The invention in its broadest aspect resides in such a process for the manufacture of acrylonitrile synthetic fibers, as comprising steps of: extruding a spinning liquid of an acrylonitrile polymer dissolved in nitric acid having a concentration of about 60–80 wt. percent from a spinneret positioned at about 1–100 mm. above the liquid surface of a coagulating bath, thus letting the extruded filaments run through the free air space preceding said spinneret and said bath surface and under such conditions that the solvent contained in the spinning liquid is subjected to substantially no evaporation; guiding the thus extruded filaments through said bath until the swelling degree of the filaments amounts to less than 350%; taking the thus coagulated and swollen filaments out of the bath; and washing the filaments by water for removing nitric acid therefrom; and for keeping the swelling degree of the thus washed filaments less than 300%.

By adopting the aforementioned improved technique, the generation of naps can be reduced to a possible minimum and the coloring performance for evenness can be highly improved, as will become clear as the description proceeds. It has been surprisingly found that in addition to the aforementioned favorable results, when the thus manufactured filaments are subjected to a turbo-stapling step, such as in a perlin machine, for the manufacture of bulky yarns by providing artificial crimp at a later stage, conventional trouble caused by the generation of so-called turbo-plies can be substantially obviated in the course of the fiber cutting process in the machine.

More specifically, bulky yarns are manufactured preferably in such a way that two kinds of fibers having different coefficients of thermal contraction are mixedly spun and the thus spun yarns are subjected to a heat treatment by contact with a heated medium such as boiling water, stream or the like, thereby causing the more contractive fiber elements to contract substantially relative to the less contractive elements, for the generation of a bulkiness of the yarns. This bulky processing technique is broadly utilized in the textile industry and for this purpose, turbo-staplers or perlin machines are used in the preparatory stage for cutting the continuously spun filaments into staple fibers. In this fiber cutting process, a tow of acrylonitrile filaments is conveyed into a thermal drafting stage which comprises two hot plates and subjected to a draft under tension at 120–160°C and then cut into fibers by application of impulsive shocks thereto by means of breaker bars. Considerable troubles are encountered frequently, however, by the generation of a substantial amount of turbo-plies which consist of waste short fibers caused by intense physical and shocking contact of the breaker bar with the filaments at the very moment of the fiber cutting operation. This generation of turbo-plies amounts generally to about 0.1% of the tow being treated upon. When the amount of the turbo-plies is large, not only the operation of the turbo-stapler may become defective, but also the fibers will be dirty and admixed with the sliver, thus resulting in a considerably reduced quality of the yarn spun therefrom.

It is also possible to a certain degree to reduce the generating amount of turbo-plies by adopting properly controlled spinning conditions for the acrylonitrile filaments being produced with using nitric acid capable of suppressing the formation of naps and strips to a possible minimum necessitates a large number of repeated experiments for the determination of the well defined and established performance of the desired effects in the above sense. Upon carrying out these practical tests, however, we have discovered an improved technique for the fulfillment of the above mentioned object to a satisfying degree.
3,636,187

3. nitric acid solution into the latter, and the thus coagulated filaments are taken out from the bath, washed with water and subjected to several steps for drafting, drying and occasional oiling, heating, crimping and others, mainly in the following three points:

4. First of all, the liquid is extruded from a spinneret which is positioned at 1–100 mm above the free liquid surface of the coagulation bath thereinto, thereby the extruded spinning liquid runs through the free air space above the bath surface without substantially any loss of the solvent contained in the spinning liquid.

5. Second, the degree of swelling of the coagulated filaments as taken out from the coagulation bath is maintained less than 350%.

6. Third, the degree of the swelling as washed with water is maintained less than 300%.

7. These and further objects, features and advantages of the invention will become more clear as the description proceeds by reference to an accompanying drawing which constitutes part of this specification, as well as several preferred numerical examples to be set forth hereinafter. It should be however noted that the embodiment shown on the drawing, and several numerical examples to follow are only illustrative and in no way limiting.

8. The drawing shows schematically in section a preferred spinning arrangement adapted for carrying out the process according to the invention.

9. In the drawing, numeral 1 denotes a feed pipe which is arranged vertically from a reservoir and a metering pump, both not being shown, a spinning liquid prepared by dissolving an acrylonitrile polymer in nitric acid of about 60–80% concentration, and at a certain predetermined rate to a spinneret which is of conventional design and formed therein a large number, for instance, 10,000 spinning orifices. The thus extruded spinning liquid is in the form of finely divided streams shown schematically at 3 and flows through the free air space from the outlet of said orifices to the free liquid surface of a coagulating bath 4 contained in a reservoir 5 and without any remarkable loss of the solvent contained in the spinning liquid, said bath comprising a dilute aqueous solution of nitric acid for instance, of 33%-concentration. The thus extruded fine streams are introduced into the bath for coagulation and then taken out by means of rotating rollers 6 and 8 mounted as shown. More specifically, these rollers 6 and 8 are driven to constantly rotate, with the filaments threaded around the bath as at 9. The concentration of the bath and the duration period of passage of the thus coagulated filaments through the bath is so selected that the degree of swelling of the filaments amounts to less than 350%. The swollen and taken-out filaments are led through a washing bath 7 consisting of water and contained in a reservoir 10 for the removal of nitric acid contained in the coagulated filaments. In this case, the duration period of passage of the filaments through the bath 7 is so selected that the degree of swelling of the filaments amounts to 300% at the highest. The filaments are then led as at 13 through guide rollers 11 and 12 driven by a drive means, not shown, and fed under tension through a drafting bath 14 comprising boiling water and contained in a reservoir 15 for subjecting filaments to a draft of 300% or more between rotating rollers 11 and 16 and then dried. The filaments at 18 are threaded around guide rollers 16 and 17 which are driven by a certain drive means, not shown. The thus drafted and dried filaments may be further processed by several additional steps for oiling, heat treating, crimping and the like.

10. In place of the regular homogeneous filaments, the products may be composite components, said to be prepared by the conjugated spinning technique. The final products may be modified to tow or staple fibers.

11. Although the true mechanism of the improvements according to the invention whereby the produced filaments may be dyed surprisingly homogeneously, generating a substantially reduced number of disadvantageous naps and providing, when treated on the turbo-stapler, a considerably reduced amount of turbo-fies, has not yet been ascertained to a reliable measure, it is believed that for this purpose the specific affinity of the acrylonitrile polymer to the nitric acid solvent, the interrelationship between the molecular orientation in the polymer solution as discharged from the spinning orifices of the spinneret and a possible minimum of the evaporation quantity of the solvent contained in the spinning liquid being kept during the passage of said liquid through the free air space from the spinneret to the free liquid surface of the coagulation bath, and finally the correlation between the specifically selected swelling degrees at the respective end of the coagulation and washing steps with the molecular orientation of the thermally drafted filaments, act in combination and in a highly delicate way for providing a highly stabilized final molecular orientation in the spun and processed filaments.

12. As was referred to hereinbefore, the spinning liquid used in the present process is a solution of acrylonitrile polymer in nitric acid having a concentration of 60–80% by wt. According to our experiments, it has been found that with nitric acid beyond the above specified range, it is very difficult to acquire the desirable effects, even when other spinning and treating conditions are adopted as suggested by the present invention.

13. When the spinneret is positioned at a closer distance than the above specified lowest limit or 1 mm, the bath liquid will arrive at the spinneret outlet along the extruded spinning liquid streams on account of the inherent surface tension of the bath liquid so that in effect the conventional dip spinning process where the spinneret is completely immersed in the bath would be brought about, thus the desirable effect attainable with the present invention would not be realized.

14. On the other hand, when the spinneret is positioned at a more distant place than the above specified upper limit or 100 mm, the spun product will represent a considerable difference in its coloring performance. In this case, the green filaments as extruded from the spinneret are liable to conjoin with each other in the course of passage through the free air space above the bath surface. In addition, it has been ascertained that the thus spun and coagulated final product represent normally a large amount of naps formed thereon. Therefore, under the above-mentioned spinning condition, it is unable to manufacture superior polyacrylonitrile synthetic fibers.

15. In this respect, sincere care must be taken to carry out the process that there is practically no evaporation of the solvent contained in the spinning solution in the course of travel thereof through the free air space and in the form of the extruded fine streams. If not, the desirable homogeneously coloring performance of the finished fibers will be lost substantially. A higher extrusion temperature will invite decidedly this kind of drawback. Similarly, a higher ambient temperature which affects upon the prevailing temperature in the free air space in the above sense must naturally be avoided. The true reason for this drawback is believed to be such that by the evaporation of the solvent to a lesser or larger degree from the extruded spinning liquid, a delicate and unknown variation in the dissolved condition of the acrylonitrile polymer in the spinning solution is thereby invited to take place in the direction towards non-homogeneity.

16. As already described, the swelling degree of the coagulated filaments at the outlet of the coagulating bath is adjusted to be less than 350%. When this specified upper-limit range is exceeded, the desired coloring performance appearing at a later step may be considerably interfered. Similarly, a large amount of naps and turbo-fies may frequently be encountered.

17. The nitric acid component contained in the coagulated filaments must be removed as much as possible therefrom.
and for this purpose the filaments are washed with fresh water. In this case, the degree of swelling of the filaments is selected to less than 300%, as was mentioned hereinbefore. With a higher degree of swelling, it has been found upon a large number of our practical experiments that substantially affected adversely and the amount of turbidity and naps will be considerably and disadvantageously increased, as with higher swelling degree at the end of the coagulation step. As an example, the amount of turbidity encountered in the process according to this invention with 0.2-0.3 g of the filaments, while the value amounts to 0.7-1.6 g if the swelling degree at this stage is selected to a higher value than above specified. These latter values are considerably inferior to those obtainable with the conventional comparative process in which acrylonitrile polymer dissolved in nitric acid is processed according to the normal wet spinning process wherein the amount of the generated turbidity will amount generally to 0.7-0.8 g per kg of the filaments produced.

Acrylonitrile synthetic fibers as produced by the process according to this invention indicate those manufactured from acrylonitrile polymers by the block copolymers by the method or the like. The acrylonitrile polymer as used herein throughout the present invention includes not only the polymer per se, but also copolymers or a mixture of said polymer and copolymers. The term "copolymer" as used throughout the present specification should be interpreted as including every copolymer (including block copolymers and graft polymers) of a copolymerizable monomer with acrylonitrile.

Representative monomers copolymerizable with acrylonitrile and employable in the present process are acrylamide; acrylamide, copolymerizable acid; acrylamide, copolymerizable acid; acrylamide, copolymerizable acid; methacrylic acid; acrylates such as methylmethacrylate, methoxyethylmethacrylate, ethylmethacrylate, methacrylate, ethacrylate, alpha-chloroacrylic acid methyl or ethyl ester; vinyl chloride, fluoro, or bromo; vinylidene chloride; methacrylonitrile, acrylamide; methacrylamide; alpha-chloroacrylamide and their alkyl substituents; methyl or ethyl vinyl ketone; vinyl carboxylates such as vinyl acetate, vinyl chloride; vinyl propionate, vinyl stearate; N-vinyl imids such as N-vinyl pthalimid, N-vinyl succinimid; methyl maleic acid esters; itaconic acid and its esters; N-vinyl carbazoles; vinyl furan; alkyl vinyl esters; vinyl ethers; sulfonic acid; and sulfonic acid esters; some of the above mentioned monomers as well.

The spinning liquid is prepared by dissolving the acrylonitrile polymer in nitric acid of about 60-80%-concentration. As for the solvent nitric acid, it is preferable to remove therefrom occasionally included nitrous compounds as carefully as possible. With the use of solvent nitric acid either having a lower concentration than 60% or a higher concentration than 80%, it is difficult to obtain the desired results even when other operating conditions should be selected within the respective limits as specified for carrying out the present invention.

Salts, acid, and, like, impurities may be included within a certain range in the solvent nitric acid without inviting an appreciably adverse effect if the solvent has a proper acid concentration as above specified.

As the process proceeds, the spinning liquid is forcibly extruded from the spinneret orifices and the temperature of the liquid should be kept between 20°C. and 50°C., preferably between -10°C. and 20°C.

The ambient atmosphere around the spinneret is generally and preferably selected to be air which constitutes an open atmospheric space. But, under certain circumstances, air may be replaced by an inert gas or gases such as nitrogen, carbon dioxide or the like which should preferably be confined in a limited space. The atmosphere in the above sense must preferably be kept between 20°C. and 50°C., advantageously between 5°C. and 35°C. It is disadvantageous that the ambient atmosphere should contain a considerable amount of moisture or water, because it will impede the evenly coloring characteristics of the manufactured filaments or the like.

The coagulation bath liquid is composed of nitric acid of 10-45 wt. percent concentration and the temperature of the bath should be kept between 20°C. and 50°C., preferably -10°C. and 0°C. Other acids, salts and like impurities may be included in the bath without any appreciable adverse effect, if the quantity of the contained impurities is within an allowable range. As shown, the bath may be of the horizontal type. Under circumstances, however, the bath may be of the vertical type such as the funnel spinning type. In the latter case, the flow velocity of the bath liquid is so selected that no considerable tension is induced in the green filaments as extruded and accompanied by the down-flowing bath liquid. Under these operating conditions, the swelling degree of the spun filaments measured at the outlet of said bath should be selected to be 350% or less.

The temperature of the water washing bath providing for the removal of the nitric acid content in the spun filaments after coagulation is set to 40°C. or less. It is naturally preferable to keep the treatment filaments under the lowest tension as possible. It is the requisite operating condition to keep the swelling degree of the filaments to be less than 300% as measured at the outlet of the water washing bath by properly selecting the coagulating conditions and the water washing conditions.

The respective swelling degrees of the spun filaments as measured at the outlets of the coagulating bath and the washing bath vary considerably depending upon the composition of the polymer, the conditions of the spinning liquid, the coagulating conditions and the like, ranging generally from about 100% to about 600%. As a general rule, the swelling degree of the filaments under treatment will decrease when the polymer contains a hydrophobic copolymer and increases with an increase of the temperature of the coagulating bath. It will decrease with an increase of polymer concentration, viscosity of spinning liquid, concentration of solvent nitric acid and that of the coagulating acid. But, the coagulation degree of these tendencies, the swelling degrees in the above sense of the filaments under spinning are conditioned to the aforementioned specific ranges.

It has been observed that also in the case of the conventional wet spinning process under utilization of solvent nitric acid as in the present case, the swelling degree of the spinning filaments will vary appreciably. But, it should be noted that in such conventional processing modes, the desirable even coloring characteristics, the generating degree of disadvantageous naps and the amount of turbidity of the filaments in the aforementioned sense do not vary considerably depending upon the above-mentioned specific operating conditions.

The water-washed filaments are subjected finally to a considerable draft of 300% or more while being heated by contact with boiling water, steam or hot air. In this case, the filaments should be dried preferably under tension to a certain degree. If the filaments not yet dried should be heated treated under slackened conditions, for instance, by contact with boiling water, the generation of naps could be increased considerably, and in addition, the dying characteristics would be adversely affected to some extent. The direction of increase of dyed specks when dyed at a later stage. The aforementioned advantageous phenomenon is found to be peculiar to the process according to this invention, in contrast to the conventional wet spinning process. Therefore it was found that for carrying out the
process in accordance with the present invention the filaments should be dried preferably under tension.

The swelling degree as used throughout the present specification is measured as follows:

Water and acid are removed from a certain selected amount of the filaments by centrifuging at 2,000 r.p.m. with a radius of rotation, 10 cm., and for 5 minutes. When the quantity of the polymer contained in the filaments is expressed by a in gms. and the contained quantity of water or water and nitric acid by b in gms., then the swelling degree "SD" is:

\[ SD = \frac{b}{a} \times 100(\%) \]

In the following, several preferred numerical examples will be given for better understanding of the inventive process.

**EXAMPLE 1**

A certain quantity of acrylonitrile polymer consisting of acrylonitrile 90% and methyl acrylate 10% was dissolved in a quantity of 70% nitric acid so as to provide a spinning solution of the polymer having a concentration of 18%. On the other hand, a coagulating bath was prepared by introducing a certain quantity of 30% nitric acid in a bath vessel such as shown at 5 on the drawing and kept at 0° C. A spinneret was held at a distance of 3 mm. from the free liquid surface of said bath and the spinning solution at 5° C., was extruded from the orifices of said spinneret and caused to travel vertically through the free air space above the bath surface into the acid bath. The temperature of the ambient atmosphere was 3° C.

The thus coagulated filaments were taken out from the coagulating bath and washed under nearly no tension with fresh water kept at 15° C. The swelling degrees of the filaments as measured upon said coagulation and water washing operations were respectively as 241% and 230%. The water washed filaments were then dried in boiling water to 700% of their length, and further oiled, dried and crimped as in the usual way.

In this way, a tow of synthetic filaments overall denier being 450,000 and monofilament denier being 3, was produced and processed further in a turbo-stapler under the following operating conditions:

- Treating temperature measured at hot plate: 140° C.
- Rate of draft: 135%
- Depth of breaker bar: 3.11

For comparison purposes, a similar tow was manufactured in accordance with the comparative conventional process and then equally treated in the same turbo-stapler. The resulting amount of turbo-flies in both cases were measured as follows:

- Amount of turbo-flies per 1 kg. of resulted fibers
  - Inventive: 0.21 gr. (0.02%)
  - Conventional: 0.80 gr. (0.08%)

**EXAMPLE 2**

An acrylonitrile polymer comprising acrylonitrile 95%, acrylamide 4.5% and sodium methally sulfate 0.5% was dissolved in 75%-nitric acid to provide a spinning solution having a polymer concentration of 14%. This spinning solution was processed in the following two different ways:

- First, the spinning solution, 3° C., was extruded through 100 orifices, each of 0.20 mm. bore, of a spinneret kept at a 5 mm.-distance above a coagulation bath consisting of 33%-nitric acid solution, −3° C., into the latter. The temperature of the ambient air atmosphere was 3° C. The thus coagulated filaments were taken out from the bath at a speed of 40 m./min., washed with fresh water at 15° C., dried under continuous tension and finally wound up on a conventional winder. The filaments thus produced represented 2 denier per filament. The swelling degrees of the filaments amounted respectively to 286% and 271%, as measured after the coagulation and water-washing operations.

- In contrast to the above-mentioned inventive process, the same spinning solutions was processed in the comparative conventional process in the following way:

  The solution was extruded from 100 orifices, each of 0.09 mm. bore, into a coagulation bath containing 33%-nitric acid, −3° C. The thus coagulated filaments were taken out from the coagulation bath at a speed of 7 m./min., washed with fresh water at 15° C., dried to 1,000% of their length in a steam atmosphere at 100° C., dried under continuous tension, and finally wound up on a conventional winder. The denier per filament amounted to 2. The degrees of swelling were measured to 316% and 294%, respectively, when measured after the coagulation and water washing operations.

The number of generated naps and the evenness of the coloring characteristics were compared for both cases. In this case, the latter data were determined by the following way:

- 200 gms. of the yarns made of these filaments were knitted on a knitting machine and the knitted products were refined with a 0.1%-aqueous solution of "Scourol 400"," a kind of non-ionic surfactant, comprising a substantial quantity of polyethylene glycol ether, and then dried. These knitted samples were dyed with "Astrazon Blue-FGL" by a dyestuff concentration: 2% of the overall weight of fibers and with a liquor ratio of 1:80 for 1.5 hours.

As for the dyeing evenness, measurements were made of the generated color specks on each of the knitted and dyed samples.

**EXAMPLE 3**

Several kinds of spinning solutions were prepared from an acrylonitrile polymer comprising acrylonitrile 93% and vinyl acetate 7% and dissolved in nitric acid of several concentrations: 50%, 60%, 70%, 80% and 85%, respectively, so as to keep the polymer concentration at 13%. Each of these spinning solutions was extruded from 100 orifices, each being of 0.09 mm. bore, of a spinneret which was kept at about 1 mm. above the free liquid surface of a coagulation bath consisting of a 35%-nitric acid solution kept at 0° C., into the bath so as to coagulate. The ambient air atmosphere was measured to 10° C. The thus coagulated filaments were taken out from the bath at a speed of 8 m./min., washed with fresh water at 18° C., dried to 1,000% of their length in a steam atmosphere at 100° C., dried under constant tension, and finally wound up by a conventional winder. The obtained results were as follows:

<table>
<thead>
<tr>
<th>Degree of swelling, %</th>
<th>Number of generated naps per 10 m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of solvent/nitric acid</td>
<td>Upon coagulation</td>
</tr>
<tr>
<td>50</td>
<td>406</td>
</tr>
<tr>
<td>60</td>
<td>311</td>
</tr>
<tr>
<td>70</td>
<td>278</td>
</tr>
<tr>
<td>80</td>
<td>243</td>
</tr>
<tr>
<td>85</td>
<td>215</td>
</tr>
</tbody>
</table>

From the foregoing comparative test results, it will be clearly seen that even if the swelling degrees in the aforementioned sense lie within the specified range as proposed by the invention, considerable amounts of gen-
erated naps and color specks will be encountered, when the concentration of the solvent nitric acid is selected to be outside the specified range.

EXAMPLE 4

An acrylonitrile polymer comprising acrylonitrile 95%, methyl methacrylate 4.5% and sodium salt of styrene sulfonic acid 0.5% was dissolved in 65%-nitric acid containing about 1% of sodium sulfate for the preparation of a spinning solution containing 15% of the polymer. Then, this spinning solution was extruded under pressure through 80 orifices each being of 0.10 mm. bore, of a conventional spinneret in the following three different ways:

A coagulating bath liquid consisting of a 39%-nitric acid solution was constantly recirculated at 2°C through a bath reservoir, and the above prepared spinning liquid, 5°C, was extruded under pressure into the bath liquid after passage through an air space, 5°C, having a travel distance about 3 mm. for the extruded solution. The thus coagulated filaments were taken out under slight tension from the bath at a speed of 7 m/min., washed with fresh water at 15°C, dried to 1000% of their length in steam at 100°C, dried under constant tension and finally wound up on a conventional winder. The swelling degrees of the thus prepared filaments were measured to 219% and 227%, respectively, at the termination of the coagulating and water-washing operations.

In a second experiment, the draft was set to about 200% in place of 1000% in the foregoing experiment. Other operating conditions were the same as above. The corresponding swelling degrees were measured in this case to be 203% and 211%, respectively.

In a third experiment, the same coagulating bath as in the foregoing second experiment was again employed and the spinning liquid was extruded from the spinneret at about 50°C, the free air space having a passage distance of about 20 mm., into the coagulation bath. The ambient atmospheric temperature around the spinneret was measured to be 50°C. Other treating conditions were the same as in the first experiment mentioned in the foregoing Example 2. The swelling degrees were measured respectively to be 296% and 300% at the end of the coagulation and water-washing operation.

The evenness of the dyeing characteristics was measured in the last-mentioned three different experiments, as in the same way in the foregoing Example 2. Kind of spinning

First
Second
Third
Number of dyed specks
5
22
51

The first experiment was carried out within the specified conditions as proposed by the present invention. The second experiment was carried into effect with a 200%-draft under tension in the coagulation bath. The third experiment was performed under such a condition that an appreciable quantity of the solvent nitric acid was dissipated in the course of travel of the extruded green filaments through the free air space. It is clear from these experiments that an application of tension onto the filaments during passage through the coagulation bath and/or a considerable evaporative loss of the solvent nitric acid from the green filaments during passage through the free or confined gaseous medium space will increase considerably the number of color specks at a later coloring step of the produced synthetic filaments.

EXAMPLE 5

An acrylonitrile polymer comprising acrylonitrile 90%, methacrylamide 5% and methyl methacrylate 5% was employed as the starting material for the preparation of the spinning liquid, and synthetic fibers were prepared therefrom in the following four different ways as shown at I, II, III and IV. The resulted filaments were tested as to the quantity of generated turbo-flies, the evenness of the coloring characteristics and the amount of generated naps, as in the several foregoing experiments. The two last mentioned data were determined as in the foregoing Example 2. Turbo-flies were measured under the following turbo-stapling conditions:

<table>
<thead>
<tr>
<th>Spinning conditions</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of polymer, percent...</td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>Concentration of solution nitric acid, percent...</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>Temperature of spinning acid solution, °C...</td>
<td>10°</td>
<td>5°</td>
<td>0°</td>
<td>5°</td>
</tr>
<tr>
<td>Concentration of coagulatibn acid bath, percent...</td>
<td>20</td>
<td>22</td>
<td>26</td>
<td>23</td>
</tr>
<tr>
<td>Temperature of coagulation bath, °C...</td>
<td>5°</td>
<td>3°</td>
<td>0°</td>
<td>0°</td>
</tr>
</tbody>
</table>

Remarks: Other operating conditions were same as in the foregoing Example 1.

Turbo-stapling conditions:

| H.T., °C... | 190 |
| H.S., percent... | 131 |
| B.D... | 3.31 |

<table>
<thead>
<tr>
<th>Degree of swelling</th>
<th>Upon coagulation</th>
<th>Upon washing</th>
<th>Amount of turbo-flies per 1 Kg.</th>
<th>Number of naps per 100 m.</th>
<th>Number of color specks per 100 m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kind of spinning</td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td>517</td>
<td>510</td>
<td>516</td>
<td>519</td>
<td>2,160</td>
</tr>
<tr>
<td></td>
<td>198</td>
<td>200</td>
<td>202</td>
<td>204</td>
<td>770</td>
</tr>
</tbody>
</table>

From the foregoing, it will be clear that in the both cases I and II where the swelling degrees were set far from the specified range as proposed by the present invention, the results were highly inferior. In the third case III where only the swelling degree of filaments as measured upon the water-washing operation is far from the recommended range, results were also considerably inferior.

EXAMPLE 6

An acrylonitrile polymer comprising acrylonitrile 90%, methyl acrylate 8% and allylsulfonic acid 2% was dissolved in 65%-nitric acid so as to provide a spinning solution having a polymer concentration of 14%, while a 35%-nitric acid solution, kept at −2°C, was recirculated through a horizontal type coagulation bath tank. Then, the spinning solution, 0°C, was extruded through 100 orifices, each being of 0.20 mm. bore, through various different air passages of 5, 25, 50 and 150 mm., into said acid bath. The ambient temperature around the spinneret was measured to 15°C. Measures were adopted to keep the ambient atmospheric air around the spinneret in a stationary condition. The thus coagulated filaments were deflected to change their travel passage direction and then taken out by means of a rotating roller from the coagulation bath at a speed of 10 m./min. Then, they were washed with fresh water at 15°C and dried 1,000 of their length in steam at 100°C. The swelling degree of the filaments was measured, respectively, to be 281% and 267% after the coagulation and water-washing operations. Then, the filaments were dried continuously under tension and finally wound up on a conventional winder. In this way, five different groups of 100 filaments, each 2 deniers, were obtained and the results were comparatively determined as in the case of the foregoing Example 2.

<table>
<thead>
<tr>
<th>Distance between spinneret and bath surface, mm.</th>
<th>Number of generated naps per 100 m.</th>
<th>Number of color specks per 100 m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>520</td>
<td>5</td>
</tr>
<tr>
<td>25</td>
<td>470</td>
<td>4</td>
</tr>
<tr>
<td>50</td>
<td>500</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>590</td>
<td>8</td>
</tr>
<tr>
<td>150</td>
<td>810</td>
<td>13</td>
</tr>
</tbody>
</table>
Throughout this specification, it must be noted that all the parts and percentages, except degree of swelling, have been given by weight.

While specific embodiments of the invention have been shown and described in detail to illustrate the application of the invention principles, it will be understood that the invention may be embodied otherwise without departing from such principles.

What we claim is:

1. A process for the manufacture of acrylonitrile synthetic fibers comprising preparing a spinning solution by dissolving a polymer selected from the group consisting of a homopolymer of acrylonitrile and copolymers of acrylonitrile and monomers copolymerizable therewith in nitric acid having a concentration of from 60 to 80 weight percent, and wherein the temperature of said spinning solution varies from —20° C. to 50° C., extruding all of said spinning solution through a spinneret which is disposed from 1 to 100 mm. above the surface of a coagulating bath through a gaseous medium into said coagulating bath, wherein said coagulating bath comprises an aqueous solution of nitric acid having a concentration of from 10 to 40 weight percent wherein the temperature of said gaseous medium varies from —20 to 50° C., wherein the temperature of said coagulating bath varies between —20 and 5° C., whereby the evaporation of nitric acid solvent of said spinning solution is substantially depressed, guiding the resulting filaments through said coagulating bath wherein the swelling of said filaments exiting from said coagulating bath is less than 350 weight percent, washing the resulting filaments having a swelling of less than 300 weight percent, stretching the filaments to at least 300% and drying the filaments.

2. A process as set forth in claim 1 wherein said gaseous medium is atmospheric air, carbon dioxide or nitrogen.

3. A process as set forth in claim 1 wherein the drying of said filaments is carried out under tension.

4. The process as in claim 1 wherein the temperature of said spinning solution varies from —10 to 20° C., wherein the temperature of said gaseous medium varies between —5 and 35° C., wherein said gaseous medium is selected from the group consisting of atmospheric air, carbon dioxide and nitrogen, and wherein the temperature of said coagulating bath varies between —10 and 0° C.

5. The process as in claim 1 wherein said polymer is a homopolymer of acrylonitrile or a copolymer of acrylonitrile with a monomer selected from the group consisting of methylacrylate, acrylamide, sodium methallyl sulfonate, vinyl acetate, methy1 methacrylate, sodium salt of styrene sulfonic acid, methacrylamide, and allyl sulfonic acid.

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