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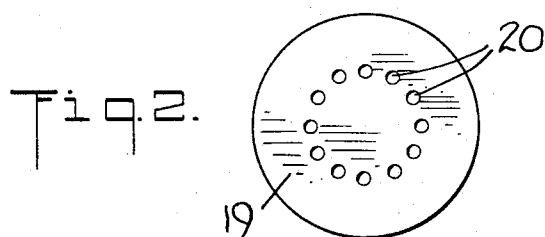
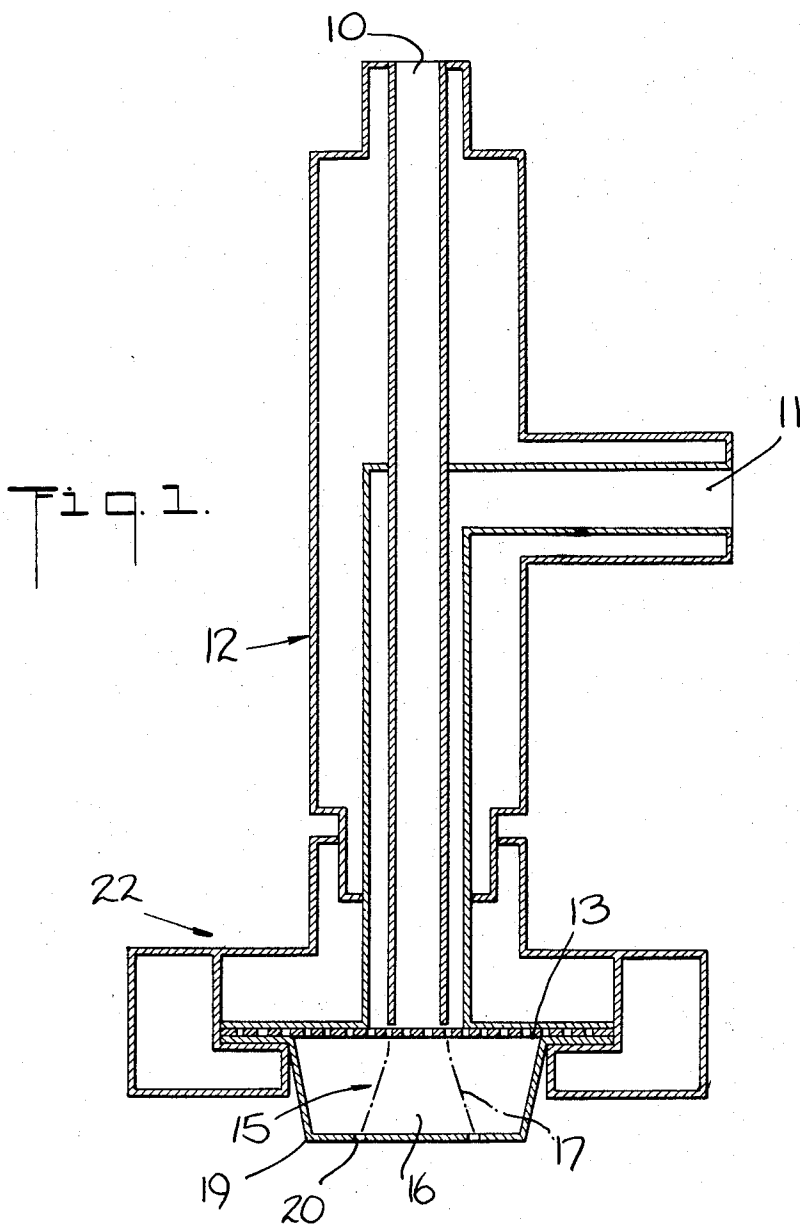
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METHOD FOR SPINNING BICOMPONENT CELLULOSE ESTERS

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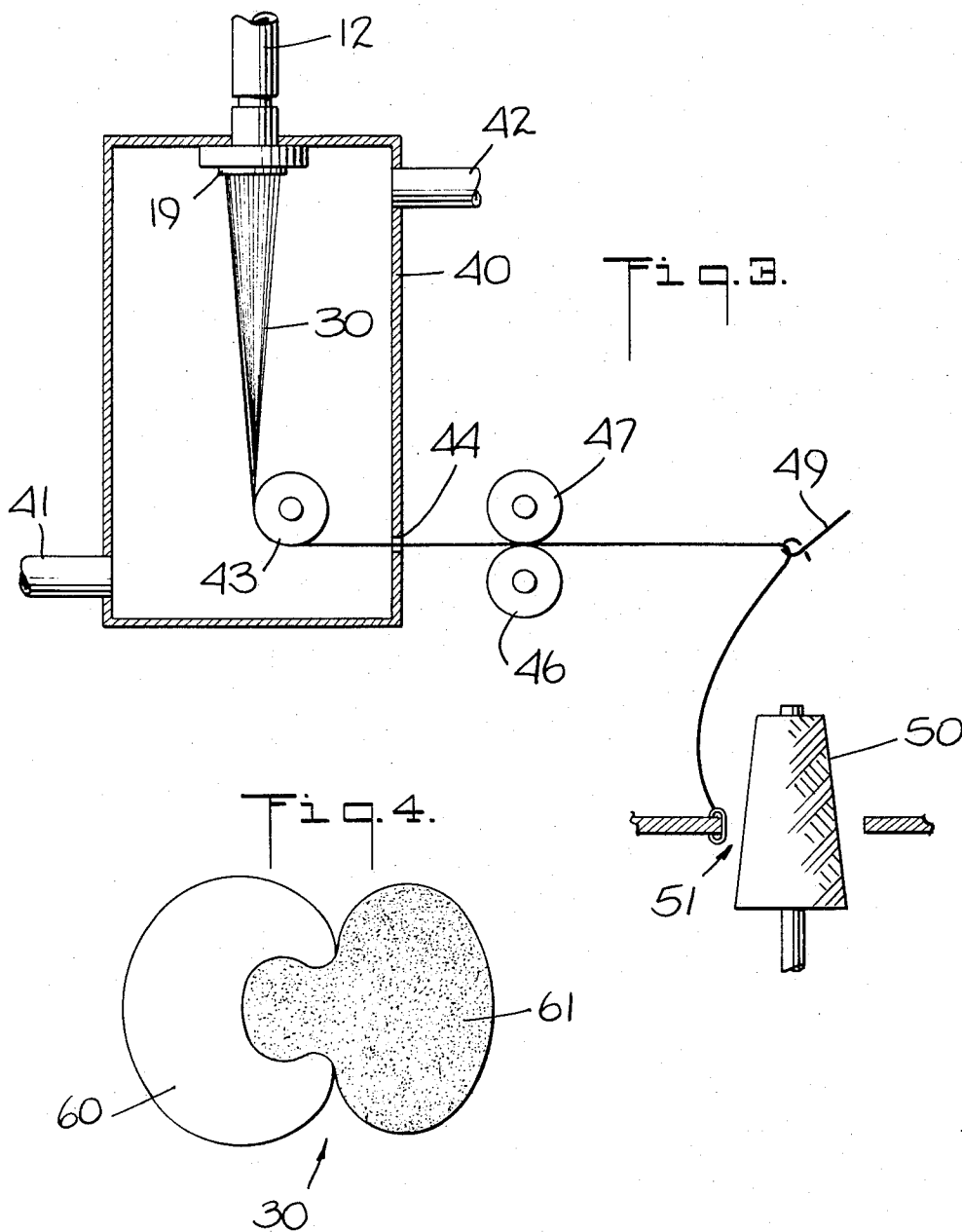
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METHOD FOR SPINNING BICOMPONENT CELLULOSE ESTERS

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This invention relates to improved multi-component filamentary materials.

It has been proposed to form bi-component filaments having a cross-section of at least two components in eccentric relationship by using two spinning solutions or melts of a filament-forming polymer which are extruded together through spinnerette orifices without substantial mixing. Processes and apparatus for accomplishing this are described, for example, in U.S. Patent Nos. 2,386,173, 2,439,813, 2,439,814 and 2,439,815.

A particularly desirable process is disclosed in application Ser. No. 178,000, filed Mar. 7, 1962 and now U.S. Patent 3,209,402, and assigned to the same assignee at the instant application, wherein multi-component filaments are formed by feeding into the upstream side of a spinnerette at least two spinning solutions of a cellulose ester such as cellulose acetate, each solution being under such pressure so as to induce laminar flow. The streams of each dope may then be brought together to form a single stream having streamlined portions which maintain their identities as separate dopes and the single stream may be passed through a filament-forming jet to form a multi-component filament. The entire disclosure of application Ser. No. 178,000 is incorporated herein by reference.

When a multi-filament yarn of bi-component filaments is desired, the two dopes are preferably in a sheath and core arrangement in conjunction with a pattern of spinnerette holes in the form of a single circle. This may be accomplished by merely transferring the two dopes to the upstream side of the spinnerette using two pipes, one of which is smaller in diameter and centered within the other, at least the smaller pipe ending some distance from the upstream face of the spinnerette plate. Thus, when one dope is transmitted through the inner pipe and the other dope through the outer pipe surrounding such inner pipe, the two dopes form an interface beyond the end of the inner pipe, which interface is substantially maintained up to the upstream side of the spinnerette plate. If, as mentioned above, the spinnerette holes form the pattern of a single circle with a center coinciding with the axis of the two lead-in pipes, it has been found that the two dopes are forced through each of such holes without substantial mixing. If the solvent of both dopes is evaporated and the filaments taken up on the downstream side of the spinnerette, as in a conventional dry spinning process, the final filaments will be composed of the two fiber-forming components of the dopes in eccentric relationship.

If one dope described in the foregoing paragraph is, for example, a cellulose acetate having an acetyl value of at least 59%, preferably at least 61%, calculated as combined acetic acid, and the fiber-forming component of the other dope is a cellulose acetate having an acetyl value of under 56%, preferably between 54 and 55%, calculated as combined acetic acid, the resulting bi-component filament will be composed of the two described cellulose acetates in eccentric relationship within the cross-section of the filaments. Bi-component filamentary material of this type may then be subjected to mildly alkaline saponification conditions, e.g., contacted with an aqueous solution of 0.1 to 3.0% sodium hydroxide at

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a temperature of 40 to 100° C. for a period of 15 to 120 minutes, to completely hydrolyze the "secondary" cellulose acetate, i.e., the cellulose acetate of lower acetyl value, to regenerated cellulose, while leaving the cellulose "triacetate," i.e., the cellulose acetate of higher acetyl value, substantially unchanged. As a result of such treatment, the secondary cellulose acetate, as it saponifies to regenerated cellulose, undergoes substantial shrinkage in length, while the cellulose triacetate component is relatively unaffected and its length therefore remains substantially constant. This causes the filament to align itself into a helical crimped configuration with the regenerated cellulose component on the inside of the helix and the longer length cellulose triacetate component on the outside. This effect is useful in obtaining a bulking, volumizing and/or texturing effect. In particular, yarn composed of cellulose triacetate-secondary cellulose acetate bi-component filaments with the components in eccentric relationship in each filament cross-section all along its length, may be woven or knitted into a relatively flat, unbulked fabric which may be handled and treated to a large extent before bulking. Subsequently, the fabric may be treated by the fabric finisher with an aqueous alkaline medium, e.g., dilute aqueous solution of sodium hydroxide to saponify the secondary cellulose acetate to regenerated cellulose while leaving the triacetate unaffected, resulting in a substantial bulking and/or texturing of the fabric. This mode of operation has the advantage of allowing a good deal of handling and treating to be carried out on the flat fabric before bulking, so that such handling and treating does not have the effect of pulling out the bulk.

Although the procedure described in the previous paragraph is very effective in inducing a crimp into the filaments by means of a saponification treatment, which treatment may be utilized in achieving bulking and texturing effects in fiber, yarn or fabric, such method has various disadvantages, among the most important of which is the fact that two separate dopes are necessary, and the relatively long period of treatment required for the saponification, usually at least half an hour. Thus, any alternative procedure which does away with the necessity of using two separate dopes of two different fiber-forming materials, and/or reduces the period of saponification would be highly desirable.

In accordance with this invention, two dopes, i.e., spinning solutions, each containing a cellulose ester and one of which contains a minor amount of a quaternary ammonium salt are cospun to form a bi-component filament, the cross-section of which contains two segments in eccentric relationship, one segment containing a quaternary ammonium salt and the other not. The filament in fiber, yarn, or fabric form is then subjected to saponification conditions to saponify the segment containing the quaternary ammonium salt which acts as a saponification catalyst while leaving the other segment unsaponified or substantially less saponified. The resulting differential shrinkage causes the filament to crimp.

In a preferred aspect of the invention, a single spinning solution or dope of a saponifiable cellulose ester, preferably cellulose acetate, is prepared, which is suitable for the formation of filamentary material by means of a dry spinning process. The dope is separated into two parts, in one of which is incorporated a minor amount of a quaternary ammonium salt. The two dopes, one of which contains quaternary ammonium salt and the other of which does not, are then used to spin a bi-component filament composed entirely of a single cellulose with one part of the cross-section of the filament containing quaternary ammonium salt and the other part in eccentric relationship to the first part within the cross-

section and containing no quaternary ammonium salt. It has been found that this material may be subjected to mildly alkaline conditions such that the part of the filament which contains quaternary ammonium salt is completely saponified to regenerated cellulose while the other part containing no quaternary ammonium salt remains either substantially unchanged or saponified to a much lower degree than the other part. Under these circumstances, the cellulose ester which is completely saponified to regenerated cellulose, undergoes substantially greater shrinkage than the other part of the filament, which causes the filament to adopt a pronounced three-dimensional helical crimp. This process may thus be used to achieve highly desirable bulking and/or texturizing effects when the material is in either the staple fiber, continuous filament yarn, or fabric form.

While the cellulose ester present in both dopes may be a secondary cellulose acetate having an acetyl value of under 56% calculated as combined acetic acid, it is preferably a cellulose acetate having an acetyl value of at least 59% by weight, most suitably at least 60% by weight, calculated as combined acetic acid, i.e., a cellulose "triacetate." It has been found that when the fiber-forming material is such cellulose triacetate, the saponification of the portion of the filament containing the quaternary ammonium salt, while leaving the portion not containing such salt unsaponified, may be very easily controlled. On the other hand, when the fiber-forming material is a cellulose acetate having an acetyl value of under 56%, e.g., 40 to 56%, calculated as combined acetic acid, i.e., a secondary cellulose acetate, the saponification of the portion containing the quaternary ammonium salt, while leaving the other portion substantially unsaponified or much less saponified, is much more difficult to control in view of the fact that secondary cellulose acetate is so readily saponified under mild alkaline conditions. However, although the process is more difficult to control with secondary cellulose acetate, it is nevertheless feasible.

In accordance with another aspect of the invention, one dope being extruded contains cellulose triacetate as the fiber-forming component and the other dope contains secondary cellulose acetate and the quaternary ammonium salt. Although this method does not have the advantage of requiring only a single dope, it does yield the advantage of substantially reducing the period required for saponification.

The dopes being extruded suitably contain about 15 to 30% by weight of cellulose ester, which, as stated above, may be the same or different in the two dopes. Preferably the solvent utilized in both dopes is composed of the same compounds, e.g. a halogenated hydrocarbon such as methylene chloride which may contain up to about 10 or 15% methanol. However, different solvents may be employed if different cellulose esters are being utilized, e.g. methylene chloride-methanol for cellulose triacetate and acetone for secondary cellulose acetate.

The quaternary ammonium salt which is incorporated into one portion of the dope being extruded, whether it contains a cellulose acetate which is the same or different from the other dope or dopes as described above, preferably quaternary ammonium halide, e.g. bromide or chloride, wherein at least one organic group is relatively long chain, e.g. has at least 8, preferably 10 to 20, carbon atoms, and is alkyl, aryl, alkaryl or aralkyl with any aliphatic groups being straight chain or branched. Up to three groups attached to the amine nitrogen of the quaternary salt are relatively short chain, e.g., contain no more than 7 carbon atoms and also may be alkyl, aryl, aralkyl or alkaryl, e.g. benzyl, and wherein the aliphatic segments may be straight or branch chain. At least two of the organic group of the quaternary ammonium salt are suitably methyl. Specific compounds which may be used are, for example, cetyl trimethyl

ammonium bromide and cetyl dimethyl benzyl ammonium bromide. The quaternary ammonium salt may be used in the dope, for example, in an amount of 0.5 to 10% by weight based on the fiber-forming material, e.g., cellulose triacetate or secondary cellulose acetate.

The saponification medium is preferably an aqueous solution of sodium hydroxide, e.g., having a concentration of 0.1 to 3.0% by weight of NaOH. However, other alkaline compounds may be used, e.g. alkali metal, alkaline earth metal or ammonium carbonates, borates, phosphates, silicates, and the like, can also be employed although they will have to be employed in greater amounts than the hydroxides because of their lesser alkalinity. The saponification liquid which is used may be at a temperature, for example, of 40 to 100° C., and the treatment may be carried out, for example, in a period of 15 to 120 minutes.

It is often desirable to incorporate into the alkaline material used to effect the saponification a small amount of an agent which increases the readiness with which the aqueous alkaline material wets the filaments. Suitable materials for this purpose are cresols or cresylic acids such as "Mercatex" or alkylated phenol-ethylene oxide condensation products known as "Triton X-100," "Igepon T" and "Igepal CA."

After the saponification treatment, the material may be subjected to further treatment using conventional procedures, e.g. washing, scouring, bleaching, dyeing, printing, etc.

The invention may be further illustrated by means of the accompanying drawing wherein:

FIGURE 1 illustrates apparatus for the practice of the invention wherein one spinning solution or dope is fed as a sheath about a core of the other dope, and either the core or sheath dope contains a quaternary ammonium salt and the other does not;

FIGURE 2 is a plan showing the face of the spinnerette used in the apparatus of FIGURE 1;

FIGURE 3 is a schematic illustration of apparatus arranged for dry spinning;

FIGURE 4 is an illustration of a typical cross-section of a bi-component filament prepared according to this invention.

Referring now to FIGURE 1, one dope is pumped into core dope tube 10 while the other dope is pumped through sheath dope tube 11, both tubes being supported by dope structuring head 12. As stated above, one of the dopes contains a quaternary ammonium salt while the other does not. The rates of flow of the dopes through tubes 10 and 11 are controlled by metering pumps (not shown) such that the flow of each dope is laminar or streamlined, rather than turbulent in character. Thus, when the dopes pass beyond the ends of tubes 10 and 11 through spinnerette dressing 13, they form a sheath 15 and a core 16 with an interface 17 coincident with core dope tube 10. The diameter of interface 17 constantly increases as it approaches the single circle of holes 20 in spinnerette plate 19. Spinnerette dressing 13 and spinnerette plate 19 are secured in place by spinnerette holder 22. The material being extruded from the spinnerette holes are composed of one portion of sheath dope 15 and one portion of core dope 16, which are converted by evaporation of the solvent into bi-component filaments.

The filamentary material of the invention may be formed by means of a dry spinning arrangement, as illustrated in FIGURE 3, wherein the two dopes are extruded through spinnerette plate 19 as described previously into dry spinning cabinet 40, into which hot air is admitted through conduit 41 and exhausted through conduit 42 along with vapors of the dope solvent. The filaments 30 pass about a guide 43 and leave the cabinet at 44 being pulled as a yarn 46 by draw rolls 47. The yarn 46 passes through a guide 49 and is twisted and taken up on a bobbin 50 by a conventional collector such as ring spinner 51.

Referring to FIGURE 4, the cross-section of the filament 30 obtained as a result of the process of this invention are composed of two different segments of fiber-forming material 60 and 61, one of which contains a quaternary ammonium salt and the other does not. This is easily determined by photomicrographs of the filament cross-section wherein one dope contains a coloring ingredient and the other does not, or the filament has been dyed with a dye which is substantive to the fiber-forming material of one segment but not that of the other.

The following examples further illustrate the invention.

Experiment A illustrates the production of a crimped filament in accordance with prior art techniques utilizing two spinning solutions or dopes containing different fiber-forming materials.

EXPERIMENT A

Two dopes were prepared in a mixture of 90% methylene chloride and 10% of methanol by weight as solvent, one containing 22.1% by weight of secondary cellulose acetate having an acetyl value of about 54.5%, while the other contains 21.9% by weight of cellulose triacetate having an acetyl value of about 61.5%, the acetyl values calculated as combined acetic acid. Using the apparatus of FIGURES 1 and 3, the cellulose triacetate dope was metered through core dope tube 10 while the cellulose secondary acetate was metered through sheath dope tube 11 at approximately equal rates such that 40 streams were extruded through 40 holes, each having a diameter of 36 microns, of spinnerette plate 19, arranged in a single circle into an evaporative atmosphere. The jet face temperature, i.e., temperature of spinnerette plate 19, was 70° C., while the temperature of the air in the vicinity of the downstream side of spinnerette plate 19 was 40° C. After substantial evaporation of the solvent, a 40 bi-component filament yarn was taken up at an initial take-up speed of 500 meters per minute. A microscopic examination of the filaments making up this yarn showed that each had a cross-section similar to that shown in FIGURE 3 with one portion being cellulose triacetate and the other being cellulose secondary acetate, the weight ratios of the components being about 1:1. This yarn was knitted into a double pique and was contacted with an aqueous solution of 0.5 weight percent of sodium hydroxide at a temperature of 85° C. for a period of 30 minutes. The fabric was then cooled and rinsed and immersed in a new bath containing 3 grams per liter of Marnel 82 and 4% based on the weight of the fabric of a disperse dye with a liquor-to-fabric ratio of 100 to 1, wherein it was allowed to remain for 2 hours at 95° C. The fabric was then extracted, loop dried at 275° C., rewet and tumble-dried. The fabric was found to develop a full bulk similar to that obtained with a secondary cellulose acetate or cellulose triacetate yarn alone, which was bulked by a mechanical treatment, e.g., false twisting.

The as-spun secondary cellulose acetate-cellulose triacetate bi-component filament yarn composed of about 50% by weight of each component had the following mechanical properties.

At 23° C. and 65% relative humidity:

Tenacity—1.39 grams per denier.

Elongation—31.7%.

Modulus—43.0 grams per denier.

At 95° C. and wet:

Tenacity—0.30 gram per denier.

Elongation—55.3%.

Modulus—8.1 grams per denier.

After the saponification treatment described above, the filaments are found by microscopic examination and testing with various kinds of dyes to be composed of cellulose triacetate substantially unmodified from the as-spun material and rayon formed by complete saponification of the secondary cellulose acetate in the same eccentric relationship in the filament cross-section as were the original sec-

ondary acetate and triacetate. This yarn had an overall acetyl value of 37.5% and a denier per filament of 4.53. Its mechanical properties were as follows.

At 23° C. and 65% relative humidity:

Tenacity—1.28 grams per denier.

Elongation—32.6%.

Modulus—36.7 grams per denier.

At 95° C. and wet:

Tenacity—0.35 gram per denier.

Elongation—44.3%.

Modulus—8.7 grams per denier.

The following example illustrates the process contemplated under this invention wherein the preparation of only a single dope with a single fiber-forming cellulose ester is required.

EXAMPLE I

A spinning solution or dope is prepared containing 20.2% by weight of cellulose triacetate having an acetyl value of 61.7% calculated as combined acetic acid dissolved in a solvent composed of a mixture of 90% by weight of methylene chloride and 10% by weight of methanol. This dope is separated into two portions in one of which is dissolved 4.5% based on the weight of the cellulose triacetate of trimethyl cetyl ammonium bromide. These two dopes, i.e., one containing trimethyl cetyl ammonium bromide while the other does not, were used to form filaments as described in Experiment A with the dope containing the ammonium salt being injected into sheath dope tube 11 while the unmodified dope is injected into core dope tube 10. The process is run so that approximately equal parts by weight of each dope are used.

The resulting yarn composed of 40 filaments each and having a total denier of about 200 is found to be composed of filaments having in their cross-section equal portions of cellulose triacetate arranged in eccentric relationship as shown in FIGURE 4, one portion of which contains trimethyl cetyl ammonium bromide dispersed throughout the cross-section while the other portion does not.

This yarn was knitted into a double pique knitted fabric which was subjected to the same saponification treatment as described in Experiment A except that the temperature of the saponification solution was 60° C. rather than 85° C. After further treating the fabric as described in Experiment A, it was found to develop a full bulk which was equivalent to that obtained by the fabric in Experiment A. Moreover, the saponified yarn of this example has mechanical properties equivalent to those of the saponified yarn described in Experiment A.

EXAMPLE II

The procedure of Example I is followed except that the quaternary ammonium salt used is cetyl dimethyl benzyl ammonium bromide in an amount of 5½ weight percent based on the triacetate. A bulked fabric is obtained similar to that obtained in Example I.

EXAMPLE III

The procedure of Example I is followed except that both dopes are solutions in acetone of 27 weight percent of secondary cellulose acetate having an acetyl value of 54.5% by weight calculated as combined acetic acid, the saponification solution contains 0.25 weight percent of sodium hydroxide and the saponification time is 15 minutes. A fully bulked fabric is obtained.

Although the preferred embodiments of the invention employ a single dope, as illustrated in Examples I to III, the process of the invention may also be carried out using two dopes each containing a different cellulose ester, e.g., the cellulose triacetate and secondary cellulose acetate shown in Experiment A with the secondary acetate dope containing quaternary ammonium salt. In this case, the advantage obtained is a much shorter saponification time than is necessary when no quaternary ammonium salt is

used to achieve equivalent bulking effects. The following example illustrates this procedure.

EXAMPLE IV

The procedure of Experiment A is followed except that the secondary acetate dope contains 2 weight percent of cetyl trimethyl ammonium bromide and the saponification time is only 10 minutes. A fully bulked fabric is obtained.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process comprising passing a spinning solution of a saponifiable cellulose ester containing a minor proportion of a quaternary ammonium salt and a spinning solution of a cellulose ester in the absence of said quaternary ammonium salt through separate zones, bringing streams of said solutions together at a common juncture under conditions such that substantially no mixing of said solutions takes place and passing a single stream containing separate portions of said solutions into an evaporative atmosphere for the solvent to form a filament composed of two portions of said cellulose ester in eccentric relationship, one portion containing said quaternary ammonium salt dispersed throughout while the other portion is free of said salt.

2. The process of claim 1 wherein said solutions are moving in laminar flow and are brought together at a common juncture to form a single stream having stream-

lined portions made up of said separate solutions, which single stream is advanced for a distance with substantially no mixing of the solutions prior to being extruded into said evaporative atmosphere.

3. The process of claim 1 wherein said cellulose ester is a cellulose acetate.

4. The process of claim 3 wherein said cellulose acetate is a cellulose triacetate having an acetyl value of at least 60.5% calculated as combined acetic acid.

5. The process of claim 4 wherein said cellulose triacetate is dissolved in a solvent comprising a major proportion of methylene chloride.

6. The process of claim 1 wherein said quaternary ammonium salt contains at least one organic group having at least eight carbon atoms.

7. The process of claim 6 wherein said quaternary ammonium salt is cetyl trimethyl ammonium bromide.

8. The process of claim 1, wherein the cellulose esters of said spinning solutions have the same average degree of substitution per unit.

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