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PROCESS FOR MANUFACTURING FIBERS AND THREADS FROM CELLULOSE TRIACETATE

Paul Ernst and Walter Fischer, Burghausen, Upper Bavaria, Germany, assignors to Celanese Corporation of America, New York, N.Y., a corporation of Delaware

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4 Claims. (Cl. 18—54)

This application is a continuation-in-part of application Serial No. 760,532, filed September 12, 1958, the disclosure of which is incorporated herein by reference.

This invention relates to producing fibers and threads from cellulose triacetate and it has for its object to provide a novel and improved process for this purpose.

Another object of the invention is to provide a simple and efficient process for producing cellulose triacetate fibers and threads having unusually high tensile strength as well as high extensibility and excellent transverse elasticity.

It is an object of the invention to permit spinning through a large number of orifices without interruption.

Other objects and advantages will become apparent from the following detailer description and claims wherein all parts are by weight unless otherwise specified.

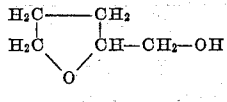
It is known to improve the relatively inferior strength of acetate fibers by stretching the threads or yarns during or after spinning, preferably while in a plastic condition. In this way resistance to tearing may be increased, but at the same time the transverse elastic properties are impaired. In particular, the stretchability is reduced, and the winding or looping strength becomes diminished.

We have now discovered a process for producing greatly improved fibers, threads and yarns from cellulose triacetate according to the wet spinning process, which have high extensibility, and excellent transverse elasticity and winding or looping strength. As a result of our process substantial advantages are obtained not only in the use of our improved product but also in processing same.

The process according to the preferred embodiment of the invention consists substantially in that a homogeneous solution of cellulose triacetate in a mixture of at least 90% methylene chloride and water-soluble monomeric glycols with 3–6 carbon atoms, their polymers and/or univalent alcohols with 1–4 carbon atoms, is spun into a homogeneous precipitation bath which comprises a mixture of not more than 70% of said glycols or the mentioned glycol derivatives, etc., as well as their mixtures, particularly semi-ethers, and the remainder of 10–15% methylene chloride as well as water. Suitable as glycols or their semi-ethers or polymers, are propanediol-1.2, 2-methylpentadiol-2.4, 3-methylpentanediol-2.4, di- and tri-ethyleneglycol, methyl- and ethylglycol as well as 3-methoxybutanol-1, as well as their mixtures.

It is preferable that the viscosity of the precipitant should not amount to more than 10 cps. and that it have a temperature of 25–40° C. The water content of said bath can only be so high that the methylene chloride is still clearly soluble; in this manner optional denier sizes, about 1–50 den., may be spun.

We have found that as semi-ether, tetrahydrofurfuryl alcohol may be employed with success in the precipitation bath in the wet spinning triacetate process. The tetrahydrofurfuryl alcohol employed,



is an interior semi-ether of the 1,4,5 pentanetriol and, under the conditions of our process, results in the production of fibers, threads and yarns having our desired high quality characteristics.

The fibers and threads of cellulose triacetate produced according to our invention correspond, with a tensile strength up to 2.5 g., with all textile requirements as regards superior elongation, cross elasticity, resistance to abrasion, winding strength, etc. A further advantage is the slight regenerative capacity of the precipitant bath, which need be heated at most to the boiling point of the water in order to recover the methylene chloride. The precipitant adhering to the fibers can be removed by washing with water without difficulty and in practice can be quantitatively recovered.

In accordance wtih another aspect of the invention it has been found that when employing spinnerettes having a large number of orifices an interruption in spinning occasionally results. This may be overcome by wet spinning into a coagulant comprising about 35 to 75% of a water-soluble glycol or derivative thereof, about 15 to 65% of methylene chloride and the balance water. Water-soluble glycols and derivatives which are employed in accordance with the invention include glycols having from 3 to 6 carbon atoms, polyglycols, ethers thereof, such as the semi-ether tetrahydrofurfuryl alcohol, or lower alkyl ethers thereof and/or esters thereof with lower fatty acids or inorganic acids.

Spinning is advantageously carried out at a temperature ranging from about 5 to 40° C. The viscosity of the coagulant advantageously is no more than about 10 centipoises and its composition and temperature are chosen accordingly.

To maintain the properties of the coagulant bath unchanged it is necessary to keep its composition from changing. During spinning a mixture rich in solvent is constantly being introduced into the coagulant thereby enriching the latter with solvent and tending to change its composition. In order to maintain the coagulant composition unchanged a mixture of glycol or derivative and water is continuously supplied to the coagulant, and simultaneously an appropriate amount of spent coagulant is withdrawn. Methylene chloride solvent is recovered from the withdrawn spent coagulant by distillation and the glycol-water residue is recirculated to the coagulant. The amount of spent coagulant which must be withdrawn is quite small as a result of the high methylene chloride content of the equilibrium coagulant and consequently recovery of methylene chloride is achieved more easily. The best fiber properties are achieved by selecting a coagulant composition close to the miscibility limit of the three components which are of limited miscibility, viz. glycols or derivatives, water and methylene chloride, since upon further addition of a relatively small amount of water or methylene chloride the coagulant mixture will separate to form two phases.

By operating in accordance with the invention it is possible to employ spinnerettes having more than 2000, e.g. 10,000 or more, orifices without interruption of spinning or clogging of the orifices.

The invention is further described in the following illustrative examples.

Example 1

A homogeneous mixture of 19 parts by weight of cellulose triacetate in a mixture of 5 parts by weight of 2-methylpentanediol-2.4 and 95 parts by weight of methylene chloride, which has a viscosity of about 100,000 cps. at 20° C., is spun through a nozzle with 1,000–2,000 apertures each of 0.07 mm. diameter with a speed of 20 m./minute in a precipitant at 35° C. which consists of 58.5 parts by weight of 2-methylpentanediol-2.4, 31.5 parts by weight of water, 10.0 parts by weight of methyl-

ene chloride. After the washing the threads are cut and dried. They have the following properties:

ET	den.	1.85
Tensile strength	g./den.	1.91
Elongation	percent	31.7
Abrasion resistance load 3 Fkm	turns	15,000
Winding strength	g./den.	1.18

Winding strength ratio 62% of the tensile strength.

In this and the other examples "abrasion resistance load 3 Fkm" means that in the determination of the abrasion resistance the load to be used is to be with a weight of 3 Fkm.

In all the examples all proportions of ingredients are by weight.

Example 2

17.9 parts of cellulose triacetate are dissolved in a mixture of 90 parts methylene chloride and 10 parts isopropanol. The solution is spun at room temperature and at a draw-off speed of 26 m./minute into a precipitant which consists of 63% of methoxybutanol-1, 27% water and 10% methylene chloride. The fiber obtained has the following values:

ET	den.	3.52
Tensile strength	g./den.	1.76
Elongation	percent	34.7
Abrasion resistance load 3 Fkm	turns	66,500

Winding strength ratio 53% of the tensile strength.

Example 3

A spinning solution of the composition 14.7 parts of cellulose triacetate, 90 parts methylene chloride, 5 parts of triethyleneglycol, and 5 parts methanol is spun from a nozzle with 48 holes of 0.07 mm. diameter into a bath consisting of 70 parts triethylene glycol, 30 parts water and 10 parts methylene chloride. The drawing off speed amounts to 20 meters per minute, the precipitation bath temperature 32° C. Washed and dried the yarn thus spun has the following characteristics:

ET	den.	1.17
Tensile strength	g./den.	2.40
Elongation	percent	23.9

Relative winding strength 47% of the tensile strength.

Example 4

In a mixture of 95 parts methylene chloride and 5 parts methanol there are dissolved 17.5 parts cellulose triacetate. The solution is spun at 32° C. into a precipitant, at a draw-off speed of 35 m./minute, the precipitant consisting of 45% ethyldigylcol, 45% water and 10% methylene chloride. The fiber obtained has the following characteristics:

ET	den.	2.32
Tensile strength	g./den.	2.14
Elongation	percent	49.3
Abrasion resistance load 3 Fkm	turns	32,000

Winding strength ratio 72% of the tensile strength.

Example 5

A solution of 14.7 parts of triacetate in 95 parts methylene chloride and 5 parts triethylene glycol is spun under the same spinning conditions as described in Example 3 in a precipitation bath consisting of 50 parts 2-methylpentanediol-2,4, 50 parts triethylene glycol, 30 parts water and 14.5 parts methylene chloride. The checking of the resulting individual yarns shows:

ET	den.	1.84
Tensile strength	g./den.	1.84
Elongation	percent	34.7

Relative winding strength 65.8% of the tensile strength.

Example 6

A homogeneous solution of 17.4 parts cellulose triacetate in 90 parts methylene chloride, 5 parts 2-methylpentanediol-2,4 and 5 parts methanol is spun in a precipitation bath at 32° C. consisting of 25 parts 2-methylpentanediol-2,4, 25 parts ethyldiglycol, 50 parts water and 7.5 parts methylene chloride. Examination of the individual yarns shows the following results:

ET	den.	2.13
Tensile strength	g./den.	2.03
Elongation	percent	37.1
Abrasion resistance load 3 Fkm	turns	46,000

Relative winding strength 65% of the tensile strength.

Example 7

A spinning solution composed of 14.7 parts cellulose triacetate, 91 parts methylene chloride, 3 parts 2-methylpentanediol-2,4, 3 parts diethylene glycol and 3 parts methanol is spun from a nozzle with 48 holes of 0.07 mm. diameter into a bath consisting of 54 parts 2-methylpentanediol-2,4, 35 parts water and 15 parts methylene chloride. Checking of the individual threads gives:

ET	den.	2.46
Tensile strength	g./den.	2.05
Elongation	percent	49.1

Relative winding strength 63% of tensile strength.

Example 8

14.7 parts cellulose triacetate is dissolved in a mixture of 90 parts methylene chloride, 5 parts diethylene glycol and 5 parts hexanediol-2,5 and spun in a bath composed of 25 parts hexanediol-2,5, 75 parts 3-methoxybutanol-1, 40 parts water and 15.5 parts methylene chloride. After the usual treatment of washing, drying and cutting the following characteristics are found on checking the individual yarns:

ET	den.	2.00
Tensile strength	g./den.	1.80
Elongation	percent	44.1

Relative winding strength 74% of tensile strength.

Example 9

A solution of 14.7 parts cellulose triacetate in 95 parts methylene chloride and 5 parts triethylene glycol is spun in a bath consisting of 50 parts triethylene glycol, 50 parts 3-methoxybutanol-1, 20 parts water and 13.3 parts methylene chloride. Yarns of the following characteristics result:

ET	den.	1.93
Tensile strength	g./den.	1.91
Elongation	percent	45.3

Relative winding strength 57% of tensile strength.

Example 10

A solution of 14.7 parts cellulose triacetate in 90 parts methylene chloride and 10 parts diethylene glycol is spun into a precipitation bath consisting of 60 parts ethyldiglycol, 40 parts 3-methoxybutanol-1, 70 parts water and 18.9 parts methylene chloride. The individual yarn tests reveal the following properties:

ET	den.	1.79
Tensile strength	g./den.	2.05
Elongation	percent	47.1

Relative winding strength 70% of tensile strength.

Example 11

The spinning solution described in Example 10 is spun into a precipitation bath composed of 30 parts diethylene

glycol, 70 parts methyldiglycol, 30 parts water and 14.4 parts methylene chloride. The resulting yarn tests show:

ET	den.	2.17
Tensile strength	g./den.	2.14
Elongation	percent	44.5

Relative winding strength 69% of tensile strength.

Example 12

A solution of 17.5 parts triacetate in 90 parts methylene chloride and 10 parts methanol is spun from a 48 hole nozzle of 0.07 mm. hole cross-section into a precipitating bath consisting of 45 parts tetrahydrofurfuryl alcohol, 45 parts water and 10 parts methylene chloride. The drawoff speed is 20 meters per minute. The precipitation bath temperature is 32° C. The washed and dried threads have the following properties:

ET	den.	2.22
Tensile strength	g./den.	2.06
Elongation	percent	34.3
Abrasion resistance load 3 Fkm	revolutions	75,000

Relative winding strength 68% of tensile strength.

Example 13

Under the conditions described in Example 12 a solution consisting of 20 parts cellulose triacetate in 90 parts methylene chloride and 10 parts 2-methylpentanediol-2,4 is spun into a precipitation bath composed of 40 parts tetrahydrofurfuryl alcohol, 30 parts 2-methylpentanediol-2,4, 30 parts water and 14 parts methylene chloride. Testing of the fibers gives:

ET	den.	2.88
Tensile strength	g./den.	2.31
Elongation	percent	33.4
Abrasion resistance load 3 Fkm	revolutions	62,000

Relative winding strength 72% of tensile strength.

Example 14

A solution such as described in Example 12 is spun into a precipitation bath consisting of 50 parts tetrahydrofurfuryl alcohol, 15 parts triethylene glycol, 35 parts water and 15 parts methylene chloride. The resulting threads reveal:

ET	den.	2.06
Tensile strength	g./den.	1.98
Elongation	percent	28.3
Abrasion resistance load 3 Fkm	revolutions	17,000

Relative winding strength 61% of tensile strength.

Example 15

As in Example 14 there is made a spinning into a precipitation bath consisting, in this case, of 50 parts tetrahydrofurfuryl alcohol, 15 parts 3-methoxybutanol, 35 parts water and 15 parts methylene chloride. Characteristics of the threads:

ET	den.	2.21
Tensile strength	g./den.	2.04
Elongation	percent	24.3

Relative winding strength 67% of tensile strength.

Example 16

The spinning solution of Example 12 is spun into a precipitation bath consisting of the following mixture: 30 parts tetrahydrofurfuryl alcohol, 45 parts ethyldiglycol, 25 parts water and 11 parts methylene chloride. The resulting threads test:

ET	den.	1.82
Tensile strength	g./den.	1.93
Elongation	percent	22.9

Relative winding strength 71% of tensile strength.

Example 17

A spinning solution of 1 part of cellulose triacetate, 3.76 parts of methylene chloride and 0.24 part by weight of methanol, which has a viscosity at 20° C. of 65,000 centipoises, is spun through a spinnerette with 2,000 apertures each of 0.07 mm. diameter into a coagulant made up of 55 parts of 2-methylpentanediol-2,4, 42 parts of methylene chloride and 3 parts of water. The temperature of the coagulant bath is 15° C. and the draw off speed of the filaments is 20 meters per minute. The filaments are continuously washed by a counter-current stream of water, are cut while still wet, lubricated and then dried.

The fiber obtained has the following properties:

Denier		1.59
Tenacity	grams per denier	2.11
Elongation	percent	16.1
Abrasion reisistance load 3 Fkm	turns	12,000
Relative loop tenacity	percent	44.5

Example 18

A spinning solution is produced of 1 part of cellulose triacetate, 4.01 parts of methylene chloride, 0.13 part of methanol and 0.13 part of 2-methylpentanediol-2,4, the solution having a viscosity of 37,000 centipoises at 20° C. The solution is spun through a ring-shaped spinnerette having 10,032 orifices each of 0.07 mm. diameter into a coagulant at 32° C. consisting of 50 parts of 2-methylpentanediol-2,4, 45 parts of methylene chloride and 5 parts of water. The resulting tow is treated as described in Example 17. The fiber obtained has the following properties:

Denier		2.16
Tenacity	grams per denier	1.87
Elongation	percent	23.5

Example 19

A spinning solution consisting of 1 part of cellulose triacetate, 3.01 parts of methylene chloride, and 0.34 part of methanol, having a viscosity of 55,000 centipoises at 20° C., is spun into a coagulant of the following composition at a temperature of 27° C.: 51 parts of ethyldiglycol having the formula $C_2H_5O—C_2H_4—O—C_2H_4—OH$, 38 parts of methylene chloride and 11 parts of water.

A tantalum spinnerette with 2,400 orifices each of 0.07 mm. diameter is employed. The draw off speed is 35 meters per minute. The fiber obtained has the following properties:

Denier		1.92
Tenacity	grams per denier	1.83
Elongation	percent	23.9
Relative loop tanacity	percent	83.1

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.

Having described our invention what we desire to secure by Letters Patent is:

1. The process which comprises wet spinning cellulose triacetate dissolved in methylene chloride into a coagulant comprising about 35 to 75% by weight of a water-soluble member selected from the group consisting of glycols containing about 3 to 6 carbon atoms, polyglycols, ethers thereof and esters thereof, about 15 to 65% by weight of methylene chloride and water to produce cellulose triacetate continuous filamentary material.

2. Process for producing filamentary cellulose tri-triacetate in a solvent comprising at least one member selected from the group consisting of water-soluble glycols containing from 3 to 6 carbon atoms, poly-lower alkylene glycols and monohydric alcohols containing from 1 to 4 carbon atoms and at least about 90% by weight of methylene chloride into a homogeneous coagulant comprising about 45 to 75% by weight of at least one member selected from the group consisting of water-soluble

glycols containing from 3 to 6 carbon atoms, semi-ethers of said poly-lower alkylene glycols, about 10 to 15% of methylene chloride and the balance water.

3. Process according to claim 2, in which the semi-ether is tetrahydrofurfuryl alcohol.

4. Process according to claim 2, in which the temperature of the precipitation bath tis 20–40° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,775,529 Bates ---------- Dec. 25, 1956

FOREIGN PATENTS

793,222 Great Britain ---------- Apr. 9, 1958
796,384 Great Britain ---------- June 11, 1958

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,081,145 March 12, 1963

Paul Ernst et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 65, strike out "acetate which comprises extruding a solution of cellulose" and insert the same after "tri-" in line 67, same column 6; column 7, line 7, for "tis" read -- is --

Signed and sealed this 28th day of April 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents