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(54) **Yarns of high loading efficiency.**

(57) A process is disclosed for increasing the Loading Efficiency of a multifilament yarn (10) by applying tension forces in a lubricating environment to align individual filaments and hold them in alignment by means of a polymeric resin included as a component of the lubricating environment.

EP 0 475 430 A1

Background of the Invention

Field of the Invention

This invention relates to a process for making flexible fiber yarns which exhibit a high tensile loading efficiency at low tensile strain and to the product of that process.

Description of the Prior Art

United States Patent No. 3,648,452, issued March 14, 1972 on the application of Young, describes impregnation of carbon fiber bundles with liquids convertible to elastic solids to make flexible and durable twisted cords.

United States Patent No. 4,095,404, issued June 20, 1978 on the application of Babayan, describes a process a process for impregnating polyamide yarns in which the yarn is impregnated with a solution of thermoplastic polyurethane resin from which the solvent is then evaporated. Several of the impregnated yarns are then twisted into a helical cable and heated above the melting point of the thermoplastic resin to bond the entire structure together.

Japanese Kokai Publication 63-135555 describes a process for improving impregnation of a fiber bundle by means of contact with a vibrating surface.

Summary of the Invention

The present invention provides a process for improving the parallel alignment of individual fibers in a fiber bundle of yarn, roving, or tow by impregnating the fiber bundle with a lubricating liquid; applying tension to the impregnated bundle; exposing the tensioned bundle to mechanical energy which promotes penetration of the lubricant into the bundle and parallel alignment of the individual fibers; and solidifying the liquid to convert it to a solid which holds the fibers in the parallel alignment. Such improvement in the alignment of individual fibers in a yarn results in increase of the loading efficiency of the yarn.

The invention, also, provides a flexible yarn, roving, or tow with improved loading efficiency characterized by a higher load at low tensile strain (less than 0.5%) than that of a yarn, roving, or tow has not been processed as described above.

Brief Description of the Drawing

The Figure is a representation of the process of this invention.

Detailed Description of the Invention

It is well-known that the tensile Load At a Specified Elongation (LASE) for individual filaments is greater than the load at the same specified elongation for a yarn, roving or tow made from a plurality of those filaments, even if the yarn, roving, or tow has not been twisted. The reasons for such a per filament loss of LASE in a fiber bundle are not entirely understood, but it is believed that the LASE of a fiber bundle is diminished somewhat due to the fact that all filaments in the bundle are not perfectly aligned with the bundle axis and thus, do not bear an equal share of the tensile forces applied to the bundle. The phenomenon of diminished LASE in fiber bundles, is particularly noticed in yarns, roving, and tows made from filaments of high tensile modulus material and at low tensile elongations (less than 0.5%). For purposes of describing this invention, fiber bundles, including yarns, roving, tows, and the like, will, hereinafter be termed yarns.

So long as the LASE of a yarn is less than the total of the LASE of individual filaments making up the yarn, some of the ability of the yarn to support a load at a given elongation is lost. The loading potential of yarns is characterized by the term "Loading Efficiency". For purposes of this invention, Loading Efficiency shall be defined as the ratio of yarn stress at 0.5% strain and filament stress at 0.5% strain times 100. Loading Efficiency and its meaning is altered somewhat by varying the percent strain at which the Loading Efficiency is determined; but, for the purpose of this invention, 0.5% strain is appropriate. To have a yarn with a high Loading Efficiency is to have a yarn in which little of the load supporting potential of the yarn has been lost.

One solution to the problem of a low efficiency structure is the use of a larger yarn to simply override the loss due to low efficiency. Whereas this solution can be used successfully in some cases, it is not

acceptable in applications in which weight, volume or cost restrictions limit the amount of fiber which can be used.

Yarns of high Loading Efficiency find special use in structures in which the tensile strain must be kept below certain a level. One such use is, for example, as reinforcement in fiber optics or electromechanical cables. Other uses include precision mechanical control cables for automotive or aerospace applications.

The process of this invention finds particular use in fibers made from aramid polymeric materials. Typical of the aramid fibers are fibers of poly(m-phenylene isophthalamide) (MPD-I) and poly(p-phenylene terephthalamide) (PPD-T). PPD-T fibers are particularly preferred for use in the process of this invention. By "PPD-T" is meant the polymer resulting from mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other diamines with the p-phenylene diamine and of small amounts of other diacid chlorides with the terephthaloyl chloride. PPD-T, also, means copolymers resulting from incorporation of other aromatic diamines and other aromatic diacid chlorides such as, for example, 2,6-naphthaloyl chloride or chloro- or dichloroterephthaloyl chloride. Preparation of PPD-T is described in United States Patent Nos. 3,869,429; 4,308,374; and 4,698,414. This invention is also useful for other high modulus fibers which are used as tensile reinforcement. These include carbon, glass, alumina, boron nitride, zirconia, and other inorganic fibers; and it is, also, useful for high modulus organic fibers such as polyethylene and polyvinyl alcohol.

The process of this invention is useful for treating continuous fibers, that is, fibers made from continuous filaments as opposed to yarns made from staple or short-cut fiber material. Moreover, the continuous fibers to be treated by the process of this invention can range from 0.1 to 20 denier per filament and the filaments can be incorporated into yarns of 100 to 10000 filaments per yarn, or more. The process is of particular value for fibers which have high initial tensile modulus: That is, in general, greater than 300 gpd. It is these fibers which are most sensitive to fiber misorientation. The process is, also, useful in the production of high loading efficiency large denier rovings and tows which are composed of a plurality of spun yarns.

The process of this invention is conducted on a moving yarn, preferably as a continuation of the spinning process, itself. The process can, however, be performed off-line by rewinding fibers which have been finished earlier and wound on spools.

Referring to the Figure, yarn 10 is drawn from supply package 11 by pull rolls 12 and 13 and is held under tension adequate for conducting the process of this invention by the force of pull rolls 19 and 20 against pull rolls 12 and 13. The tension from pull rolls 19 and 20 draws yarn 10 around various direction changing rolls 14 to lubricating liquid applicator 15 and mechanical energy applicator 16. After application of lubricating liquid and mechanical energy, yarn 10, now impregnated with lubricating liquid and with individual filaments aligned, is drawn around additional direction changing rolls 17 into and through oven 18, where the lubricating liquid is dried or cured to yield a solid, flexible, polymeric yarn matrix material. From pull rolls 19 and 20, yarn 10, as the product or this invention, is drawn to windup station 21 to be packaged.

Overall, the process includes application of tension to the yarn to be treated and contact of the yarn with a lubricating liquid. The lubricating liquid can he applied either before or after the tension. After the tension and the lubricating liquid have been applied, energy is introduced to the yarn and the lubricating liquid to cause the liquid to be incorporated throughout the yarn encasing each filament and to cause the individual filaments to become aligned with each other. The lubricating liquid is dried while maintaining the yarn under tension.

Tension can he applied to the yarn by any of several well known means such as by drawing the yarn through adjacent nip rolls or in several wraps around pairs of pull rolls. The amount of tension applied should be, in any case, greater than that which is expected during use of the yarn; but should not be so great as to break individual fibers. The tension generally applied in practice of this invention is from 1 to 5 grams per denier. It should be noted that, during the fiber alignment process, the tension will decrease and if a constant tension apparatus is not being used, the final tension should not drop below the tension expected in use of the yarn. If the tension applied is less than the in-service tension or if the tension drops below the in-service tension during processing, the full benefit or the process of this invention will not be realized. Alignment tension is applied to the yarns so that any filaments which are misplaced or located in some non-parallel attitude in the yarn formation, will have an opportunity later in the process to become aligned.

The lubricating liquid with which the yarn is treated, can be any liquid which provides filament to filament lubrication and the capability to be dried or cured into a flexible solid material such that the individual filaments have an opportunity to slide into parallel arrangement with their neighbors before the liquid is dried or cured and will be held in that parallel arrangement after the liquid is dried or cured. The lubricating liquid is usually a polymer solution or a latex made from some elastomeric material; but such is

not required. Lubricant liquids have been made from organic solutions of polyurethanes, styrene-butadiene rubber, natural rubber. Also latices of materials such as polyfluoroethylenepropylene, vinyl polymers, acrylic rubber, polyvinylacetates, polyurethanes and natural rubber have been utilized as lubricating liquids. Because it is preferred that the lubricating liquid will contain a material which will permit retention of the parallel formation of individual filaments after solidifying, it is preferred that the lubricating liquid have a polymeric, preferably elastomeric, material, as at least one component. Particularly preferred as the elastomeric component is acrylic and polyurethane rubber. When solutions or latices are utilized as the lubricating liquid, care must be exercised that the concentration of material is low enough to permit maintaining a viscosity of the liquid which can easily impregnate the yarn to be treated.

The concentration of the elastomer must also be high enough so that a sufficient amount is provided between the fibers to immobilize them in their preferred aligned positions. This generally will require greater than 5% elastomer, by volume, in the yarn. For the purposes of this invention, there is no upper limit to the amount of elastomer incorporated in to the bundle. However, an upper limit will be dictated by economic and processing considerations. In order to maintain flexibility of the product yarn from this process, the elastomeric component should have sufficiently low modulus. Otherwise, the product may be too stiff and of limited usefulness for the application described above. Although relatively stiff and inflexible matrix polymers could be used, it has been found that the elastomer is preferred to have a tensile modulus less than 1000 psi at 100% elongation. It is desirable that the elastomer have low stress relaxation so that the product will retain the high loading efficiency during transit and storage prior to use. It is also desired that the elastomer retain its flexibility at any low temperature which would be encountered during use. Otherwise, the yarn will become stiff and generally unusable at such low temperatures.

Once the lubricating liquid has been contacted with the yarn and tension applied, mechanical energy is applied to the yarn and liquid in order to cause the lubricant liquid to wet the individual filaments and to make its way into the interstitial spaces in the yarn structure. The mechanical energy serves a two-fold purpose. First, it is useful to ensure that each filament is completely wetted by the lubricant liquid and that the yarn is completely impregnated by the liquid; and second, the mechanical energy serves the purpose of providing the driving force necessary to cause non-parallel filaments to slip into parallel formation, once lubricated and under tension. This energy can be applied by any of a number of methods, such as by passing the wetted yarn through a comb, over rolls or around pins. The impregnating and aligning energy can also be introduced by vibrational forces such as can be provided through the use of a piezoelectric transducer operating at frequencies up to and including the ultrasonic range.

Once the mechanical energy has been applied in an amount adequate to cause impregnation of the yarn by the lubricating liquid and alignment of individual filaments, the impregnated yarn is further processed to solidify the impregnant into the elastomeric material needed to hold the filaments in an aligned configuration. Solidification can be accomplished by evaporating the solvent from a resin solution, evaporating the dispersing liquid; curing the resin in a latex resin; curing an uncured resin; and the like. Tension is maintained on the impregnated yarn while the yarn is exposed to conditions designed to evaporate solvent contained in the lubricating liquid and/or cure, coagulate or fuse any resin dissolved or dispersed in that solvent. As a general rule, the conditions for drying and curing merely involve heating the yarn to a temperature of 100 to 250 ℃. The time needed will depend on the amount and type of solvent and the curing reactivity or melting point of the elastomeric resin. Heating can be accomplished by any commonly used method such as convection, radiation or induction. If heat treatment of fibers under tension is desirable to increase their initial modulus, the conditions described above can be adjusted to accomplish such heat treating.

Test Methods

Denier. The denier of a filament is calculated from its fundamental resonant frequency determined by vibrating a 2-4 centimeter length of filament under tension with changing frequency (ASTM D1577-66, part 25, 1968). The denier of a yarn is the weight, in grams, of 9,000 meters of the yarn.

Stress at 0.5% strain. For conduct of Examples herein, tensile testing of yarns was on an INSTRON Model 1122 tensile tester with 100 kg capacity flat faced pneumatic clamps which had been surfaced with fine crocus cloth. Specimen length was nominally 500 or 700 mm. Cross head speed was 20mm/min.

Tensile testing of single filaments was also conducted on the INSTRON Model 1122 tensile tester fitted with 500 gm capacity pneumatic clamps at a full scale load of 100 gram-force. Specimen length was nominally 254 mm. Cross head speed was 20 mm/min. To facilitate clamping and handling, the filament ends were mounted onto cardboard tabs with a cyanoacrylate adhesive.

All tensile testing was done at 55 RH and 25 ℃.

General testing methodology, data collection, and analysis was carried out in the same manner for both the yarns and single filaments. The yarn or filament specimen was mounted into the clamps to insure that there was no prestress on the yarn or filament. The movement of the cross head was then initiated while a computer monitored the stress and the cross head displacement. The beginning of the test was taken as the point at which the stress reached 0.1 gpd. The specimen length at that point was computed based on the original distance between the clamps plus the displacement of the cross head prior to reaching the 0.1 gpd stress. The origin of the stress versus strain curve was subsequently located by means of a linear regression of the first ten stress/strain data pairs. By this method, the stress versus strain curves were computed.

Loading Efficiency.
(L.E.%) is defined as follows:

$$(L.E.\%) = \frac{(\text{yarn stress at } 0.5\%)}{(\text{filament stress at } 0.5\%)} \times 100$$

Description of the Preferred Embodiments

Example 1

In this example, a yarn made from poly(p-phenylene terephthalamide) was treated by the process of this invention and that yarn was compared with untreated yarn. The yarn was a commercially-available, 1140 denier, aramid fiber product sold by E. I. du Pont de Nemours & Co., Wilmington, DE, USA, under the trademark designation "Kevlar 149".

The single filament and yarn stress at 0.5% elongation for the untreated yarn were determined to be 5.8 and 4.7 grams per denier, respectively. The loading efficiency (L.E.%) for the untreated yarn (control) was 81%.

The yarn was processed using the machine schematically shown in the Figure. A tension of 3 kilograms force was applied to the yarn by adjusting the relative speeds of the pull roll assemblies. A metered quantity of a FEP fluorocarbon resin dispersion was applied to the yarn by means of a slotted tube. The yarn was then contacted with a vibrating surface driven by a piezoelectric transducer at 40,000 Hz. An additional amount of the same fluorocarbon resin dispersion was applied to the yarn and then the yarn was passed through a radiant oven in order to evaporate the water and fuse the resin. The residence time in the oven was 30 seconds. The oven set point temperature was 300 ※C. The final impregnated yarn was approximately 45% resin. The FEP fluorocarbon resin dispersion was a 55%, by weight, aqueous dispersion of polyfluoroethylenepropylene sold by E. I. du Pont de Nemours & Co., Wilmington, DE, USA, under the trademark designation "Teflon 120".

The stress at 0.5% elongation of the treated yarn is shown in Table 1. The L.E. of the yarn, based on the properties of the filaments from the starting yarn, was 100%.

Example 2

The same yarn was treated as in Example 1 except that the applied tension was 5 kg force, the oven residence time was 60 seconds, and the final product was 70% resin The L.E. was, again, 100% (See of Table 1).

TABLE 1

	Example 1	Example 2
Treating Conditions		
Tension,kgf	3.0	5.0
Oven Temperature, ※C	300	275-300
Time, seconds	30	60
% Resin	45	70
Stress at 0.5% strain		
mean, gpd	5.8	5.8
standard deviation	0.3	0.2
n	4	5
L.E., %	100	100

Example 3

The same yarn as was used in Example 1, was treated using a vinyl resin latex. The oven set point temperature was 290 ※C and the yarn residence time in the oven was 12 seconds. The final product was 20% resin. Three runs were made at different tension levels (1.6, 2.6 and 3.8 kg force). The L.E. of the product yarns were 86%, 93%, and 100%, respectively and show the influence of tension in this process (See Table 2). The vinyl resin latex was a 50 %, by weight, latex of ethylene/vinyl chloride copolymer sold by Air Products and Chemicals, Inc., Allentown, PA, USA, under the trademark designation "Airflex TL60".

TABLE 2

	Run 1	Run 2	Run 3
Treating Conditions			
Tension, kgf	1.6	2.8	3.6
Oven			
Temperature, ※C	290	290	300
Time, seconds	12	12	13
% Resin	20	20	20
Stress at 0.5% strain			
mean,gpd	5.0	5.4	5.8
standard deviation	0.2	0.1	0.1
n	5	5	7
L.E., %	86	93	100

Example 4

The same yarn as was used in Example 1 was treated using acrylic and nitrile rubber latices. The oven set point temperature was 500 ※C and the yarn residence time in the oven was 5.3 to 6.0 seconds. The final products were 20% to 27% resin. The L.E. of the product yarns (See Table 3) were 95% and 100%.

TABLE 3

	Nitrile Rubber*	Acrylic Rubber**
Treating Conditions		
Tension, kgf	2.3	4.0
Oven Temperature, ※C	500	500
Time, seconds	5.3	5.3
Resin, %	20	27
Stress at 0.5% strain		
mean, gpd	5.5	5.9
standard deviation	0.3	0.1
n	10	7
L.E., %	95	100

* Nitrile rubber latex sold by B. F. Goodrich under the trademark designation "Hycar 1578".

** Aqueous dispersion of:

1 weight part acrylic rubber latex sold by B. F. Goodrich under the trademark designation "Hycar 21260";

1 weight part kaolin;

1 weight part water; and

0.2 weight part surfactant.

Claims

1. A process for increasing the loading efficiency of a yarn comprising the steps of:
   a) applying alignment tension to the yarn;
   b) contacting the yarn with a lubricating liquid;
   c) exposing the yarn under tension and the lubricating liquid in contact with the yarn to mechanical energy;
   d) solidifying the lubricating liquid while maintaining the yarn under tension.

2. The process of claim 1 wherein the tension applied to the yarn is 1 to 5 grams per denier.

3. The process of claim 1 wherein the lubricating liquid is a solution of resin and solvent which is solidified in step (d) by evaporating the solvent.

4. The process of Claim 1 wherein the lubricating liquid is a latex of resin in dispersing liquid.

5. The process of Claim 1 wherein the energy is vibrating energy.

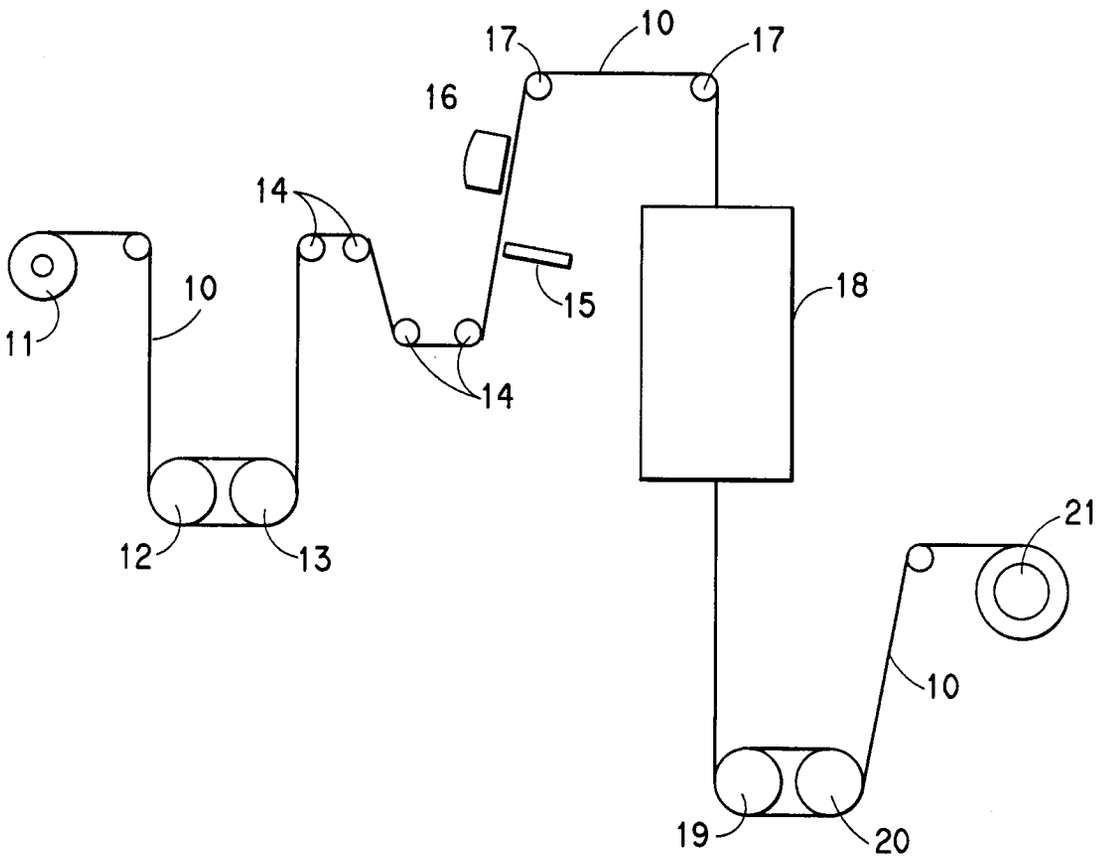
6. A process for increasing the loading efficiency of a fiber bundle comprising the steps of:
a) applying alignment tension to the fiber bundle;
b) contacting the fiber bundle with a lubricating liquid;
c) exposing the fiber bundle under tension and the lubricating liquid in contact with the fiber bundle to mechanical energy;
d) solidifying the lubricating liquid while maintaining the fiber bundle under tension.

7. The process of claim 6 wherein the tension applied to the fiber bundle is 1 to 5 grams per denier.

8. The process of claim 6 wherein the lubricating liquid is a solution of resin and solvent which is solidified in step (d) by evaporating the solvent.

9. The process of Claim 6 wherein the lubricating liquid is a latex of resin in dispersing liquid.

10. The process of Claim 6 wherein the energy is vibrating energy.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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 91115546.3

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP - A - 0 080 843 (WHITE) * Claims; page 2, line 24 - page 3, line 3 * --	1,6	D 06 M 10/10 D 06 B 13/00 D 02 J 1/20 D 06 M 15/70 D 06 M 23/10
A	US - A - 3 807 273 (KURTZ) * Claims * --	1,6	
A	US - A - 4 522 774 (DONNELLY) * Claims * --	1,6	
A	GB - A - 2 118 478 (RHOVYL) * Claims * --	1,6	
A	EP - A - 0 067 387 (BADISCHE CORPORATION) * Claims * --	1,6	
D,A	US - A - 3 648 452 (YOUNG) * Claims * ----	1,6	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 06 M
D 06 B
D 02 G
D 02 J
D 01 H
B 65 H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	02-12-1991	BECKER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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