 of smaller diameter. Idler-separator roll 8' is employed as in FIG. 1 and two supplemental separator rolls 19, 20 are added. A steam tube, shown at 9', has a steam inlet connection 21, condensate trap 22 and condensate return 23. In operation, yarn 1', drawn in snubbing contact with pin 6, passes in multiple wraps around the large diameter part 17 of draw roll 7' and separator roll 8'. The yarn then traverses steam tube 9', changes direction over roll 20 and passes in multiple wraps around the smaller diameter portion 18 of draw roll 7' and separator roll 19. The hot relaxed yarn is then wound up as shown in FIG. 1.

The spinneret shown in FIG. 3 includes a spinneret plate 31 and a distribution plate 32. Plate 32 has a central cavity 33 and a ring-shaped cavity 34, each of which is adapted to receive a molten polymer under pressure and distribute it to one of the annular channels 35, 36 in plate 31. Channels 35, 36 discharge through passages 37, 38 to alternate holes in a circular pattern. In this manner, the filaments are intermingled as they leave the spinneret and may be packaged as at 2 or, in a coupled process, quenched and forwarded to feed roll 4.

An alternate method of intermingling the filaments from the different polymers comprises bringing together the different filaments either before or after drawing, passing the filament bundle through the steam tube, then passing the filaments through an air jet to intermingle and interlace the filaments prior to passage around roll 11. Such a procedure has been described by Bunting and Nelson in their U.S. Patent No. 2,985,995. If desired, the heating and interlacing may be combined in one step by using hot air or steam in an interlacing jet, as described by Dahlstrom and Wert in their U.S. Patent No. 3,069,836.

The boil-off shrinkage of the filaments, as referred to herein, is determined by subjecting a measured length of the filament to boiling water for 15 minutes, drying and again measuring the length of the filament. The percentage reduction in length is calculated and referred to as the boil-off shrinkage.

The degree of loopiness due to differences in retraction of the different filaments may be determined by examination of the yarn under a microscope or other source of magnification. Before making such observations, the yarn package is held at 75° F. and 72% RH for 15 hours. It is then removed from the package and observed in a relaxed condition.

The instantaneous room temperature retraction of the filaments after removal from the package is determined by separating the freshly wound yarn into two bundles, each containing the filaments from one polymer composition. Each of the bundles is then placed in an Instron tester under the same tension, in grams/denier, as prevailed during the winding of the yarn, the sample length (distance between the jaws of the tester) being 10 inches. The sample is held under this tension for 15 hours at 75° F. and 72% RH. The tension is then reduced to zero and the instantaneous reduction in length of the sample recorded. The difference in instantaneous retraction between the different filament bundles provides an objective indication of yarn loopiness under zero tension. Obviously, the test may be run using single filaments if desired.

The curves shown in FIG. 4 are obtained by measuring the percentage instantaneous retraction at various degrees

of hot relaxation (according to the procedures of Examples I-IV) in the range of 0 to 15%, preferably at intervals of 3 to 4%, plotting the data obtained and connecting the points with a smooth curve. The curves for polyhexamethylene adipamide (66), the copolymer of polyhexamethylene adipamide and polyhexamethylene isophthalamide (66/6I), and the melt blend of polyhexamethylene adipamide and polyvinyl pyrrolidone (66/PVP) have been shown for purposes of illustration.

The stress decay characteristics of the filaments may be determined by separating the different filaments from one another, placing each separate filament bundle in an Instron tester using a 10-inch sample length, adjusting the tension (stress) on the filament bundle to 0.229 gram/denier and recording the decrease in stress while holding the filaments at constant length, in a 75° F. and 72% RH environment, until it becomes essentially constant. This will usually require 10 hours or more. The stress decay characteristics are substantially the same, for the purposes of this invention, if the stress levels as determined above differ by no more than 0.020 g.p.d. after 15 hours for filaments having an initial modulus of about 22 g.p.d.

The difference in stress level which is permissible will, of course, depend on the initial modulus of filaments since the initial modulus is indicative of the rate at which the yarn structure elongates with increasing load or retracts with decreasing load in the very early stages of elongation. Practically, initial modulus is determined from the stress-strain curve (obtained when the yarn is elongated 2% in a yarn tester and then unloaded) by multiplying the load at 1% elongation on the unloading curve by 100 and dividing by the denier of the yarn. The stress decay characteristics are substantially the same, for the purposes of this invention, if the ratios of stress to initial modulus for the different filaments differ by less than 0.001.

EXAMPLE I

A 48% aqueous solution of hexamethylene diammonium adipate (66 nylon salt) and 0.3 mol percent, based on the salt, of a 25% aqueous acetic acid solution (viscosity stabilizer) are charged to an evaporator and concentrated to 60% at atmospheric pressure, which corresponds to a final temperature of about 105° C. The 60% salt solution is transferred to an unstirred autoclave with steam atmosphere and heated in the closed autoclave until the steam pressure reaches 250 p.s.i. (requiring about 20 minutes). When this pressure is reached, steam is bled off, maintaining 250 p.s.i. pressure, and heating is continued until the concentration of salt is 90%, which corresponds to a temperature of 230° C. At this point, the charging of 33% by weight (based on final polymer weight) of a 30% aqueous solution of polyvinyl pyrrolidone is started and completed over a period of 15 minutes. The polyvinyl pyrrolidone has a molecular weight of about 125,000 and is of sufficient purity to be stable against discoloration and cross-linking at high temperatures. After the charge is completed, the heating and bleeding off at 250 p.s.i. are continued until the temperature reaches 245° C. At this temperature, the pressure reduction is started and continued over a period of about 90 minutes until the temperature has reached 270° C. and the pressure has been reduced to atmospheric. Heating at atmospheric pressure is continued until 275° C. is reached to complete the polymerization. The autoclave is discharged by bringing it to 100 p.s.i. pressure of inert gas (nitrogen and carbon dioxide) and discharging molten polymer as a ribbon by extrusion through a narrow slit. The ribbon is quenched on a water cooled casting wheel and cut into 1/2-inch flakes. The melt blended polymer flake has a relative viscosity of 34.7 and a polyvinyl pyrrolidone content of 9%.

Flake of 66 nylon having a relative viscosity of 39.5 is prepared in the conventional manner. It and the nylon/

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polyvinyl pyrrolidone flake are melted separately in screw melters and extruded from alternate holes in a spinneret of the type shown in FIG. 3. The spinneret has 34 holes so that 17 filaments of 66 nylon and 17 filaments of 66 nylon/N-polyvinyl pyrrolidone filaments are extruded. The filaments are quenched by passing air transversely across the filament bundle as described in U.S. 2,273,105 and then wound into a package in the conventional manner. The filaments are subsequently withdrawn from the package and drawn as illustrated in FIG. 1 to a ratio of 3.46. The yarn is then passed through a steam tube at 423 yards/minute and permitted to relax as illustrated in FIG. 2. The steam tube is $2\frac{1}{16}$ inches in length and is supplied with superheated steam at 275° C. and 12 p.s.i. For purposes of comparison, yarns with the various degrees of relaxation given in Table I were prepared. These yarns were twisted $\frac{1}{2}$ Z-turn per inch using a ring twister of conventional design. The denier per filament is 2.0. When the yarn is removed from the package, the filaments having various degrees of relaxation retract instantaneously to the extent indicated in FIG. 4. The percentage instantaneous retraction is determined after removal from an Instron tester as previously described. As shown in FIG. 4, the retraction of the filaments from the two different polymer compositions is substantially the same where the hot relaxation is about 12%. There is no loop formation and no difficulty in handling or processing the relaxed yarn into fabrics.

When the stress decay properties for the different filaments from this yarn are determined as described previously, the stress after 15 hours and the stress/modulus ratio for the 66 nylon and 66 nylon/N-vinyl pyrrolidone filaments are substantially the same at 12% hot relaxation, as shown in Table I. Where this condition prevails, no difficulties are encountered in processing the yarn into fabrics. However, where the hot relaxation treatment is omitted or when the degree of relaxation is considerably different from that prevailing at the point of coincidence of the curves for the two polymer compositions, the yarn is found to be very difficult to process into fabrics and is judged not to be of commercial quality in this respect.

The initial modulus of the hot relaxed 66 nylon filaments is 22 g.p.d. and T_g is $80 \pm 5^\circ$ C.; corresponding values for the 66 nylon/N-vinyl pyrrolidone filaments are an initial modulus of 21 g.p.d. and a T_g of $90 \pm 5^\circ$ C.

When a sample of the 12% hot relaxed yarn is placed in boiling water for 15 minutes, the boil-off shrinkage of the 66 nylon filaments is 7.2% while that of the 66/polyvinyl pyrrolidone filaments is 10.8%.

A plain weave fabric having a loom construction of 96 x 68 is woven from the 12% relaxed yarn and finished in the conventional manner by scouring in a relaxed condition at the boil and heat setting in the conventional manner. The resulting fabric has a warm, dry hand as compared to a conventional nylon fabric of similar construction. The fabric bulk is 2.4 cc./gram as compared to 2.0 cc./gram for a conventional nylon fabric of the same construction when measured by the standard BSI method.

Table I

Hot relaxation, percent	15-hr. stress, g.p.d.		Stress/modulus		
	66 nylon	66/PVP	66	66/PVP	Difference
None.....	0.192	0.108	0.0087	0.0051	0.0036
4.....	0.175	0.104	0.0080	0.0050	0.0030
8.....	0.136	0.086	0.0062	0.0041	0.0021
12.....	0.053	0.053	0.0024	0.0025	0.0001
15.....	0.000	0.026	0.0000	0.0012	0.0012

EXAMPLE II

Yarn is prepared, drawn and passed through a steam tube, all as described in Example I. It is then passed through an air jet, as described by Dahlstrom and Wert, to intermingle and interlace the filaments. During the

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heating and interlacing steps, the yarn is permitted to relax 12% by appropriate regulation of the relative speeds of the rollers (FIG. 2). The interlaced yarn is then wound into a package in the conventional manner without twisting. When it is removed from the package, the filaments retract about 0.25% and the retraction is substantially the same for all of the filaments, i.e., no loops in the filaments are observed.

When a sample of the yarn is immersed in boiling water for 15 minutes and the boil-off shrinkage of the various filaments determined, it is found that the nylon/polyvinyl pyrrolidone filaments shrink 10.8% while the nylon filaments shrink only 7.2%.

When the yarn is woven into fabric and scoured, the fabric characteristics are found to be substantially as described in Example I except that the fabric has a softer and smoother hand.

EXAMPLE III

Example I is repeated except that the steam tube of FIG. 2 is replaced by an air jet supplied with hot air at 410° C. and 13 p.s.i.g. to relax and interlace the filaments. The filaments are permitted to relax 12% and then wound into a package without twisting. When the yarn is removed from the package, the filaments retract about 0.25% but the retraction of the various filaments is substantially the same. No loops are observed and the yarn is easily processed into fabric. When yarn samples are subjected to boiling water for 15 minutes and the boil-off shrinkage of the filaments measured, it is found that the nylon/polyvinyl/pyrrolidone filaments shrink 10.8% while the nylon filaments shrink only 7.2%. When the interlaced yarn is woven into fabric as described in Example I the fabric is found to exhibit the same characteristics as the fabric of Example II.

EXAMPLE IV

A 48% aqueous solution of hexamethylene diammonium adipate (66 nylon salt) is charged into an evaporator. A 40% aqueous solution of hexamethylene diammonium isophthalate (6-I), prepared by combining equimolar proportions of hexamethylene diamine and isophthalic acid, is added to the evaporator in sufficient amount to provide 8% by weight of hexamethylene diammonium isophthalate based on the total weight of dry salt present. The salt solution is then evaporated to a 75% concentration level, at which point the temperature is about 138° C. The 75% salt solution is then charged to an autoclave and heated to a temperature of about 242° C. and 250 p.s.i. pressure, about 85 to 90 minutes being required for this operation. The pressure is then reduced over a period of 85 minutes to atmospheric pressure and the temperature increased to 270-275° C. The polymer is then held for 40 minutes at this temperature and extruded in the form of a ribbon which is quenched on a water-cooled casting wheel and cut into $\frac{1}{2}$ -inch flakes in the conventional manner. The polymer has a relative viscosity of 40.

The 66/6-I flake and 66 nylon flake of 45 relative viscosity prepared as described in Example I are melted separately, extruded, quenched and wound as described in Example I except that the filaments are extruded through spinneret orifices of the type described in U.S. 2,939,201 to produce trilobal cross sections having a modification ratio of 2.3, a tip radius of 0.225 and a lobe angle of $\pm 18^\circ$. The filaments are subsequently withdrawn from the package, drawn to a ratio of 2.47 and then given a hot relaxation treatment as described in Example I, the degree of relaxation being varied as shown in FIG. 4. The different yarns are then interlaced with an air jet, as described by Dahlstrom and Wert, and wound into packages in the conventional manner under a tension of 16 grams. When the yarns are removed from the packages, after 15 hours storage at 75° C. and 72% RH, and examined under a microscope, it is observed that the yarn which is given 11% hot relaxation

has no loops due to difference in instantaneous retraction of the various filaments but that the yarns relaxed at the other percentages shown in Table II are loopy. The 66 nylon filaments are separated from the 66/6-I copolymer filaments and the instantaneous retractions determined on an Instron tester as previously described. When the retraction is plotted against percent hot relaxation as shown in the FIG. 4, it is found that the data for 66 and for the 66/6-I filaments lie on different curves which intersect at 11% relaxation.

When samples of the yarn which was relaxed by 11% are subjected to boiling water for 15 minutes, the boil-off shrinkage of the 66 nylon filaments is 7.6% while that of the 66/6-I filaments is 11.3%.

The initial moduli of both the 66 nylon and the 66/6-I filaments are 22 g.p.d. The latter have a T_g of $95 \pm 5^\circ \text{C}$.

When the stress decays of the different filaments are determined as described in Example I, the stress level after 15 hours is 0.073 g.p.d. and the stress/modulus ratio is 0.0033 for both sets of filaments where they are given 11% hot relaxation, but these values are different under other conditions (Table II).

When the yarn which was given 11% hot relaxation is processed into fabric, no difficulty with loopiness is encountered whereas the yarns relaxed at 4% and 15% were difficult to process due to loopiness.

A plain weave fabric of 96 x 68 loom construction is prepared from the 11% hot relaxed yarn and finished in the conventional manner by scouring in a relaxed condition at the boil and heat setting. The resulting fabric has a warm, dry hand and higher bulk (2.3 cc./gram) when compared with a conventional nylon fabric of the same construction (2.0 cc./gram).

Table II

Hot relaxation, percent	15-hr. stress, g.p.d.		Stress/modulus		
	66 nylon	66/6-I	66	66/6-I	Difference
None-----	0.192	0.165	0.0087	0.0075	0.0012
4-----	0.175	0.150	0.0080	0.0068	0.0012
8-----	0.136	0.110	0.0062	0.0050	0.0012
11-----	0.073	0.073	0.0033	0.0033	0.0000
15-----	0.000	0.026	0.0000	0.0012	0.0012

EXAMPLE V

Flakes of 66 and 66/6-I nylons, both having a relative viscosity of 32, are prepared as described in Example IV except that a 25% aqueous solution of an antistatic agent, nonyl phenoxy capped polyethylene ether alcohol of about 1600 molecular weight, is added to the autoclaves during polymerization in sufficient amounts to provide concentrations of 2.5% by weight in both the 66 and 66/6-I flake. The antistatic agent is added when the temperature reaches 235°C . The autoclaves are equipped with a stirrer to provide a satisfactory dispersion of the antistatic agent in the polymers.

The 66 and 66/6-I flakes are melted separately and extruded from the same spinneret as in Example IV to form seven 66 filaments and seven 66/6-I filaments. The substantially equidimensional filaments are then quenched in the conventional manner and converged at a guide to form a yarn. The yarn is then passed twice around a feed roller with its associated separator roller and thence to a draw roller having a higher peripheral speed whereby the yarn is drawn to a ratio of 3.0. The draw roller is located in a heated compartment having an air temperature of 150°C . From the draw roller, the yarn is passed around a second roller in the heated compartment and then back around the draw roller, the second roller having the same peripheral speed as the draw roller so that the yarn is subjected to a constant length heat treatment. The yarn then passes from the

heated compartment directly to and around a roller having a lower peripheral speed whereby the yarn is permitted to retract 2.5% in length. The hot relaxed yarn is then passed through an interlacing jet as in Example IV and wound into a package in the conventional manner. The denier of the final yarn is 40.

When the yarn is removed from the package after 15 hours storage at 75°C and 72% RH, no loop formation is observed, indicating that the room temperature retraction and hence the stress decay levels of the filaments are substantially equivalent. The 66 nylon filaments are characterized by an initial modulus of 32.3 g.p.d., a 15 hour stress level of 0.207 g.p.d. and stress/modulus ratio of 0.0064. By comparison, the 66/6-I filaments exhibit an initial modulus of 31.8 g.p.d., a 15-hour stress level of 0.192 and a stress/modulus ratio of 0.0060. Thus, the ratios differ by only 0.0004. The filaments exhibit a difference in shrinkage in boiling water of about 3%.

When the yarn is knit into a tricot fabric and the fabric finished in the conventional manner, the fabric has much better covering power and a generally better appearance than conventional nylon tricot fabric. The accumulation of static electricity under conditions of low humidity is much less than with conventional nylon fabric and comparable to cotton.

As shown in the foregoing examples, the yarns of this invention lead to a substantial improvement in the aesthetic qualities of fabrics without the attendant difficulties of the prior art yarns which have not been commercially acceptable due to the small loops which form when the yarn is removed from the package for processing into fabric.

The yarns disclosed herein consist of filaments from different polymer compositions, the different filaments having the characteristic that their viscoelastic properties at room temperature, i.e., in the range of about 20 to 35°C ., are substantially the same but, at higher temperatures, i.e., 100°C or higher, are different. This desirable effect is accomplished by a critical selection of polymer compositions and appropriate treatment of the filaments. The polymer compositions employed should each have 70% or more monomer units of the same class as the major proportion of monomer units of the other composition. By the same class is meant that the monomer units are of one of the well-recognized classes such as the amide units in polyamides or the ester units in polyesters. It is, of course, desirable that the monomer units be identical but different units in the same class may be selected in certain cases. Preferably, one of the compositions consists substantially entirely of the same monomer units, i.e., is a homopolymer, while the other polymer composition contains from 5 to 30% by weight of a different monomer unit. Thus, the second composition may be a copolymer containing 5 to 30% of monomer units which are different from the major proportion of the monomer units in the composition. Instead of being a copolymer, the second composition may be a melt blend (Example I) containing 5 to 30% of a different polymer.

Although it is desirable that one of the polymer compositions consist essentially of the same monomer units, it is possible in some cases to employ copolymers or melt blends in both compositions provided that one of the compositions contains at least 5% more of a particular monomer unit than the other.

Suitable constituents for preparing the compositions of this invention are the fiber-forming, melt-spinnable synthetic polymers such as polyamides, polyesters and polyolefins. The preferred classes are polyamides and polyesters of the type described in U.S. Patents Nos. 2,071,250; 2,071,253; 2,130,523; 2,465,319; 2,130,948; 2,190,770 and elsewhere. The preferred polyamides for use as the major constituent of the compositions are polyhexamethylene adipamide, known commercially as 66

nylon, and polycapromide, known commercially as 6 nylon.

The two polymer compositions preferably have maximum work loss temperatures (T_g) which differ by no more than 30° C. As referred to herein, T_g is that temperature (above 0° C.) at which maximum mechanical work loss occurs in a filament. It is a polymer property which is related to molecular structure and arrangement. The manner in which T_g is related to maximum mechanical work loss is given in "Die Physik der Hochpolymeren," A. S. Staverman and F. Schwarzl, Band IV, Springer-Verlag, Berlin, 1956, Chapter I.

A further requirement is that the two polymer compositions used in preparing the filaments be sufficiently different in viscoelastic properties at the higher temperatures to insure a differential shrinkage in boiling water of a least 1%. This may be readily accomplished by using as one of the compositions a copolymer containing a minor proportion of monomer units which are considerably different from the major proportion of the monomer units. Likewise, this objective may be accomplished by adding to a homopolymer a second homopolymer or copolymer which differs considerably in chemical composition but which is capable of being melt blended with the composition.

Polymers which are particularly suitable for melt blending in minor proportion with the polyamides and especially with polyhexamethylene adipamide or polycapromide are the poly(N-vinyl amides). The preferred poly(N-vinyl amides) are the polyvinyl lactams, such as N-vinylpyrrolidone, N-vinylpyrrolidone, N-vinyl valerolactam and homologically related compounds.

Copolyamides which are suitable for use in this invention are those in which the minor constituent varies considerably in chemical structure from the major constituent. Thus, various copolyamides based on 66 nylon may be prepared by replacing, in the polymerization, part of the hexamethylene diamine with another amine such as m-xylylene diamine or parts of the adipic acid with another acid such as sebacic acid. Many other combinations are known in the art.

When the viscoelastic properties of the two compositions at the higher temperature are sufficiently different to provide the shrinkage differences required by this invention, the properties of the filaments at lower temperatures will almost always differ to some degree and must be equalized by appropriate treatment. In the exemplified hot relaxation procedures, this equalization has been accomplished by heating the filaments at appropriate stages in the processing to relieve certain strains in the polymer structures which act at room temperature to give differences in retraction when the filaments are removed from the yarn package. Surprisingly, it has been found that by heating the yarns sufficiently to bring about a critical degree of retraction subsequent to drawing, the differences in viscoelastic properties at room temperature are substantially eliminated while the differences which occur at higher temperatures are affected only moderately if at all. The equalization of viscoelastic properties at room temperature which is believed to be a phenomenon relating to the amorphous areas of the filaments is best expressed in terms of the stress relaxation behavior of the filaments when they are loaded to about the same level of tension, as in the winding operation, and held at constant length. Under these conditions, the stress or load required to hold the yarn at constant length is observed to decrease with time until it becomes substantially constant after a period of about 10 hours or more. For practical purposes, a comparison of the residual stress or load after 15 hours is sufficient to detect any differences in stress relaxation behavior. The filaments from the different polymer compositions should, after hot relaxation, show substantially the same level of stress decay at the end of 15 hours to be satisfactory for the purposes of the invention. By substantially the same level is means that a

variation of no more than about 0.02 g.p.d. exists for a yarn having a modulus of about 22 g.p.d.

In order that the yarns of this invention display the desired properties, the initial moduli of the filaments from the different polymer compositions must be approximately the same, i.e., they should not differ by more than 10%.

As indicated above, the relaxation treatment required to achieve similarity in viscoelastic properties at room temperature is quite critical. In the procedure of Example I, the percentage of relaxation must not vary more than about 1.5% from that existing at the point of coincidence of the two relaxation-retraction curves shown in FIG. 4. The preparation of similar curves for filaments spun from other suitable compositions or of corresponding curves for filaments hot relaxed according to the procedures of Example V should be apparent from the present disclosure. They should also provide the requisite information for selecting operable polymer systems and for making appropriate process adjustments in accordance with the teachings of this invention.

In practice, the desired percentage relaxation after drawing is fixed by controlling the relative peripheral speeds or diameters of power driven rollers on either side of the heating zone. Heat is applied to the yarn by any suitable means, the temperature and time of exposure being regulated so that the yarn retracts sufficiently to run smoothly on the rollers without any slackness. In the case of combinations of filaments which exhibit wide differences in boil-off shrinkage, the retraction permitted in hot relaxation must usually be higher. While the upper limit of retraction is dictated by the differences in the filaments in the yarn being processed, in general, retractions in the range of 5 to 15% are required in the procedure of Example I.

As indicated previously, intermingling of the filaments may be accomplished by spinning the different filaments from the same spinneret so that the filaments are interspersed as produced or separate filament bundles may be intermingled by passing them through an air jet or other device where they are subjected to the action of a turbulent fluid which interlaces and intermingles the filaments. When the filaments are interlaced in this manner, the conventional twisting of the yarn may be omitted and it is found surprisingly that the fabrics prepared from the interlaced yarns of this invention dye more uniformly than those prepared from twisted yarns.

Where the filaments are all extruded from the same spinneret, the different filaments are obviously drawn at the same time and to the same degree; however, when different filament bundles are brought together, these bundles may be drawn or undrawn. It is preferable in most cases that the filaments be drawn to about the same extent.

Preferably, the filaments are of nonround cross section, cross sections of heart shape, cruciform shape, multilobal shape (Examples IV and V) and the shield shapes of U.S. Patent No. 2,939,202 being superior to round sections. Improvement in fabric luster and hand are realized by the use of such nonround cross-sectional shapes. The optimum shapes for this purpose appear to be the trilobal shapes disclosed and claimed in U.S. Patent No. 2,939,201, those having modification ratios of 1.8 to 3.0, tip radii of 0-0.5 and lobe angles of 0-60° being particularly desirable.

The yarns of this invention preferably contain a durable antistatic agent. The antistatic agent should be present in a concentration of at least 2% by weight of the filament and may be added to either or both of the polymeric compositions used in producing these yarns. Suitable antistatic agents include the high molecular weight poly(alkylene ethers), i.e., those in the molecular weight range of 1300 to 200,000.

The poly(alkylene ethers) which may be employed are either ethylene oxide, propylene oxide or ethylene oxide-

propylene oxide condensation products, i.e., the products contain from two to three carbon atoms in the alkylene group with two of the carbon atoms being intralinear carbon atoms connecting intralinear ether-oxygen atoms. Preferably, the poly(alkylene ether) is an ethylene oxide polymer which may be terminated or "capped" by hydroxyl groups or by one or more ether end groups of the formula —OR, where R is an alkyl, aryl, or aralkyl group, such as methyl, ethyl, i-octyl, decyl, lauryl, tridecyl, nonylphenyl, dodecylphenyl, phenyl, naphthyl and the like. Residues of coupling compounds or chain-initiating agents, such as bis-phenol, may be present. Indeed, when the specified number of ethylene oxide units are present, copolymer constituents in addition to those mentioned may be included in the polymer chain. Other elements or radicals may be introduced into the R groups provided they are not reactive with the hydrophobic polymer, e.g., halogen, especially fluorine, a phosphite or phosphate to decrease flammability, and hypophosphite or phosphinate to improve light durability. The necessity for the absence of groups which are reactive with the hydrophobic polymer will be readily apparent since durability, molecular weight, and other physical properties of the hydrophobic polymer are adversely affected by copolymerization with poly(alkylene ether).

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A filamentary yarn comprised of a plurality of intermingled, differentially shrinkable, drawn, continuous filaments of two different compositions, the first composition being polyhexamethylene adipamide, the second composition being taken from the group consisting of (1) a melt blend of polyhexamethylene adipamide and polyvinyl pyrrolidone and (2) a copolymer of hexamethylene adipamide and hexamethylene isophthalamide, said filaments being characterized as to viscoelastic equality by stress/modulus ratios differing by no more than 0.001.

2. A filamentary yarn comprised of a plurality of intermingled, differentially shrinkable, drawn, continuous filaments of two different compositions, the first composition being polyhexamethylene adipamide, the second composition being taken from the group consisting of (1) a melt blend of polyhexamethylene adipamide and polyvinyl pyrrolidone and (2) a copolymer of hexamethylene adipamide and hexamethylene isophthalamide, said filaments being characterized as to viscoelastic equality by substantially equal instantaneous retractions and initial moduli.

3. A filamentary yarn comprised of a plurality of intermingled, differentially shrinkable, drawn, continuous filaments of two different compositions, the first composition being taken from the group consisting of polyhexamethylene adipamide and polycaprolactone, the second composition being taken from the group consisting of (1) copolymers of said first composition containing from 5–30% of another monomer and (2) melt blends of said first composition with from 5–30% of another thermoplastic synthetic polymer, said filaments being characterized as to viscoelastic equality by substantially equal instantaneous retractions at room temperature.

4. The yarn of claim 3, said filaments being further characterized by stress/modulus ratios differing by no more than 0.001, one of said compositions containing at least 2% by weight of a high molecular weight polyalkylene ether as an antistatic agent.

5. The yarn of claim 4 wherein the temperature of maximum work loss (T_g) for the different filaments differs by no more than 30° C. and said compositions each contain at least 2% by weight of a high molecular weight polyalkylene ether as an antistatic agent.

6. Packaged filamentary yarn in the form of intermingled, differentially shrinkable, drawn, continuous filaments of two different compositions, the first composition comprising a polymer selected from the group consisting of polyhexamethylene adipamide and polycaprolactone, the second composition being selected from the group consist-

ing of (1) copolymers of said first composition containing from 5–30% of another monomer and (2) melt blends of said first composition with from 5–30% of another thermoplastic, synthetic polymer, said filaments being characterized by substantially equal instantaneous retractions at room temperature and by substantially equal initial moduli.

7. The yarn of claim 6, said filaments being further characterized by stress/modulus ratios differing by no more than 0.001, said first and second compositions each containing at least 2% by weight of a capped polyethylene ether alcohol having a molecular weight of about 1600 as an antistatic agent.

8. In a process which includes intermingling filaments of polyhexamethylene adipamide in a bundle with filaments of a composition taken from the group consisting of (1) a melt blend of polyhexamethylene adipamide and polyvinyl pyrrolidone or (2) a copolymer of polyhexamethylene adipamide and polyhexamethylene isophthalamide, the steps of: drawing the bundle and substantially equalizing the room temperature stress decay properties of the different filaments in the drawn bundle by hot relaxation, the percentage relaxation being substantially that at which the relaxation-retraction curves for the different filaments coincide.

9. In a process which includes intermingling filaments of two different synthetic polymeric compositions in a bundle, the steps of: drawing the bundle and substantially equalizing the room temperature stress decay properties of the different filaments in the drawn bundle by hot relaxation, the first of said compositions consisting essentially of a polymer taken from the group consisting of polyamides and polyesters, the second of said compositions consisting essentially of at least 70% of said first composition and at least 5% of a different thermoplastic synthetic polymer, the different filaments being characterized by substantially equal initial moduli, the percentage relaxation being substantially that at which the relaxation-retraction curves for the different filaments coincide.

10. The process of claim 9 wherein said first composition is a polyamide, said second composition is taken from the group consisting of melt blends and copolymers of said polyamide and another thermoplastic synthetic polymer, and said equalizing step comprises relaxing the drawn bundle in a heated atmosphere to retract by from 5–15% of the drawn length.

11. The process of claim 10 wherein said equalizing step comprises relaxing the drawn bundle in a heated atmosphere to retract by from 9.5–13.5% of the drawn length.

12. The process of claim 11 wherein said second composition is a melt blend of said polyamide and polyvinyl pyrrolidone.

13. The process of claim 11 wherein said second composition is a copolymer of said polyamide and polyhexamethylene isophthalamide.

14. The process of claim 9 wherein said first composition is a polyamide, said second composition is taken from the group consisting of melt blends and copolymers of said polyamide and another thermoplastic synthetic polymer, and said equalizing step comprises a constant length heat treatment followed directly by a relaxation to retract from 2–10% of the drawn length.

15. A process comprising the steps of: gathering a plurality of filaments spun from two different compositions, one of said compositions being polyhexamethylene adipamide, the other being a random copolymer of hexamethylene adipamide and hexamethylene isophthalamide, said copolymer containing about 10% by weight of hexamethylene isophthalamide units; drawing said filaments; substantially equalizing the room temperature stress decay properties of the different filaments by successively heating them in their advance through a constant length zone and then relaxing the heated filaments to retract by about

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2.5% of their drawn length; intermingling the filaments in a bundle; and packaging the bundle.

References Cited by the Examiner

UNITED STATES PATENTS

2,461,094 2/1949 Taylor ----- 57—140
2,956,330 10/1960 Pitzl ----- 28—72 X
2,979,883 4/1961 Waltz ----- 57—140

5

14

3,003,222 10/1961 Pitzl ----- 28—72
3,036,988 5/1962 Knospe ----- 260—45.5
3,039,171 6/1962 Hume et al. ----- 28—72
3,061,998 11/1962 Bloch ----- 57—140
3,069,836 12/1962 Dahlstrom et al. ----- 57—140
3,088,794 5/1963 Bonner ----- 264—210 X
3,097,181 7/1963 Glickman ----- 260—42

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