United States Patent

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Osaka, Japan
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[33] Japan
[31] 43/18823, 43/77274 and 44/9535

[54] **HEAT-TREATING PROCESS OF THERMOPLASTIC FIBERS**
4 Claims, 14 Drawing Figs.

[52] **U.S. Cl.** **28/72.1**
[51] **Int. Cl.** **D02q 1/00**
[50] **Field of Search** 28/1.2, 72, 72.1, 76

[56] **References Cited**
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Primary Examiner—Louis K. Rimrodt
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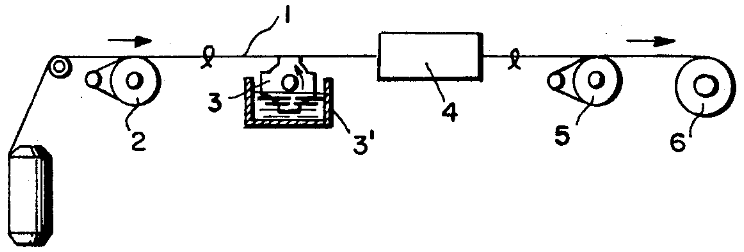
ABSTRACT: This invention relates to a heat-treating process of thermoplastic fibers. According to the invention, prior to passing the thermoplastic fibers continuously through a high-temperature atmosphere maintained above the melting point of the fibers at a high speed, a liquid having a relatively large latent heat of vaporization or specific heat which is inert to the fibers is nonuniformly applied to the fiber surfaces. Thus pretreated fibers exhibit, after the aforesaid heat treatment, nonuniform dyeability (this property is expressed as "different dyeability" in the specification) and/or nonuniformly crimped state. Also conjugate fibers having nonuniform latent crimpability can be prepared in accordance with the subject process.



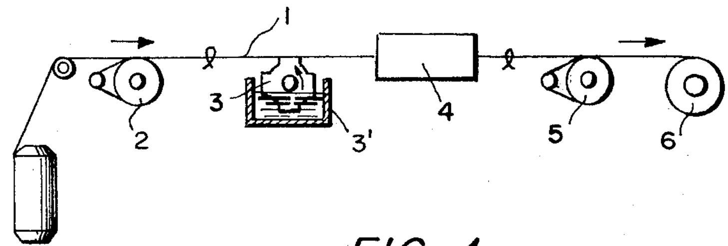


FIG. 1

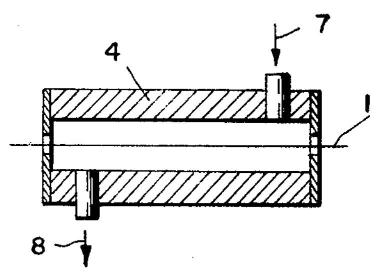


FIG. 2

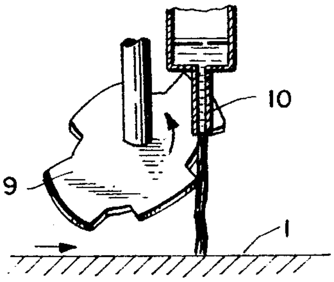


FIG. 3

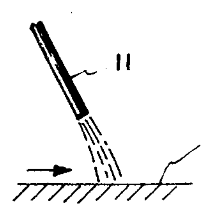


FIG. 4

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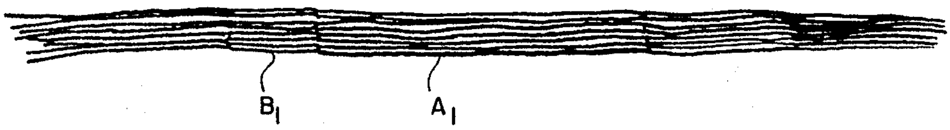

FIG. 5

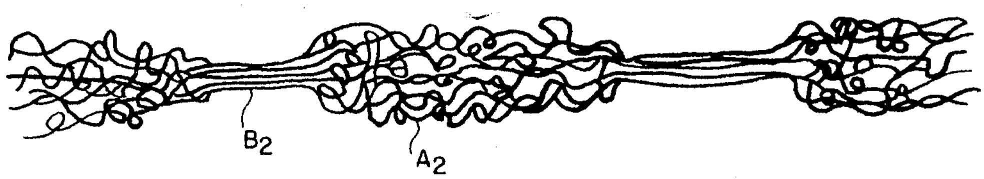

FIG. 6

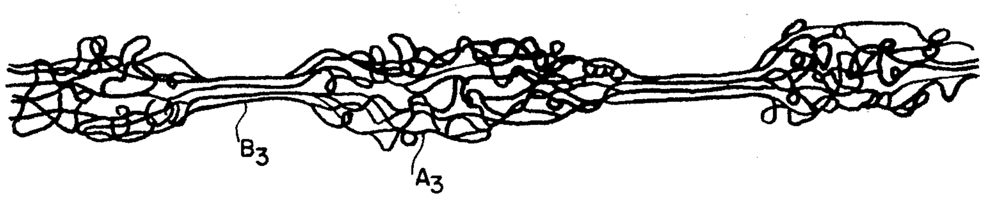

FIG. 7

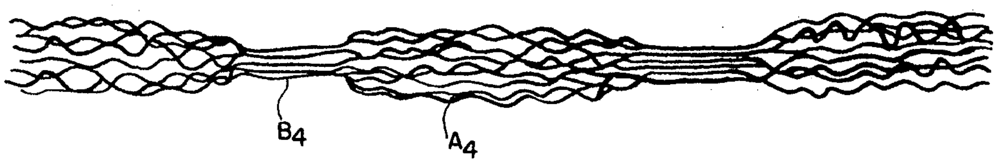

FIG. 8

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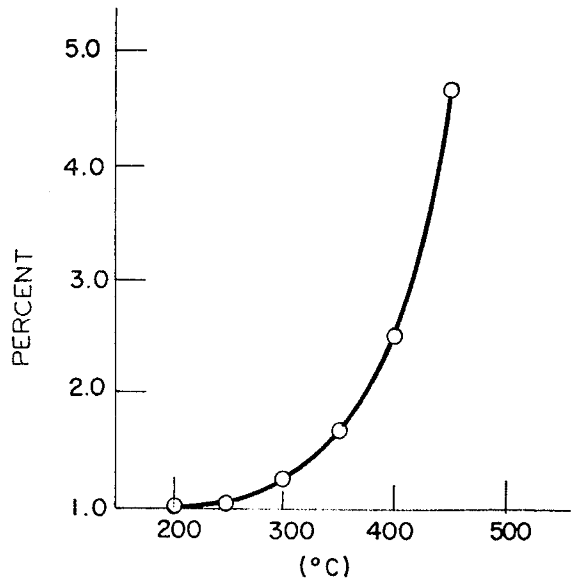

FIG. 9

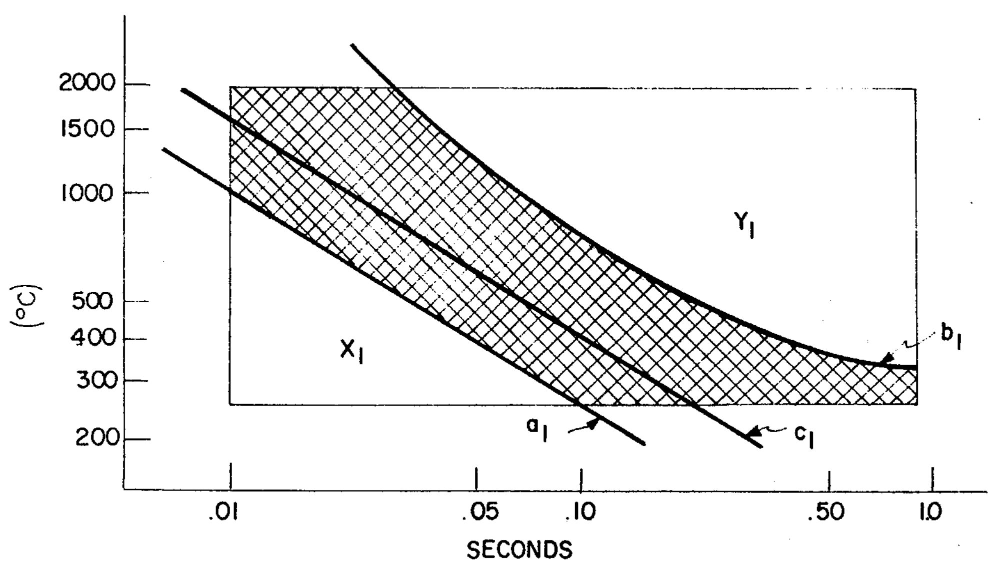

FIG. 10

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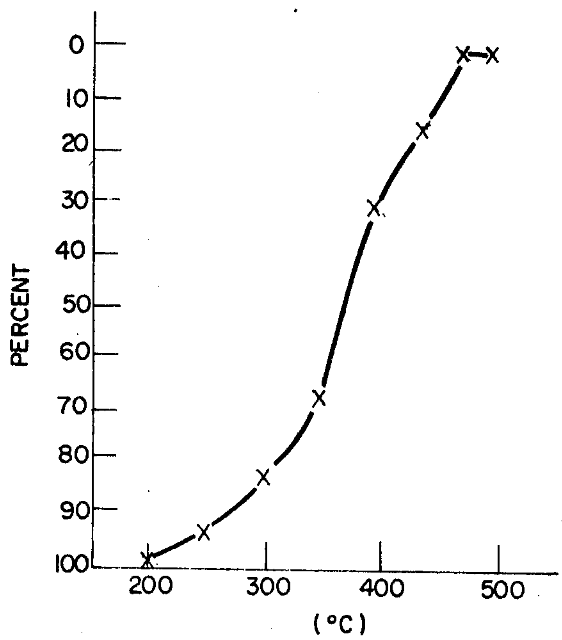

FIG. 11

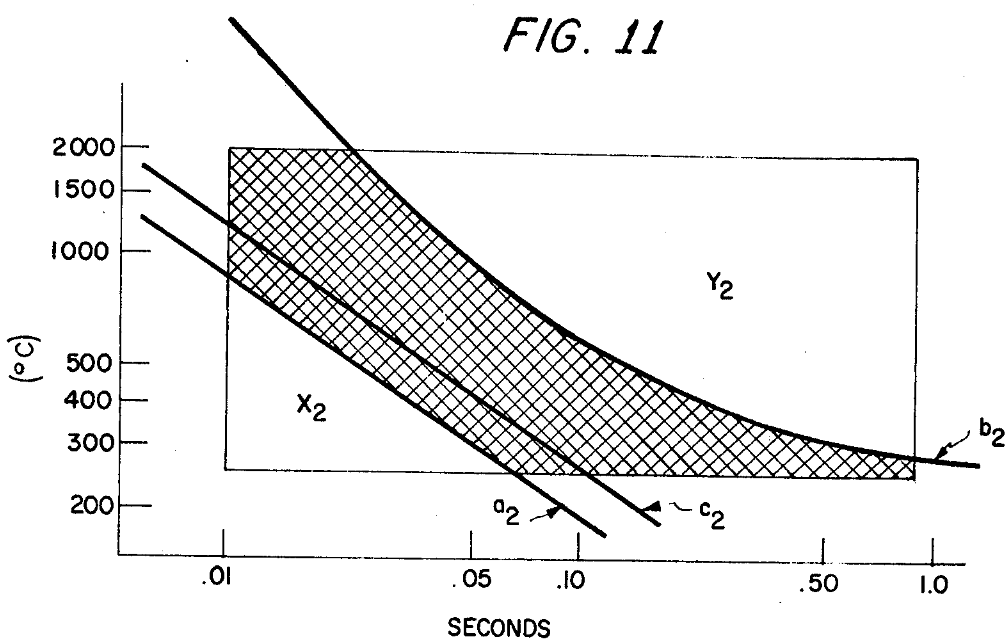

FIG. 12

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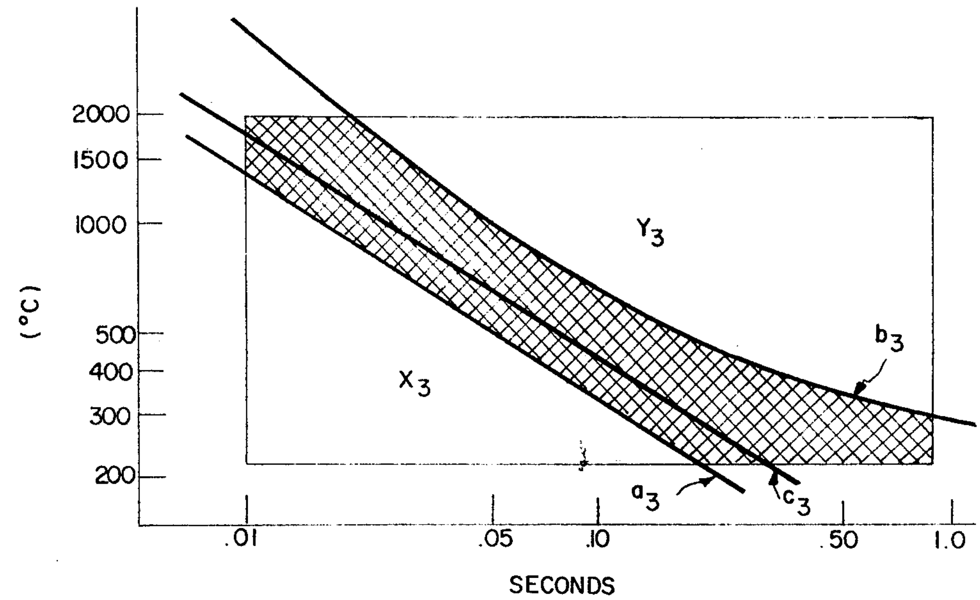

FIG. 13

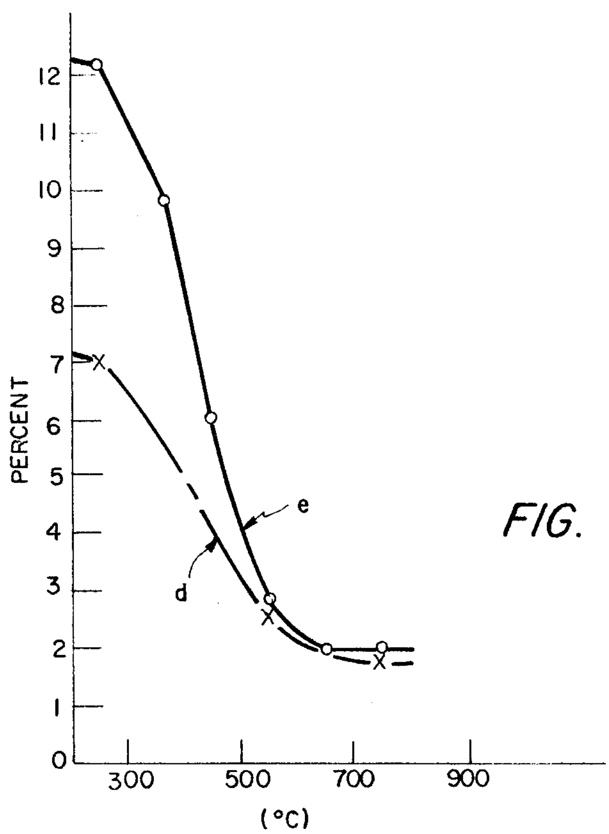

FIG. 14

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HEAT-TREATING PROCESS OF THERMOPLASTIC FIBERS

As the result of our initial researches on methods for imparting different dyeability, to polyester fibers, the following two facts are discovered: that the dyeability of polyester fibers can be remarkably improved by heat-treating the fibers at temperatures higher than the melting point thereof, while retaining their mechanical properties at practically satisfactory level; and that the dyeability of the fibers is greatly improved in proportion to the rising of the temperature in the above-mentioned high-temperature treatment. Such remarkable dyeability improvement cannot be achieved at temperatures below the melting point of the fibers. It was also found that if fibers are treated with a liquid having a large latent heat of vaporization or specific heat prior to the above-mentioned high-temperature treatment and the said high-temperature treatment of fibers to which such liquid has been sufficiently applied is performed for a period of time within a critical range where the above high-temperature treatment may be allowed with respect to non-liquid-applied fibers, the dyeability of the treated fibers is not affected by such treatment. We tried to make a skillful use of the above phenomena to provide various fancy fibers. That is, we nonuniformly applied onto the fiber surfaces an inert liquid such as water, before said heat treatment. The liquid should never have any dissolving ability of the fibers to be treated, under the treating conditions. Water is the optimum liquid, for both handling and economical reasons. The term "nonuniform application" denotes the state wherein such a liquid is applied onto the entire surfaces of the thermoplastic fibers to be treated, with the pickup varying along the direction of axis and/or the circumferential direction of the fibers; or the state wherein the liquid is applied intermittently onto the fiber surfaces along the axial direction, with uniform or varying pickup. If expressed in more concrete manner, in a typical example, liquid-applied portions (A) and non-liquid-applied portions (B) are formed on the fiber surface. Manner of forming the portions (A) and (B) is not critical. For example, the portions (A) and (B) may be arranged alternately at regular intervals along the longitudinal direction of the fibers. Or, the portions (B) may be present at random in the portion (A). Our expected result of heat treating the so pretreated fibers at the already described high temperatures was that, while the portions (B) would exhibit high dyeability since they directly contact the high-temperature atmosphere, the portions (A) would be shielded from the action of heat by the liquid covering the same portions. Furthermore, since the heating time to be employed is extremely short, the fibers themselves are scarcely heated during the heat treatment, if they are covered by the liquid. Thus the quantity of heat applied to the portions (A) would be very low, while that applied to the portions (B) would be high. We reasoned that consequently the dyeability of the portions (A) would be low, while that of the portions (B) would be high.

With the foregoing expectations we practiced the described pretreatment and heat treatment of thermoplastic fibers, and obtained fibers showing distinctly different dyeabilities, which proved correctness of our concept. The dye pickup was less at the portions (A), and much more at the portions (B).

Then we attempted to determine the correlations of the inert liquid application with crimp retention of already crimped fibers, and with latent crimpability of conjugate fibers. Thus we applied an inert liquid intermittently to crimped fibers and conjugate fibers having latent crimpability, and then subjected them to the high-temperature heat treatment, to find that the existing crimps and latent crimpability are retained intact at the portions (A), but those properties in the portions (B) deteriorated or vanished. Particularly when the fibers having latent crimpability are treated in boiling water or steam in relaxed state after the heat treatment, intermittent crimps are formed along the direction of fiber axis.

As has been described in the foregoing, the present invention succeeded in the preparation of fibers having nonuniform dyeability and/or nonuniform crimping property, by the combined steps of nonuniformly applying a liquid having a relatively large latent heat of vaporization or specific heat, such as water, onto the surfaces of thermoplastic, synthetic fibers, and heat-treating the same fibers at the specified high temperatures for an extremely short time.

The invention also succeeded in the preparation of fibers having nonuniform latent crimpability, by applying the same process to conjugate fibers having latent crimpability.

Referring now to the drawings:

FIG. 1 is a schematic view showing one example of the apparatus suitable for practicing the subject process,

FIG. 2 is a schematic view showing one example of the apparatus for heating the fibers in accordance with the invention,

FIGS. 3 and **4** are the schematic views showing modifications of the apparatus for applying the liquid onto the fibers,

FIG. 5 is an enlarged side view of one example of dyed polyester fibers having different dyeability, which has been prepared in accordance with the invention,

FIG. 6 is an enlarged side view nonuniformly crimped fibers obtained by applying the process of this invention to already crimped, thermoplastic fibers,

FIG. 7 is an enlarged side view of dyed fibers exhibiting both nonuniform crimpability and different dyeability, which are obtained by applying the subject process to already crimped polyester fibers,

FIG. 8 is an enlarged side view of the fibers obtained by applying the subject process to conjugate fibers having latent crimpability and thereafter treating them in boiling water in relaxed state,

FIG. 9 is a graph showing the relationship between the heat-treating temperature and relative dyeability of polyester-type fibers,

FIG. 10 is a graph showing the empirically obtained correlation of heat-treating temperature and time of polyester-type fibers,

FIG. 11 is a graph showing the empirically obtained correlation of heat-treating temperature and residual crimp ratio demonstrated by crimped polyethylene terephthalate fibers,

FIG. 12 is a graph showing the empirically obtained correlation of heat-treating temperature and time of crimped polyethylene terephthalate fibers,

FIG. 13 is a graph showing the empirically obtained correlation of heat-treating temperature and time of crimped poly-ϵ-capramide fibers,

FIG. 14 is a graph showing the correlation of the heat-treating temperature with shrinkages of polyethylene terephthalate fibers and polyethylene terephthalate-isophthalate fiber in boiling water.

An embodiment of the invention will be explained hereinbelow, referring to FIG. 1. In the drawing, yarn **1** is fed from the feed rollers **2**, passed through the heating device **4** via a liquid supply roller **3**, and withdrawn by winder **6** via takeup rollers **5**.

In the embodiment, the liquid can be applied to the yarn intermittently along the axial direction thereof, by the use of roller **3** provided with regular or irregular teeth, at least the teeth portion thereof being immersed in the liquid stored in the bath **3'**. Thus, while the roller **3** is rotated in a fixed direction, the yarn **1** is advanced, contacting with the upper points of the teeth. The liquid pickup of the yarn varies depending on such factors as advance rate of the yarn, rotation speed of the roller and shape and number of teeth. It is also possible to employ plural liquid supply rollers to effect various liquid application patterns along the axial direction of yarn or fiber. The liquid application device is obviously not limited to the roller **3** employed in the embodiment of FIG. **1**, but any suitable device may be used so far as the described purpose of liquid application is accomplished. For example, the liquid may be allowed to fall down in fine streams on the running yarn **1** from a small-diameter tube **10**, the liquid flow being intermittently interrupted by a sector **9** which is rotating in the direction of arrow, as illustrated in FIG. 3. With that device also the nonuniform application of the liquid along the axial direction of yarn can be achieved. Similarly to the case of roller 3, plural sectors 9 may be used to produce various nonuniform liquid application patterns. Again, as shown in FIG. 4, a spray 11 may be used in place of the roller 3. In that case, various nonuniform liquid application patterns along the axial direction of yarn can be obtained likewise, by continuous or intermittent spraying of the liquid.

The heat treatment of thus pretreated yarn is affected in the heating device 4. As the heating medium, a gaseous substance is most preferred. Thus, a gaseous substance of the desired high temperature, such as air, nitrogen or steam, etc., is filled in a cylindrical room 4 as illustrated in FIG. 2. In order to maintain a constant heat-treating temperature, the gas of predetermined temperature may be supplied from the entrance 7 at one end of the cylindrical room 4, and the said gas may be discharged through an exit 8 at the opposite end. Similar heating effect can be obtained by means other than the device of FIG. 1, such as irradiation of running yarn with infrared rays, or installation of electrothermic wire in the surrounding walls of a cylindrical heating chamber.

The temperature of heat treatment in accordance with the present invention is not lower than the melting point of the thermoplastic synthetic fibers to be treated. The "heat-treating temperature" refers to the temperature of the heating medium in the vicinity of the fiber surfaces under treatment in the heating zone, which can be determined by conventional means, with a thermocouple, for example.

The effect of such heat treatment depends mainly on the temperature employed and the duration time. The higher is the temperature, the less is the time required for achieving the desired effect. The time can be determined from velocity of yarn passing through the heating zone and length of the heating zone. The time should be instantaneous, in the order of one-hundredth to one-tenth of a second. Too short a heat-treating time, however, fails to achieve the satisfactory result. Whereas, excessively long treating time will cause complete melting of the fibers, rendering the process inoperable.

Generally speaking, it is necessary that the treating temperature is within the range from melting point of the treated fibers to 2,000° C., and the time is in the range from 0.01—0.9 second. When the latter is longer than 0.9 second, the portions of the treated fibers not shielded by the inert liquid tend to be molten, and shielding effect of the liquid at the other portions is reduced or nullified, since the temperature is so high as not lower than, the melting point of the fibers. Thus, appropriate heat-treating time is not longer than 0.9 second, in accordance with the basic concept of the invention to instantaneously subject the fibers remarkably nonuniform properties by the high-temperature treatment, and also from the standpoint of economical operation.

Obviously, the shorter is the treating time, the higher becomes the efficiency of the subject process. Whereas, in accordance with the invention it is required to apply an inert liquid to the fibers in advance of the heat treatment, with controlled nonuniformity, which must be done at a high speed, keeping up with the yarn velocity in the heating zone. Thus, from the practical operability for smoothly imparting optionally controlled liquid application pattern, it is recommended to allow the heat-treating time of at least 0.01 **second**.

When the temperature exceeds 2,000° C., difficulties for maintaining stable operation increase. Various problems must be solved as to heating element, refractory material and heat-insulative material, etc., before provision of an apparatus for heating at above 2,000° C. with stability. At such high temperatures, simple and effective heat insulation is difficult. From the foregoing practical reasons, heat-treating temperatures not exceeding 2,000° C. are preferred.

In practicing the subject process, thereof, the heat-treating temperature and time should be selected from the above-specified ranges, regardless the type or size of the fibers to be treated. Appropriate combination of the temperature and time varies somewhat, depending on the desired product as follows.

1. Preparation of differently dyeable fibers

An example of polyester fibers to which the subject process has been applied is shown in FIG. 5. The specimen is that which is dyed after the heat treatment. In that embodiment, particularly the imparting of different dyeability is aimed at. In FIG. 5, the portions A, Showing low dyeability are those which were applied with the liquid, and consequently not or little heated. Whereas, the portions B, showing high dyeability were not applied with the liquid and therefore, heated directly. Such different dyeability in accordance with the invention can be conveniently imparted to such polyester fibers from homo- or co-polyesters in which all or predominant portion of acid component is terephthalic acid, and all or predominant portion of glycol component is ethylene glycol; and fibers from the blends containing such homo- or co-polyesters as the main components. Such fibers are prepared by conventional spinning and subsequent drawing with optional heat treatment. Multifilamentary yarns are particularly preferred. The polyester fibers treated in accordance with the subject invention exhibit distinct different dyeability, and simultaneously retain mechanical properties satisfactory for various practical usages.

The correlation of heat-treating temperature with relative dyeability is as illustrated in FIG. 9. The data of FIG. 9 are provided by a polyethylene terephthalate yarn heated in high-temperature air for 0.15 second, under a tension of 0.08 g./d. It can be clearly understood from the graph that the satisfactory dyeability is obtained in the heated air of temperatures above the melting point of the sample yarn (260° C.). The dyeability remarkably improves with the temperature rise above the melting point. That tendency is invariably very distinct. Referring back to FIG. 5, the portions A_1 applied with the liquid in advance are little influenced by the heat during the heat treatment, and consequently exhibit little heat treatment effect, that is, low dyeability. In distinct contrast, the portions B_1 are directly heated and showed high heat treatment effect, that is, high dyeability. Thus, when so treated yarn is dyed, distinct difference in color shades is observed between the portions A_1 and B_1.

In the foregoing, the term "relative dyeability" refers to the values determined as follows. The sample fibers are dyed in a boiling dye bath of Dispersol Fast Scarlet B, 4 percent o.w.f. for 30 minutes, and 50 mg. of the dyed fibers are dissolved in 20 cc. of ortho-chlorophenol. The "relative dyeability" is determined by measuring the optical density of thus obtained solution of 515 mμ., expressed in index number with reference to so measured optical density of nontreated sample fibers as 1.

When the subject process is applied to polyester fibers, the heat-treating time (t) expressed by second differs for each specific type of fibers. For example, for large denier fibers, longer (t) is required. Taking an example of a multifilamentary yarn of 75 **deniers**/36 filaments, it is empirically established that the upper and lower limits of (t) can be determined by the following equations, in which T(° C. is the treating temperature and Tm(°C.) is the melting point of the polyester fibers.

As to the lower limit of (t);

$$\log T - \log Tm = -0.592 - 0.588 \log t \ldots (a_1).$$

As to the upper limit of (t);

$$\log(T - Tm) = 1.576 - 1.085 \log t \ldots (b_1).$$

If the relative dyeability is 1.5;

$$\log T - \log Tm = -0.390 - 0.588 \log t \ldots (c_1).$$

The relationships of the above three empirical equations are illustrated in FIG. 10, in which the axis of abscissae denotes (t) and that of ordinates, T. In this case Tm is 260° C. The line (a_1) shows the lower limit, and line (b_1) shows the upper limit. In the X_1 area below the lower limit, the heat treatment is ineffective, and in the Y_1 area above the upper limit, the process becomes inoperable.

From practical reasons, in case of the multifilamentary yarn of 75 deniers/36 filaments, the area filled with double diagonal lines on FIG. 10 may be considered as denoting the optimum application range of this invention. It can be easily understood that, when the denier of the fibers to be treated is increased, the said area on the graph is shifted to the side of higher temperature and longer time. Likewise, when the total denier of the fiber is decreased, the area is shifted to the side of lower temperature and shorter time. This general rule also applied in the below-described cases (2) and (3).

2. Preparation of nonuniformly crimped fibers

For the preparation of nonuniformly crimped fibers in accordance with the invention, a prerequisite must be filled. That is, the thermoplastic fibers to be treated must be crimped in advance. Of course the crimping as a pretreatment is effected substantially uniformly, over the entire length of the fibers. As an example, product of applying the subject process to a crimped thermoplastic fiber is illustrated in FIG. 6, in which densely crimped portions A_2 and scarcely crimped portions B_2 appear alternately along the axial direction. The portions A_2 are those to which an inert liquid was applied in advance, and which were hardly heated. Before the practice of subject process, the entire fibers were in crimped state as the portions A_2. After the nonuniform liquid application and a high temperature treatment in accordance with the present invention, the crimps in portions B_2 (which were directly heated) vanished.

In order to determine the formation mechanism of this nonuniform crimps, we have carried out the experiments necessary for determining the variation in crimping status accompanying the temperature variation in a high-temperature treatment of conventional crimped fibers which are not applied with any inert liquid. The results of the experiments are given in FIG. 11. The sample fibers employed in the experiments were polyethylene terephthalate fibers of 50 deniers/24 filaments, which were crimped by false twist method at 210° C. The sample fibers were heated in air for 0.12 second, and the correlation of heat-treating temperature with residual crimp ratio was investigated. As the heating apparatus, a cylindrical electric oven of 30 cm. in length and 2.1 cm. in inner diameter was employed. The "residual crimp ratio" was determined as follows:

$$\text{Residual crimp ratio } (\%) = \left(\frac{L-l}{L-l_0}\right) \times 100$$

Before the relaxation in boiling water, a fixed length of sample fiber under a tension of 0.1 g./d. was taken. After the relaxation treatment the length of the same specimen under a tension of 0.1 g./d. was expressed by L. Also in the above equation, l is the length of untreated fiber and l, that of the treated fiber, both measured under a tension of 0.001 g./d. after the relaxing treatment in boiling water.

Referring to FIG. 11, the axis of abscissae represents heat-treating temperature, and that of ordinates, the above residual crimp ratio. From the graph it can be understood that the crimps are reduced or eliminated within extremely short time, by the heat treatment at temperatures above the melting point of the fibers (in the illustrated case, 265° C.).

From the foregoing experimental results, it can be understood that the change in crimping status of the portions B_2 referring to FIG. 6 is perfectly logical, and that the portions A_2, which were shielded by the liquid from the heating effect, retain the original crimped state is also theoretically persuasive.

The nonuniformly crimped state of the fibers obtained in accordance with the invention is furthermore variable by such practices as nonuniform liquid application over the entire surfaces of the crimped fibers, intermittent but regular liquid application along the axial direction of the fibers, intermittent and irregular liquid application, etc.

It has been also discovered that particularly in the heat treatment of crimped polyamide fibers, elimination of crimps is more effectively achieved when the fibers are overfed into the heating zone. As has been described as to the preparation of differently dyeable fibers in the preceding item (1), the heat-treating effect depends mainly on the treating temperature and time. That is, less time is required for achieving the intended result, under higher temperatures, increasing efficiency of the process. In any case it is necessary for obtaining the intended fibers of irregular crimps, to secure definite difference in crimping states of the fiber portions applied with an inert liquid, and of the portions not applied with the liquid. In terms of residual crimp ratio, the difference should preferably correspond to that of at least 15 percent. The conditions of such a treating system should be selected in consideration of the above requirement. For example, when experiments are run as to a polyethylene terephthalate fibers which have been crimped by false twist method at 190° C., having 50 deniers/24 filaments, the following empirical equations are obtained as to upper and lower limits of the heat-treating time (t).

As to the lower limit;

$\log T - \log Tm = -0.775 - 0.652 \log t \ldots (a_2)$.

As to the upper limit;

$\log(T - Tm) = 1.424 - 1.100 \log t \ldots (b_2)$.

If the desired residual crimp ratio is 70 percent,

$\log T - \log Tm = -0.636 - 0.652 \log t \ldots (c_2)$.

The relations of the above three empirical formulae can be illustrated as in FIG. 12, in which the axis of abscissae represents (t), and that of ordinates, T. The line (a_2) indicates the lower limit, and line (b_2), the upper limit. In the area X_2 below the lower limit, the heat treatment is ineffective, and at the area Y_2 above the upper limit, the subject process is inoperable. Similarly to FIG. 10, in FIG. 12 also the area filled with double diagonal lines denotes the scope within which the subject process is conveniently operable.

Also taking an example of heat-treating a poly-ε-capramide fibers of 70 deniers/12 filaments which have been crimped by false twist method at 160° C., the following empirical equations are established.

As to lower limit of (t);

$\log T - \log Tm = -0.435 - 0.612 \log t \ldots (a_3)$.

As to upper limit of (t);

$\log(T - Tm) = 1.791 - 0.853 \log t \ldots (b_3)$.

When the desired residual crimp ratio is 70 percent;

$\log T - \log Tm = -0.318 - 0.621 \log t \ldots (c_3)$.

The relations of the above three equations are illustrated in the graph of FIG. 13, in which the conveniently operable range corresponds to the area filled with double diagonal lines. (In that case Tm is 223° C.) The thermoplastic, synthetic fibers to which the above differential crimping can be applied include all the fibers made of thermoplastic polymers, such as polyester, polyamide, polyvinyl, and polyolefin fibers, etc. The manner of crimping and processing given to the fibers as a pretreatment to the subject process is not critical. That is, crimped fibers prepared by any known method such as false twist, edge crimp, etc. are usable.

According to the invention, the differing degree of crimping states can be optionally varied over a wide range, from distinct contrast to slightly visible difference. When the product fibers are formed into knit or woven goods, the exhibit excellent properties such as unique feeling and hand, appearance, and high bulkiness.

3. Preparation of differently dyeable, nonuniformly crimped fibers

In the above item (2), subject process is applied to already crimped thermoplastic fibers to produce nonuniformly crimped fibers. Such an embodiment is also practicable with crimped polyester fibers, in which the crimps in the liquid-applied portions are retained intact, and crimps in the other portions are reduced or eliminated. Whereas, in item (1), when ordinary, noncrimped polyester fibers are subjected to the present process, the fibers are imparted with different dyeability. That is, the portions in the fibers directly exposed to the heat are dyed deeply. We therefore inferred that such different dyeability would be imparted also to crimped polyester fibers. The correctness of this inference is already proven with numbers of experiments. That is, when the subject process is applied to already crimped polyester fibers, and the resulting nonuniformly crimped fibers are dyed, the product is dyed with a color of different shades. An example of such a product is illustrated in FIG. 7.

Referring to the drawing, the portions A_3 were applied with an inert liquid, and therefore were scarcely heated, consequently exhibiting little difference in crimp density and dyeability from those of the untreated crimped fibers. Whereas, the portions B_3 were directly exposed to the heating, in which the crimps are eliminated and high dyeability is exhibited.

As in the foregoing, when the subject process is applied to crimped polyester fibers, nonuniformly crimped and nonuniformly dyed product is obtained.

4. Method for imparting latent nonuniform crimpability to conjugate fibers

Latent, nonuniform crimpability can be imparted to conjugate fibers also in accordance with the present invention. This particular embodiment is applicable to latently crimpable conjugate fibers which exhibit crimps when heat-treated in relaxed state, for example, polyester and polyamide conjugate fibers. The material conjugate fibers may be undrawn, drawn, or heat-treated under conditions as will not render the fibers crimped, preceding the application of subject process. It is well known that in such latently crimpable conjugate fibers obtained by simultaneous melt-spinning of polymers having different thermal shrinkages through the same orifice, the density and size of crimps developed upon a relaxed heat treatment depend largely on the difference in thermal shrinkages of the components of the fiber. Therefore, it is easily inferrible that the crimp development will be variable by altering the thermal shrinkage of the component or components before the relaxed heat treatments. Whereas, we have found that thermal shrinkage of thermoplastic fibers greatly reduces upon application of a high temperature, heat treatment in accordance with the present invention. In FIG. 14, the correlation of reduction of shrinkage in boiling water with the heat-treating temperature is demonstrated, as to fibers of polyethylene terephthalate and copolymers thereof. In the graph of FIG. 14, the axis of ordinates represents the shrinkage of fiber in boiling water, and that of abscissae, heat-treating temperature in accordance with the present invention. Also "*d*" denotes the polyethylene terephthalate fibers of 75 denier/36 filaments, and "*e*," a copolymer fibers of polyethylene terephthalate containing 10 wt. percent of isophthalic acid on the basis of total acid components, of 75 denier/36 filaments. The treating time employed was 0.04 second at all temperatures. For example, a conjugate fiber composed of the polyethylene terephthalate and polyethylene terephthalate-isophthalate copolymer having thermal shrinkages in boiling water, respectively, 7 percent and 12.3 percent possesses latent crimpability. When the high-temperature heat treatment is applied to that fiber, however, the difference in thermal shrinkages of the components is reduced with the temperature rise in the heat treatment, and the latent crimpability of the conjugate fiber is changed. In the embodiment illustrated in FIG. 14, the difference in thermal shrinkages can be reduced to substantially zero. The conjugate fiber whereupon loses the latent crimpability.

Thus, when the nonuniform liquid application and subsequent heat treatment of the subject process are applied generally to latently crimpable conjugate fibers, the difference in thermal shrinkages of the components of the fibers at the portions directly exposed to the heat changes appreciably, that is, normally decreases. Consequently, when so treated fiber is further heat treated in relaxed state, crimps are developed differently on the liquid-applied portions from those on the portions not applied with the liquid. Normally the latent crimpability on the latter portions are reduced or completely eliminated.

As an example, the product of an embodiment in which an inert liquid is applied to a latently crimpable yarn at regular intervals along the axial direction thereof is shown in FIG. 8. Of course the drawing shows the state of the yarn after a boiling water treatment for approximately 30 minutes in relaxed state, following the treatment of this invention. By the boiling water treatment, the yarn thus developed crimps in the portions A_4 which were applied with the liquid and consequently received little effect of heat. In the drawing, B_4 denotes the portions of the yarn directly exposed to the heat.

In the foregoing heat treatment of latently crimpable fibers, tension is a significant factor for achieving the intended result. In certain cases the crimps in the conjugate fibers develop during the heat treatment, if the fibers are kept free of tension. Therefore, it is necessary to exert a tension as will prevent such crimp development in the fibers, i.e., at least 1×10^{14} g./d., on the fibers during the heat treatment.

The common advantages of the subject invention in the above-described various embodiments (1) through (4) are as follows. This invention is continuously operable at a very high speed, e.g., fibers can be processed accordingly at a rate as high as 1,000 m./min. The process can be practiced as one stage of a series of continuous treatments, following, drawing step or various crimping process; or, can be practiced as a separate, independent treatment; with simple operation and high efficiency. It is also possible, in accordance with the invention, to impart different dyeability and/or crimpability to thermoplastic fibers at optionally varied degrees.

Example 1

A drawn and heat-set polyethylene terephthalate yarn (75 denier/36 filaments, inherent viscosity 0.62, Δn=0.161) was passed through an electrically heated cylindrical tube 30 cm. long and having an inside diameter of 1.9 cm. and was heat-treated continuously by being drawn through heated air of 400° C. at a takeup speed of 70 meters per minute under a tension of 0.27 g./d. At this time the yarn was sprayed with water at a point 10 cm. before the entrance to the heated tube, as shown in FIG. 4. The so obtained treated yarn, when dyed (30 minutes in a boiling dye bath containing 4 percent o.w.f. of Dispersol Fast Scalet B, also the same in the subsequent examples), showed a marked pepper-and-salt pattern of deep and light shades. The so treated yarn had a tenacity of 4.8 g./d., an elongation of 19.5 percent and a Young's modulus of 76.5 g./d. (The yarn before treatment had a tenacity of 4.9 g./d., an elongation of 25.9 percent and a Young's modulus of 88.9 g./d.) On the other hand, when, by way of comparison, the experiment was carried out changing only the treatment temperature to 250° C., a gradation in shade was not observed.

Example 2

An un-heat-set polyethylene terephthalate yarn (75 denier/36 filaments, inherent viscosity 0.61, Δn=0.141) was heat treated with the same apparatus, conditions and procedure as employed in Example 1. A marked pepper-and-salt pattern of deep and light shades appeared in the so obtained yarn when dyed. The so obtained yarn had a tenacity of 4.6 g./d., an elongation of 20.4 percent and a Young's modulus of 77.2 g./d. (This yarn, before treatment, had a tenacity of 4.6 g./d., an elongation of 28.8 g./d. and a Young's modulus of 75.3 g./d.)

Example 3

The polyethylene terephthalate yarn used in Example 2 was treated as in Example 1 excepting that a treatment temperature of 750° C., a takeup speed of 300 meters per minute and a tension at the time of treatment of 0.027 g./d. were employed. A distinct pepper-and-salt-like gradation in shade was observed in the treated yarn upon dyeing, and this yarn had a tenacity of 3.9 g./d., an elongation of 32 percent and a Young's modulus of 43.2 g./d.

Example 4

The polyethylene terephthalate yarn used in Example 1, in being heat-treated employing a heat treatment apparatus as used in Example 1, was first applied water intermittently along its longitudinal axial direction with a liquid imparting device such as shown in FIG. 3 and thereafter was submitted continuously to a heat treatment in heated air of 580° C. under a tension of 0.27 g./d. at a takeup speed of 150 meters per minute. The so obtained yarn upon being dyed exhibited marked gradation in shade at a periodicity of 15 centimeters. Further, the deep color portion of the treated fiber had a tenacity of 4.7 g./d., an elongation of 22.6 percent and a Young's modulus of 77.4 g./d. and thus retained its mechanical properties to an extent as to be fully adequate for practical purposes.

Control 1

The experiment was operated exactly as in Example 4, excepting that a treatment temperature of 300° C. was used. However, in this case the treatment time was insufficient and, as a result, a pattern in which there was a gradation in shade did not appear in the treated yarn upon being dyed. On the other hand, when the same experiment was attempted but with a treatment temperature of 1,200° C., the heat treatment effects were too excessive, with the consequence that the yarn melted and broke to render it impossible of continuing the experiment.

Example 5

A polyethylene terephthalate yarn imparted crimps by false twist method (150 denier/48 filaments) was treated in heated air of 450° C. at delivery and takeup speeds of 150 meters per minute, using the heat treatment apparatus as employed in Example 1. At this time carbon tetrachloride was intermittently applied to the yarn by using the apparatus shown in FIG. 3, the application being accomplished by allowing the carbon tetrachloride to flow down as a fine stream at before the entrance to the heated tube and intermittently cutting this stream at a point above the yarn. The so treated yarn turned out to be one having at intervals of about 10 meters about 50 centimeters of portions where the crimp was slight. The knit product of the so treated yarn exhibits an intriguing appearance as compared with that knit from the untreated yarn.

Example 6

A poly-ε-capramide yarn (70 deniers/12 filaments) imparted crimps by false twist method was treated at a treatment temperature of 800° C. and delivery and takeup speeds of 300 meters per minute, using the heat treatment apparatus as used in Example 1. At this time water was applied intermittently as well as irregularly to the yarn by contacting the yarn with a piece of felt at before the entrance to the heated tube by which water was constantly fed to the yarn by capillarity and by disposing at a point immediately before the point at which the piece of felt contacts the yarn a means for intermittently separating said piece of felt from the yarn. The so treated yarn turned out to be one having at intervals of 5 meters to 10 meters portions about 50 centimeters in length where the crimp was slight.

Example 7

A poly-ε-capramide yarn identical to that of Example 6 was treated with the same heat treatment apparatus as used therein, at a treatment temperature of 500° C. and delivery and takeup speeds of 100 meters per minute, water being applied in this case with the liquid imparting apparatus shown in FIG. 1. The so treated yarn turned out to be one having intermittently along its longitudinal direction portions about 50 centimeters in length which were completely devoid of crimps and other portions about 5 meters to 10 meters in length where crimps identical to those in the yarn originally fed were retained intact.

Example 8

A polyethylene terephthalate yarn identical to that of Example 5 was heat treated using the heat treatment apparatus employed in Example 1, the treatment being carried out continuously in heated air of 700° C., at delivery and takeup speeds of 150 meters per minute and with application of substantially no tension. At this time water was applied intermittently and irregularly to the yarn by the provision, as shown in FIG. 1 at a point 10 centimeters before the entrance to the heated tube and longitudinally of the yarn, of two rollers having partially cutaway portions, the two rollers being operated at different peripheral speeds in applying the water. The so-treated yarn turned out to be one having portions intermittently and randomly spaced wherein there were completely no crimps for a distance of 3 centimeters to 20 centimeters at intervals of 0.3 meter to 20 meters. Those portions of the yarn to which water had been applied retained intact the crimps that were present in the originally fed yarn. The knit product obtained by knitting this treated yarn loosely became a very artistic knit goods having lacelike diaphanous portions.

In addition, this treated yarn, as a result of its possession of a greater heat treatment effect than that of the yarn of Example 5, possesses conjointly the property of developing a pattern having a gradation in shade upon dyeing.

Example 9

A polyethylene terephthalate yarn (75 denier/36 filaments) imparted crimps by false twist method was treated using the heating apparatus as used in Example 1, a temperature of the heated air of 650° C. and liquid paraffin as the liquid applied but otherwise by the same procedure and under identical conditions as in Example 8. The so treated yarn, as in the case of the yarn of Example 8, had intermittently and at random portions with no crimps at all and fused partially and other portions in which the crimps of the originally fed yarn were retained intact. When this yarn was dyed, the portions without the crimps were dyed to a very deep shade, thus indicating the possession of different dyeability. The woven goods of this treated yarn not only possess artistry as in the case of that of Example 5, but also present as interesting appearance because of its different dyeability.

Example 10

A polyethylene terephthalate yarn identical to that of Example 9 was treated by means of the same apparatus as employed therein and under identical conditions. At this time carbon tetrachloride was intermittently applied with the liquid-imparting apparatus as used in Example 6. The so treated yarn turned out to be one in which appeared in alternation portions about 30 centimeters in length with practically no crimps at all and portions 5 meters to 20 meters in length wherein the crimps present were observed to somewhat less than in the originally fed yarn.

Example 11

A 50-total-denier, 24-filament polyethylene terephthalate yarn having crimps imparted by false twist method was treated using the apparatus as in Example 1, a treatment temperature of 600° C. and delivery and takeup speeds of 300 meters per minute. At this time water was applied to the yarn at a point 10 centimeters before the entrance to the heated tube using a pair of water-imparting rollers having indentations and rotating at different peripheral speeds. The so-treated yarn turned out to be one having intermittently and at random portions 3 centimeters to 5 centimeters having no crimps, which were spaced at intervals of 30 centimeters to 2 meters.

On the other hand, when the experiment was carried out changing the treatment temperature to 1,300° C. and the treatment speed to 900 meters per minute, a similar intermittently crimped yarn was obtained. However, in this case, the portions from which the crimps had disappeared became straighter than that of the case above described.

Control 2

Example 11 was repeated except that a treatment temperature of 270° C. and a treatment speed of 300 meters per minute were used. In this case, due to the fact that the treatment time was insufficient, the crimps of those portions to which water was not applied were not changed in the least, i.e., they were in an identical state as before the treatment. Hence, a gradation in shade did not develop upon dyeing.

On the other hand, when the same experiment was attempted but with a treatment temperature of 950° C. and a treatment speed of 300 meters per minute, the heat treatment effect was so excessive that the yarn melted and broke to render it impossible to continue the experiment.

Control 3

Example 6 was repeated except that a treatment temperature of 400° C. In this case, due to the insufficiency of the treatment time, no change whatsoever was noted in the crimps of the portions to which water was not applied. On the other hand, when the same experiment was attempted with a treatment temperature of 1,000° C., the heat treatment effect being so great the yarn melted and broke to render it impossible to continue the experiment.

Example 13

A drawn side-by-side type latently crimpable conjugate yarn (45 denier/7filaments) composed of polyhexmethylene adipamide (m.p. about 265° C.) and 20 wt. percent hexamethylene sebacamide-copolymerized polyhexamethylene adipamide (m.p. about 230° C.) was heat treated in heated air of 600° C. at delivery and takeup speeds of 150 meters per minute, using the apparatus as used in Example 1. At this time water was applied unevenly along the longitudinal axial direction of the yarn as in Example 7. When the so treated yarn was submitted to a relaxation treatment for 30 minutes in boiling water, crimps were developed unevenly along the axial direction of the yarn in correspondence to the foregoing water-applied portions.

Example 14

A latently crimpable conjugate yarn identical to that of Example 13 was heat treated by using the heat treatment apparatus as in Example 1 at a heat treatment temperature of 900° C. at delivery and takeup speeds of 300 meters per minute. At this time water was applied intermittently along the longitudinal axial direction of the yarn, as in Example 4, at a point before the entrance of the yarn to heated tube. When the so treated yarn was treated for 30 minutes in boiling water in its relaxed state, crimps were developed at regular intervals along the axial direction of the yarn.

Example 15

A drawn side-by-side type latently crimpable conjugate yarn (75 denier/12 filaments) composed of polyethylene terephthalate (m.p. about 260° C.) and 10 wt. percent isophthalic acid-copolymerized polyethylene terephthalate (m.p. about 240° C.)was heat treated as in Example 13 by passing the yarn through heated air of 910° C. at delivery and takeup speeds of 300 meters per minute and applying water using liquid-imparting rollers. When the so treated yarn was submitted to a relaxation treatment for 30 minutes in boiling water, crimps were developed at random along the longitudinal axial direction of the yarn.

Example 16

Carbon tetrachloride was sprayed against the latently crimpable conjugate yarn of Example 15 using the sprayer shown in FIG. 4, following which the yarn was heat-treated in heated air of 400° C. by using the heat treatment apparatus as in Example 1 at delivery and takeup speeds of 70 meters per minute. When the so treated yarn was submitted a relaxation treatment for 30 minutes in boiling water, an irregular and complicated crimp pattern was developed along the axial direction of the yarn.

We claim:

1. A method of heat-treating thermoplastic fibers having a crimped configuration so as to impart nonuniform crimp thereto, which process comprises nonuniformly applying to said thermoplastic fibers a liquid which is inert to said thermoplastic fibers, has a relatively large latent heat of vaporization and substantially no dissolving action for said thermoplastic fibers, and subsequently subjecting said thermoplastic fibers having said inert liquid nonuniformly thereon to a noncontact heat treatment atmosphere maintained at a temperature above the melting point of said thermoplastic fibers for a period of 0.01 to 0.9 seconds, so as to remove the crimp of said thermoplastic fibers at those portions where said inert liquid is not applied.

2. The method of claim 1 wherein said inert liquid is water.

3. The method of claim 1 wherein the temperature of said atmosphere is up to 2,000° C.

4. The method of claim 1 wherein said thermoplastic fibers are polyester fibers.