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PROCESS

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This invention relates to artificial fibers and fabrics and more particularly to the production of a new synthetic wool.

This invention has as an object the preparation of artificial, wool-like filaments, fibers, yarns, fabrics, etc. Another object is the preparation of wool-like products of good dyeing characteristics, high degree of crimp, good retentivity of crimp both wet and dry, and superior heat stability, strength, uniformity, and freedom from shrinkage and low moisture regain. A further object is the preparation of wool-like products having such desirable characteristics and at the same time unattacked by moths. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a filament of a synthetic linear superpolymer, preferably a superpolyamide, in a cold-drawn, swollen, relaxed condition, is exposed to a heated, indifferent fluid for a time sufficient to crimp the filament.

The filaments to which the crimping process of the present invention is applied and from which the new wool-like products are made, are derived from synthetic linear polymers of the type described in U. S. Patents 2,071,250—2,071,253 and 2,130,948. Of the synthetic fiber-forming polymers (i. e. superpolymers) described in these patents, the polyamides have been found most valuable in attaining the objects of the present invention. These polyamides are of two types, those derived from polymerizable monoamino-monocarboxylic acids or their amide-forming derivatives, and those derived from suitable diamine-dibasic acid mixtures or their equivalents.

Before considering the present invention in detail, it is advantageous to indicate the nature of the polymers used and to define certain terms and tests mentioned throughout the description. A property of the fiber-forming synthetic linear polymers which is especially utilized in this invention is their ability to be spun into filaments which can be cold drawn into oriented filaments. The term "cold drawing" is applied to the process of elongating the filaments by the application of stress while in the solid state, i. e. at a temperature below the melting point of the polymer. The cold drawn filaments show definite orientation along the fiber axis whereas the undrawn

filaments are substantially unoriented. The term "filament" as used herein will refer to both oriented and unoriented filaments or threads which are drawn from the polymers regardless of whether the filaments or threads are long (continuous) or short (staple), while the term "fiber" will refer more specifically to the oriented filaments (long or short). The fibers are in general more useful in the manufacture of yarns and fabrics than are the undrawn filaments. The term "crimped" filament or fiber will be used to indicate that the filament or fiber is not straight but possesses a crinkled, curled, spiral, helical, or serrated form.

Having explained the various terms to be used, the invention will now be described in detail and with particular reference to synthetic linear polyamides, since these polymers yield the most satisfactory artificial wool. The filaments used as starting material may be prepared from the polyamides by any method of spinning, e. g., by the melt, dry, or wet processes. Wool-like fibers can be prepared from filaments of almost any diameter, but filaments having deniers in the neighborhood of 0.5 to 20.0 are most useful. The invention can be applied to single filaments or to a plurality of filaments. In the latter case the filaments may be twisted into a thread although this affects the nature of the crimp in the final product. The filaments may be bright or dull and may contain other substances. If the filament is not cold drawn prior to contact with the heated fluid crimping takes place, but the product is not as finely crimped and the crimp has a tendency to be lost in further operations, e. g., carding. The filament is preferably drawn to at least 200%, i. e. to twice the original length, in order to withstand further operations. A draw of 300% or better however gives superior results.

The filaments are drawn and then swollen or swollen and then drawn. They are in a swollen, drawn condition at the beginning of their exposure to the heated indifferent liquid. The swelling may be done with any mild swelling agent, e. g. aniline, benzyl alcohol, but preferably with a neutral, hydroxylated, associated, low molecular weight, water soluble, readily volatile (i. e. below 100° C.) liquid which is a non-solvent for the polymer such as water, methanol, ethanol,

the propanols and mixtures thereof, i. e. water and lower alkanols or mixtures thereof.

The swollen drawn filament is then brought in contact in a relaxed condition with the heated, indifferent, fluid. By "indifferent fluid" is meant a liquid, gas or vapor which is chemically inert toward the polymer. Suitable liquids include hydrocarbons, chlorinated hydrocarbons, esters, polyhydric alcohols, metals such as mercury or molten Wood's metal, and ethers. The indifferent fluid when a liquid should be immiscible or not readily miscible with the swelling agent with which the filaments are wetted and should be readily removed from the filaments by evaporation or by washing. When water is used as the swelling agent, turbine oil and castor oil are among the most suitable liquid crimping baths. When methanol is used as the swelling agent, these two oils, tetrachloroethylene and Hi-flash naphtha are most suitable as liquid crimping baths. The indifferent fluid may be a superheated vapor. The particular vapor to be used is dependent likewise to a certain extent upon the nature of the swelling medium for the filaments. When water or methanol is used as the swelling medium, tetrachloroethylene or Hi-flash naphtha vapor baths are most satisfactory. Gases such as nitrogen, argon, carbon monoxide, etc. may also be used. In general liquids are preferred because of the readiness of heat transfer, etc.

The most satisfactory temperature for the indifferent fluid is dependent to some extent upon the nature of the same, the nature of the filaments being crimped, and the nature of the swelling agent. Temperatures between 90 and 250° C. may be employed. When liquid crimping baths are used, the best temperature is generally between 90° and 170° C. for polyhexamethylenedipamide filaments. If methanol is the swelling agent used with the same type of filaments, the best results with liquid crimping baths are always obtained below 150° C. and in most cases at 100-120° C. When water is used as the swelling agent with liquid crimping baths, again with polyhexamethylenedipamide filaments, temperatures above 150° C. are always required to obtain the best results. For any one crimping bath methanol as the swelling agent allows the use of the lowest temperature for optimum crimp; ethanol requires a somewhat higher bath temperature, and water still higher. When hot vapor baths are used as the crimping baths, the temperatures required are generally between 150° and 250° C. Here again the optimum temperature to be used depends upon the nature of the crimping bath, the nature of the swelling medium, the nature of the filaments being crimped, and the time for which the filaments are subjected to the action of the vapor bath. In using liquid crimping baths the liquid should be used at a temperature at least 20° C. and preferably at least 30° C. above the boiling point of the swelling agent used. It should therefore boil at least this increment above the boiling point of the swelling agent and preferably at an even higher temperature.

The crimp produced in the fibers is largely spiral in character, although some flat crimps (in one plane) are also present. The number of crimps per inch depends to some extent upon the fineness of the filaments, the nature of the polymer of which they are composed, the nature of the swelling agent, the nature of the crimping bath, the crimping bath temperature, etc. Un-

der proper conditions the number of crimps per inch may vary between 4 and 20 per inch. In general, the number of crimps per inch, their size, and their permanence can be made equal to or superior to those of natural wool.

The tensile strength of the filaments is affected by the process as shown by representative data in the table.

TABLE

Effect of crimping with hot liquid bath upon tenacity of filaments from hexamethylenedipamide polymer

Crimping bath	Swelling agent	Crimping bath temperature °C.	Tenacity, g. per filament
None—control.....	None.....		19.1
Turbine oil.....	95% methanol.....	110	16.6
Do.....	Water.....	160	10.1
Tetrachlorethylene.....	95% methanol.....	100	19.2
Do.....	do.....	110	18.4
Lauryl alcohol.....	do.....	130	16.7
Do.....	do.....	150	16.3
Do.....	Water.....	160	14.3
Castor oil.....	95% methanol.....	120	12.2
Do.....	Water.....	160	10.7
Hi-flash naphtha.....	95% methanol.....	100	18.3
Do.....	do.....	120	16.2

It will be noted that when suitable swelling agents and crimping baths are chosen the decrease in tenacity of the crimped filament is slight.

The retentivity of the crimp in fibers prepared by the process of this invention is equal to that of natural wool. No subsequent setting process is required to produce this permanence in the crimp. During the treatment of the filaments with the hot crimping bath they should be subjected to very slight or no tension in order that they may crimp freely and produce crimp of satisfactory fineness. The amount of tension which the filaments will tolerate while being subjected to the crimping baths is dependent, of course, to some extent upon the crimping conditions. Under conditions which will produce the best crimp, the filaments will tolerate a larger amount of tension and still produce satisfactory crimp than under conditions which are not as ideal. In general, the tension on the filaments during treatment with the crimping bath should be less than 0.5 mg./denier and preferably less than 0.2 mg./denier.

The polyamide wool fibers prepared by the above method are similar to those described in the copending applications, Miles S. N. 125,940, now U. S. 2,197,896, and Hardy and Miles S. N. 183,922. They have excellent elastic properties, show fiber orientation when examined by X-rays, are quite insensitive to moisture, have good resistance to solvents and chemical reagents, show little tendency to lose strength on aging, and have good dyeing characteristics. The polyamide wool can be dyed with the dyes used for wool; in general, the dyeings are more fast than in the case of natural wool. Unlike wool, the polyamides can be dyed with dyes which are used in an alkaline medium. Moreover, the polyamide wool fibers and fabrics have good heat insulating properties. In resiliency and crease retention the polyamide wool fibers and fabrics are similar to natural wool. The polyamide wool fibers of this invention generally have tenacities ranging from 3 to 4 grams per denier, values much greater than those of wool itself. An outstanding property of the polyamide wool as com-

pared with other known synthetic wools is that it retains its crimp when wet.

Having thus outlined the principles and purposes of the invention it is further illustrated in the following non-limitative examples.

EXAMPLE I

A sample of 600-denier, 30-filament dull polyhexamethylene adipamide yarn was drawn 313% and cut into 4.7-inch staple of approximately 5 denier per filament. The staple was swelled by immersing it in water for a few minutes. It was then pressed free of excess water and immersed in turbine oil at 160° C. until no more crimp formed in it. It was removed from the oil, washed free of oil, and allowed to dry. The resulting material was of an excellent, wool-like, spiral crimp equal in permanence to that of natural wool.

EXAMPLE II

A sample of 300-denier, 20-filament bright polyhexamethylene adipamide yarn was drawn 200%, and cut into 4-inch staple of approximately 5 denier per filament. This material was swelled by soaking it for a few minutes in 95% methanol-5% water. Excess swelling agent was pressed off and the material was immersed in turbine oil at 110° C., and held until no more crimp formed in the material. It was then removed, washed free of oil and allowed to dry. The material so prepared possessed an excellent wool-like crimp. It had a tenacity of 13.3 g./filament compared to 16.6 g./filament for untreated fiber.

EXAMPLE III

Example II above was repeated with the exception that the swollen polyhexamethylene adipamide filaments were immersed in a tetrachloroethylene bath at 100° C. instead of in turbine oil. In this case no washing of the filaments was required because the crimping bath medium was volatile and evaporated leaving the filament clean. The material produced was of an excellent wool-like crimp. Its tenacity was 14.8 g./filament and its retentivity of crimp by the test described in applications Serial Nos. 125,940 (filed February 15, 1937) and 183,922 (filed January 7, 1938) was 76%.

EXAMPLE IV

A sample of continuous 600-denier, 30-filament dull polyhexamethylene adipamide yarn was drawn 313%. It was swelled by immersion in 100% methanol for a few minutes and then immersed in a tetrachloroethylene liquid bath at 110° C. until no more crimp formed in the filaments. When it was removed and the tetrachloroethylene allowed to evaporate, the material was found to be a clean, finely crimped, wool-like substance. Its tenacity was 18.2 g./filament as compared to 19.1 g./filament for the untreated filaments. Its crimp retentivity was 89%.

EXAMPLE V

A sample of 300-denier, 20-filament bright polyhexamethylene adipamide yarn was drawn 200% and cut into 4-inch staple of approximately 5 denier per filament. It was swelled by immersing it for a few minutes in 95% ethanol-5% water. The excess swelling agent was pressed off and the material immersed in a bath of liquid Hi-flash naphtha at 110° C. until no more crimp formed in the filaments.

The Hi-flash naphtha evaporated, leaving the filaments clean. The material had a very good, wool-like, spiral crimp which was permanent in boiling water.

EXAMPLE VI

A sample of continuous 440-denier, 30-filament bright polydecamethylene adipamide yarn was drawn 250% and swelled by wetting it with water. It was then passed continuously between squeeze rolls which eliminated the excess of swelling agent and onto an endless screen belt. While on the belt it was passed under a spray of mineral oil at 150° C., which caused it to crimp spontaneously into a very good, helical, wool-like crimp.

EXAMPLE VII

A sample of 600-denier, 30-filament dull polyhexamethylene adipamide yarn was drawn 313% and cut into 4.7-inch staple of approximately 5 denier per filament. It was swelled in 95% methanol and immersed in Hi-flash naphtha vapors at 150° C. where it crimped spontaneously into a very good, wool-like material of 19.0 g./filament tenacity as compared to 19.1 g./filament for the untreated fibers. The crimp was permanent to boiling water and to all standard textile processing.

EXAMPLE VIII

A sample of continuous 300-denier, 20-filament bright polyhexamethylene adipamide yarn was drawn 200%, swelled with water, passed continuously through squeeze rolls to remove the excess of water, and then led continuously through a chamber containing di-n-butyl ether vapors at 250° C. This treatment produced, spontaneously, a good crimp in the filaments.

Although this invention has been described with particular reference to polyamides, it is applicable broadly to fiber-forming synthetic linear polymers. To obtain products useful in the textile field, however, the melting point of the polymers should be above 110° C. so that they can be washed with boiling water. The most useful products are obtained from polymers having a melting point above 220° C. As examples of fiber-forming synthetic polymers might be mentioned polyesters, polyacetals, polyethers, polyester-polyamides, and other co-polymers. The preparation of polymers of this class is described in detail in the patents referred to above.

The fiber-forming polyamides or superpolyamides described in the above mentioned patents are the most useful of the linear condensation polymers for conversion into the wool-like products of this invention. Of these polyamides a valuable class for use in the preparation of wool-like fibers comprises those derived from diamines of formula $\text{NH}_2\text{CH}_2\text{RCH}_2\text{NH}_2$ and dicarboxylic acids of formula $\text{HOOCCH}_2\text{R}'\text{CH}_2\text{COOH}$ or their amide-forming derivatives, in which R and R' are divalent hydrocarbon radicals free from olefinic and acetylenic unsaturation and in which R has a chain length of at least two carbon atoms. An especially valuable group of polyamides within this class are those in which R is $(\text{CH}_2)_x$ and R' is $(\text{CH}_2)_y$ wherein x and y are integers and x is at least two. As examples of polyamides which fall within one or both of these groups might be mentioned polytetramethylene adipamide, polytetramethylene sebacamide, poly-

pentamethylene sebacamide, polyhexamethylene adipamide, polyhexamethylene β -methyl-adipamide, polyhexamethylene sebacamide, polyoctamethylene adipamide, polydecamethylene adipamide, polydecamethylene p-phenylene diacetamide, and poly-p-xylylene sebacamide. This invention is also applicable to fiber-forming polyamides derived from polymerizable monoaminomonocarboxylic acids or their amide-forming derivatives, including the lactams, such as 6-aminocaproic acid, caprolactam, 9-aminononanoic acid, and 11-aminoundecanoic acid. It is also within the scope of this invention to prepare wool-like fibers from mixtures of preformed polyamides and from interpolymers or copolymers derived from a mixture of polyamide-forming reactants, e. g., a mixture of two diamines with one or more dicarboxylic acids, or a mixture of a diamine, a dicarboxylic acid, and an amino acid.

It is evident from the discussion and examples that a considerable degree of latitude is permitted in the mode in which the invention may be practiced. The process can be carried out as a batch process or as a continuous process. One method of carrying out the process continuously consists of cold drawing the filaments continuously as they come from the spinning cell, passing them continuously either after they have been cut into staple or not, as may be preferable, into a bath of the swelling medium used, removing them continuously from this bath by means of an endless belt which carries them between squeeze rolls to eliminate the excess of the swelling medium, and passing them continuously through a spray of the hot crimping liquid or a chamber containing the hot vapors of a vapor quenching bath, and finally dumping them continuously into a washing machine if necessary or into a baling machine if washing is not required. In this way the transformation of the polyamide polymer into a final crimped fiber is made a continuous process.

While the process of this invention is applicable to filaments of synthetic linear condensation polymers generally, it will be apparent that the optimum operating conditions will vary somewhat with different filaments depending upon their properties and the manner in which they were prepared and treated. The optimum conditions for each polymer can be worked out experimentally, the essential features of the process being those outlined above.

Liquid crimping baths which may be used include mineral oils of all types, castor oil, tetrachloroethylene, glycerol, triacetin, dimethylene, pentaerythrite, lauryl alcohol, oleic acid, sebacic acid, actyl alcohol, butyl carbitol, triethanolamine, Hi-flash naphtha, Turkey red oil, etc. Vapor crimping baths which are suitable include Hi-flash naphtha, toluene, n-amyl alcohol, di-n-butyl ether, tetrachloroethylene, methylhexyl ketone, and other similar materials. In general, the most suitable liquid and vapor crimping baths are those which are not miscible with the liquid which has been used as the swelling agent for the polyamide filaments.

As has been previously stated, the crimping bath temperatures which are suitable are dependent to a certain extent upon the nature of the swelling agent used for the polyamide filaments, the nature of the filaments themselves, and upon the nature of the crimping bath. With liquid crimping baths temperatures between 90° and 170° C. are most suitable, while with vapor

crimping baths temperatures between 150 and 250° C. are most satisfactory.

The diameter of filaments which can be used in the practice of this invention may vary widely and includes, in fact, any filament of a size suitable for ordinary textile usage. Filament deniers of 1 to 20 are of widest usefulness. As the diameter of the filament increases the crimp produced by the process of this invention tends to become correspondingly coarser. The wool-like fibers may contain delusterants. The delusterant may be inorganic or organic. It is also possible to carry out the process of this invention using polyamide filaments containing other types of materials, for example, plasticizers, resins, oils, pigments, cellulose derivatives, dyes, etc. When staple fibers are used in the process they may be of widely varying lengths, although lengths of $\frac{1}{2}$ inch to 10 inches are most useful. The process, however, is equally suitable for staple or continuous filaments.

The length of time for which the filaments must be treated with the liquid or vapor crimping bath is dependent upon the nature, diameter, and bulk of the filaments, the amount and nature of the swelling agent which they contain, the nature and temperature of the crimping bath, etc., and must be worked out for any set of these conditions. However, the crimp ordinarily appears rapidly (within a fraction of one second to several seconds) and increases to a maximum at which it remains regardless of the additional time for which the filaments may be subjected to the crimping conditions. Increasing the time, therefore, beyond this point of maximum crimp does no harm except to gradually decrease the fiber tenacity.

The wool-like fibers obtained in accordance with the process of Examples IV, VI, and VIII are continuous. Yarns and fabrics can be readily formed from these fibers. By using the process described in the other examples, staple crimped fibers are obtained and these staple fibers can be formed into yarns and fabrics by standard textile procedure for staple fibers. Fabrics prepared in this way have a more fuzzy appearance and feel than those prepared from the continuous fibers. If desired, other types of staple fibers can be admixed therewith, e. g., cotton, wool, linen, rayon, or silk staple.

This invention provides a convenient and economical method for the preparation of artificial wool-like fibers. In comparison with previously proposed methods of crimping superpolymer and particularly superpolyamide filaments the process is simple and economical, especially because it can be applied to fibers in bulk, particularly to staple filaments which can be prepared cheaply. It requires no unusual or intricate equipment. The swelling agents and crimping baths used may be of cheap materials or may be economically recovered.

The artificial wool-like fibers prepared by the method of this invention are fully equal to natural wool in crimp retention, heat insulating properties, and dyeing characteristics, and are superior to wool in strength, heat stability, uniformity of characteristics, freedom from shrinkage, and low moisture regain. Unlike wool, they are not attacked by moths. The synthetic wool-like products of this invention are quite stable at 150° C., whereas natural wool decomposes quite rapidly at this temperature with liberation of ammonia, hydrogen sulfide and carbon bisulfide. The process by which the artificial

fibers of this invention are made is of such a character that modifying agents, for example, delusterants and plasticizers, can be readily incorporated therewith. The fibers of this invention can be easily formed into yarns of the worsted type. These yarns can be knitted or woven into fabrics, rugs, and the like. If desired, other types of fibers and yarns, for example viscose rayon, acetate rayon, cotton, silk, and wool, can be used in conjunction with the crimped polyamide fibers in the preparation of fabrics. Ordinary, i. e., straight, polyamide fibers and yarns can also be used with the crimped polyamide products. In contrast to other known synthetic wools, the product of this invention retains its crimp when wet. A bundle of crimped polyamide fibers when wet and squeezed will spring back instead of remaining packed as will crinkled or crimped cotton, viscose rayon, cellulose acetate rayon, or any other known wool substitute. This is also true of the corresponding fabrics.

These wool-like products are similar to those prepared by the process of Hardy and Miles S. N. 183,922, filed January 7, 1938, and may be used for the same purposes and in the same ways.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Process for crimping a filament of synthetic linear superpolymer which includes the steps of treating the filament with a swelling agent and exposing the filament in its oriented state while swollen with said agent and in a substantially relaxed condition to an indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said swelling agent.

2. Process for crimping a filament of synthetic linear superpolyamide which includes the steps of treating the filament with a swelling agent and exposing the filament in its oriented state while swollen with said agent and in a substantially relaxed condition to an indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said swelling agent.

3. Process for making a wool-like filament which comprises impregnating an oriented filament of a synthetic linear superpolyamide with a neutral, hydroxylated, low molecular weight, water soluble, volatile non-solvent liquid, and exposing the so impregnated filament, while it is in a substantially relaxed condition, to contact with an indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said impregnating liquid.

4. Process for making a wool-like filament which comprises impregnating an oriented fila-

ment of a synthetic linear superpolyamide with an alkanol having less than four carbon atoms and exposing the so impregnated filament, in a substantially relaxed condition, to contact with an indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said impregnating liquid.

5. Process set forth in claim 1 in which said heated indifferent liquid is substantially immiscible with said swelling agent.

6. Process for making a wool-like filament which comprises impregnating an oriented filament of a synthetic linear superpolyamide with methanol, and exposing the so impregnated filament, while it is in a substantially relaxed condition, to contact with a heated indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said impregnating liquid.

7. Process for making a wool-like filament which comprises impregnating an oriented filament of a synthetic linear superpolyamide with water, and exposing the so impregnated filament, while it is in a substantially relaxed condition, to contact with a heated indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said impregnating liquid.

8. The process of claim 2 in which said superpolyamide is polyhexamethylene adipamide.

9. The process of claim 6 in which the temperature of the indifferent liquid is between 100 and 150° C.

10. The process of claim 6 in which said superpolyamide is polyhexamethylene adipamide, said indifferent liquid is tetrachloroethylene, and said temperature is between 100 and 120° C.

11. The process of claim 7 in which said temperature is about 160° C.

12. The process of claim 7 in which said superpolyamide is polyhexamethylene adipamide, said indifferent liquid is a mineral oil, and said temperature is about 160° C.

13. Process for crimping staple fiber of synthetic linear superpolymer which includes the steps of treating the staple fiber with a swelling agent and exposing the fiber in its oriented state while swollen with said agent and in a substantially relaxed condition to an indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said swelling agent.

14. Process for crimping staple fiber of synthetic linear superpolyamide which includes the steps of treating the staple fiber with a swelling agent and exposing the fiber in its oriented state while swollen with said agent and in a substantially relaxed condition to an indifferent liquid whose temperature is at least about 20° C. above the boiling point of the said swelling agent.

15. The process of claim 14 in which the said superpolyamide is polyhexamethylene adipamide.

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