Dec. 2, 1969 FROCESS FOR THE PRODUCTION OF POLYURETHANE ELASTIC FIBER HAVING LESS ADHESIVITY Filed Sept. 22, 1964 3,482,010

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3,482,010 PROCESS FOR THE PRODUCTION OF POLY-URETHANE ELASTIC FIBER HAVING LESS ADHESIVITY Takeshi Yasui and Kanji Matsubayashi, Kurashiki, Japan, assignors to Kurashiki Rayon Company Limited, Kurashiki, Japan, a corporation of Japan Filed Sept. 22, 1964, Ser. No. 398,260 Claims priority, application Japan, Sept. 30, 1963, 38/51,845 10 Int. Cl. D01f 7/06; D01d 5/06 U.S. Cl. 264-130 **3** Claims

ABSTRACT OF THE DISCLOSURE

A process for the preparation of less adhesive polyurethane elastic fiber by treating the polyurethane elastomer or spun polyurethane elastomer fiber with aliphatic hydrocarbon derivatives having from 4 to 50 carbon atoms. 20

This invention relates to a process for producing a polyurethane elastic fiber having less adhesivity which is characterized by either carrying out the spinning in a medium 25selected from an aliphatic hydrocarbon derivative containing from 4 to 50 carbon atoms such as carboxylic acid esters, amides, nitriles, alcohols, aldehydes, ketones, amines, urethanes, ureidos, halides, sulfonic acid esters, and mixture, emulsion or solution containing thereof; or 30 treating the fiber obtained by spinning the polyurethane elastomer by a conventional process with the abovementioned medium.

The object of the invention is to produce a polyurethane elastic fiber freed from adhesive property while facilitating 35 spinning or winding operation of mono- and multifilament yarn and further rendering the production of staple fiber thereof possible.

The polyurethane elastic fibers produced by prior process have very strong adhesivity that they have been almost 40 impossible to obtain a yarn smoothly or continuously from a winder bobbin. Independent of its production processes, such as wet-spinning, dry-spinning, semi-meltspinning, melt-spinning etc., the spun yarn unavoidably adheres not only between each filament but also between yarns, i.e., between single yarn bundle extruded from the 45 same nozzle when they are taken up by a bobbin, thus making such operations badly annoying.

A number of improvements have hitherto been tried in order to overcome these problems, but no pronounced 50 resolution has been proposed up to now. One of those trials involves the sprinkling or the spraying of talc or the like inorganic substances, but it causes troubles of scattering fine dust with only advantage of preventing the yarn from adhesion to give only doubled multifilament yarn, and no effective method has been accomplished for preventing the adhesion between monofilament yarns. If such problems have been solved further development of polyurethane elastic fibers will be expected according to their excellent and particular physical properties. For instance, the success in producing the polyurethane elastic staple 60 fiber of the size as little as a few or several deniers in commercial scale will contribute to a great extent in a field of spinning or textile industry due to its adaptability in mixed-spinning etc.

After numerous investigations, the inventors have ⁶⁵ found an effective method for preventing the troublesome adhesion not only of yarns as well as of each single filaments in an easy manner and accomplished the invention. 70

The invention will be explained more clearly by means of an example.

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A spinning solution was prepared by dissolving in 88 parts of dimethylformamide 12 parts of a polyurethane elastomer consisting of polyester having the molecular weight of 1,910 with both terminal hydroxyl groups of butandiol having intrinsic viscosity of 0.96 dl./g. in dimethylformamide at 30° C. with adipic acid, diphenylmethane diisocyanate and methylenedianiline. The solution was extruded into a coagulating bath through a nozzle having 100 holes each having a diameter of 0.08 mm. at a speed of 5 cc./min. The coagulating bath contained a homogeneous emulsion prepared by emulsifying 30 parts of sebacic acid amide into 70 parts of water by using a commercial nonionic-anionic dispersion agent, and further adding the emulsion thus prepared into 90 parts of water. The fiber thus spun was water-washed as usual and wound on a bobbin rotating at the speed of 10 m./min. The fiber thus wound on the bobbin could be not only taken out smoothly but also obtained as completely separated single yarn.

A cross section of the yarn thus taken up is diagrammatically illustrated in the drawings, of which

FIG. 1 is an enlarged cross sectional view of a polyurethane elastic fiber obtained by the process of the invention. and

FIG. 2 is the similar cross sectional view of the fiber without using the material according to the invention obtained by usual wet-spinning process. These figures indicate the state of the fiber whether each single filament is separated or adhered together.

Referring to FIG. 1 each single yarn is completely isolated from each other. For the sake of comparison, the same solution was spun in water or 1 to 70% aqueous solution of dimethylformamide and the construction of the cross section of the resulted fiber is shown in FIG. 2 which shows complete adhesion of each single yarn. In this case, the shape of the cross section of the fiber is liable to become flat due to the pressure imposed by a first guide or roller, and that causes trouble in subsequent weaving operation. Moreover, each yarn adheres firmly together when leaving the yarn wound on a bobbin at that state and thus makes unwinding operation extremely difficult or almost impossible.

As is evident from FIG. 1, the use of the medium of the invention in a coagulating liquid can only eliminate the adhesive troubles of yarns or filaments.

The invention is hereinabove explained by the effect upon the use of such medium in a coagulating bath in wet-spinning, but the same effect is obtainable by treating the fiber, which has been spun in a conventional process, in a second third or fourth bath containing such medium with satisfactory adhesion-preventing effect, especially in preventing the adhesion between yarns, compared to that obtained without using such medium.

The treatment can aso be carried out by either evenly $_{55}$ spraying, padding or coating the fiber with the medium upon melt, semi-melt or dry-spinning operation thereof, or by passing the fiber in a bath containing the medium, or by attaching the medium evenly on the fiber surface by using an application roll before winding. The amount of the medium to be attached to the fiber is usually 0.005-100% by weight based on the dry weight of a usual fiber, more preferably within 0.05-5%. Thus the inventors have found that it is effective for preventing the adhesion to attach to the spun yarn aliphatic acid amides, carboxylic acid esters, nitriles, alcohols, aldehydes, ketones, amines, urethanes, ureidos, halides and sulfonic acid esters, which compounds have from 4 to 50 carbon atoms. These substances are shown as follows.

The aliphatic carboxylic acid esters having 4-50 carbon atoms. These substances are shown as follows.

capronate, tetradecyl carpronate, pentadecyl capronate, heptyl enanthate, octyl enanthate, hexyl caprylate, heptyl 3,482,010

caprylate, octyl caprylate, amyl pelargonate, heptyl pelargonate, heptyl caprylate, heptyl undecanate, vinyl laurate, heptyl laurate, dodecyl laurate, octadecyl laurate, heptyl myristate, heptyl palmitrate, octyl palymitate, dodecyl palmitate, cetyl palmitate, octadecyl palmitate melissyl palmitate and monoalcohol esters such as methyl, ethyl, propyl, isoacyl, tert.-butyl, heptyl, octyl, hexadecyl, heptadecyl, octadecyl, oleyl, hexacosyl, allyl, cholester respectively of stearic acid, petroselinic acid, octadesenic acid, oleic acid, elaidic acid, ricinoleic acid respectively or tetracosyl lignocerate, melissyl myristate and the like mono alcohol ester or mono or diester of cebacic acid and the like mono or dicarboxylic acid ester of dibasic acid or glycerine ester of the above carboxylic acid or ester of carboxylic acids such as methyl ester of 2-oxystearic 15 acid: or

Aliphatic alcohols such as nonyl alcohol, capryl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, eicosanol, decanol-2, tridecanol-2, cetyl alcohol, melissyl alcohol, or 10-undecenol-1, 12-tri-20 decenol-1, oleil alcohol, elaidyl alcohol, linoleyl alcohol, linolenyl alcohol and the like unsaturated alcohols or octane diol, nonane diol, decane diol, eicosane diol, and the like diols; or

Aldehydes, such as butyl aldehyde, hexyl aldehyde, 25 octyl aldehyde, nonyl aldehyde, dodecyl aldehyde;

Ketones such as methyl butyl ketone, methyl hexyl ketone, ethyl butyl ketone, and dinonyl ketone; or

Aliphatic nitriles, such as capronitrile, enanthnitrile, caprylonitrile, peralgonnitrile, undecanenitrile, lauroni- 30 trile, tridecanenitrile, myristonitrile, pentadecanenitrile, palmitonitrile, margalonitrile, stearonitrile, oleonitrile; or

Aliphatic amides, such as hexyl amide, heptyl amide, octyl amide, nonyl amide, decyl amide, undecyl amide, lauryl amide, stearic acid amide, oleic acid amide, renolic 35 acid amide or acyl or their acyl sulfanyl amide, oxyethyl amide: or

Aliphatic amines, such as hexyl amine, heptyl amine, octyl amine, tridecyl amine, tetradecyl amine, pentadecyl amine, hexadecyl amine, dococyl amine or diamyl amine, 40 diheptyl amine, didecyl amine, didodecyl amine, dihexadecyl amine, dioctadecyl amine or tributyl amine, trioctyl amine, tridodecyl amine, trioctadecyl amine, or N-methyl-heptyl amine, N,N-dimethyl hexyl amine, N, N-diethyl palmityl amine, trilauryl amine, tristearyl $_{45}$ amine, N-tridecyl aniline, N-undecyl-N-methyl aniline, N-palmityl-N-methyl aniline, 1.8-diamino octane, 16-oxypalmityl amine and the like; or

Aliphatic sulfonic acid esters such as methyl octadecane sulfonate: or 50

Aliphatic ureidos or urethanes such as monoureido of said carboxylic acid such as lauric acid monoureido, tridecanoic acid monoureido, sylistic acid monoureido, palmitic acid monoureido, stearic acid monoureido, oleic acid monoureido, elaidic acid monoureido, linolenic acid 55 monoureido, ricinoleic acid monoureido, erucic acid monoureido or capryl alcohol, undecyl alcohol, lauryl alcohol, myristyl alcohol, pentadecyl alcohol, cetyl alcohol, stearyl alcohol, nonandecyl alcohol, 10-undecenol-1, 11-dodecenol-1, 12-tridecenol-C, oleyl alcohol, 60 eraidyl alcohol, decanediol, heptadecanediol, octadecanediol and the like urethanes of higher alcohol, a-naphthyl urethane or phenyl urethane or hexyl urethane, tetramethylene diurethane, hexamethylene diurethane of various kinds of alcohols such as methyl alcohol, ethyl 65 alcohol and octyl alcohol and higher urethanes, such as tetramethylene diurethane, hexamethylene diurethane;

Octadecyl chloride, chlorinated paraffin and the like halogenates may be used. They may contain aromatic nuclei such as benzene nuclei. 70

A solution or emulsion of above substances may also be employed. A mixture of two or more of above substances, i.e., the aliphatic, carboxylic acid esters, amides, nitriles, alcohols, aldehydes, ketones, amines, ureidos, urethanes, halides, sulfonic acid esters etc., such as natural 75 tween yarns but also between single filaments.

wax may be employed. A water-insoluble substance as above explained is particularly suitable for the invention. Above substances may be easily removed, if desired, from the fiber by washing or extraction with a surface active agent, aqueous solution, an organic solvent etc., however, the removal is not always necessary and the fiber can be used directly to the finishing or weaving processing.

The polyurethane elastic fiber according to the invention is so-called polyurethane elastomer or fiber consisting

mainly thereof and said polyurethane elastomer consists 10 of polymer glycol and polyisocyanate having usually a secondary transition point below 50° C., and a chain-growth agent such as diamine, diol, water etc. The formation of said polyurethane elastomer may be carried out either prior to spinning or during spinning, i.e., by so-called reactive spinning.

The polymer glycols having the secondary transition point below 50° C. to be used include polyesters, polyethers, polyetheresters, polyacetals etc. having the moleuclar weight of 500 to 5,000.

The invention will be explained further in detail by the following examples which are not limitative.

EXAMPLE 1

A spinning solution was prepared from a solution in 90 parts dimethylformamide of 10 parts of polyurethane polymer having intrinsic viscosity of 0.73 dl./g. at 30° C. in dimethylformamide, with the polymer being consisted of polyester having both terminal hydroxyl groups and the molecular weight of 2,660 prepared from ethylene glycol/propylene glycol (70/30 molar ratio) and adipic acid, phenylmethane diisocyanate and o-toluidine.

An emulsion was prepared separately by dispersing 35 parts cetyl palmitate in 40 parts water by using a nonionic surface active agent available on the market and added in the amount of 7% into water of coagulating bath for wet-spinning. The spinning solution was then spun in the coagulating bath in the manner same as in Example 1. The fiber thus obtained showed complete separation not only between yarns but between single filaments as well and it was cut into staple fibers.

EXAMPLE 2

Spinning solution was made of 80 parts of dimethylformamide in 20 parts polyurethane polymer consisting of polybutylene glycol having the molecular weight of 1,134, diphenylmethane diisocyanate and ethylene diamine and having intrinsic viscosity of 0.69 dl./g. at 30° C. in dimethylformamide. The spinning solution was extruded in a spinning tube maintained at 175° C. at a rate of 12 cc./min. through a spinneret having 20 holes each in diameter of 0.1 mm. The fiber was treated before it enters into a guide below the spinning tube with a solution of 20 parts stearic acid amide in 80 parts methanol by means of an application roll to contain 1% thereof, and taken up at a speed of 50 m/min. The fiber thus obtained showed substantial separation not only between yarns but also between single filaments.

EXAMPLE 3

Polyurethane polymer having intrinsic viscosity of 0.96 dl./g. at 30° C. in dimethylformamide was prepared from polycaprolactone of the molecular weight of 1,240, tolylene diisocyanate and bisphenol-A, and melt spun by extruding it at 190° C. through 10 holes spinneret each in diameter of 0.2 mm. at a spinning speed of 1 g./min. An aqueous emulsion of 20 parts paraffin wax in 30 parts water emulsified by using 10 parts of nonionic-anionic surface active agent available on the market was applied to the fiber under the spinning tube prior to entering into a guide with an application roll to attach 2% of the emulsion. The fiber wound showed the separation not only be-

EXAMPLE 4

Myristonitrile was used instead of paraffin wax in Example 4. The fiber taken up therefrom showed entirely no adhesion not only between yarns but between single filaments as well similarly to Example 3.

EXAMPLE 5

15 parts of polyurethane polymer having the intrinsic viscosity of 0.95 at 30° C. in dimethylformamide prepared from polybutylene formal, diphenyl methane diisocyanate 10 and ethylene glycol were dissolved uniformly in tetrahydrofuran at 50° C. by stirring for 4 hours, and the resulted solution was extruded into a spinning tube maintained at 100° C. through a nozzle of 20 holes each in diameter of 0.2 mm. An emulsion of 15 parts of lauryl 15 alcohol in 40 parts water emulsified by using 45 parts of an anionic surface active agent was sprayed on the fiber prior to entering into a guide under the spinning tube to attach 0.2% of the emulsion, then the fiber was taken up at a rate of 200 m./min. No adhesion took place between 20 yarns as well as single filaments.

EXAMPLE 6

A spinning solution was prepared from 88 parts of dimethylformamide dissolved in 12 parts of polyurethane ²⁵ polymer consisting of polypropylene glycol, diphenyl methane diisocyanate and tetramethyl methylene dianiline. An emulsion prepared by emulsifying 25 parts of cetyl alcohol phenyl urethane in 45 parts of water by using 30 parts of a nonionic-anionic surface active agent was added in an amount of 7% to a coagulating bath containing water and evenly dispersed therein. The above spinning solution was extruded in a bath at a speed of 3 cc./min. through a nozzle having 100 holes each in diameter of 0.08 mm. and taken up at a speed of 10 m./min. after waterwashing. The fiber thus obtained showed no adhesion between yarns and single filaments, and was cut to provide staple fibers.

What we claim is:

1. A process for the production of less adhesive polyurethane elastic fiber, which comprises treating conventionally spun polyurethane elastomer fiber with a compound selected from the group consisting of aliphatic ni6

triles having 4 to 50 carbon atoms and aliphatic urethanes having 4 to 50 carbon atoms.

2. A process according to claim 1, wherein said compound is an aliphatic nitrile having 4 to 50 carbon atoms.

3. A process according to claim 1, wherein said compound is an aliphatic urethane having 4 to 50 carbon atoms.

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