



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : D01F 2/30, 1/10, C08K 5/05 C08K 3/22 // C08L 1:12	A1	(11) International Publication Number: WO 93/13250 (43) International Publication Date: 8 July 1993 (08.07.93)
(21) International Application Number: PCT/US92/11208 (22) International Filing Date: 21 December 1992 (21.12.92) (30) Priority data: 816,338 31 December 1991 (31.12.91) US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventors: SEO, Kab, Sik ; 2413 Essex Drive, Kingsport, TN 37660 (US). LANDRY, Christine, Joanne ; 50 Havenwood Hollow, Fairport, NY 14450 (US). COLTRAIN, Bradley, Keith ; 95 South Ridge Trail, Fairport, NY 14450 (US). CLOYD, James, Dale ; P.O. Box 124, Jonesborough, TN 37659 (US).		(74) Agent: MONTGOMERY, Mark, A.; 343 State Street, Rochester, NY 14650-2201 (US). (81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CELLULOSE ESTER SHAPED ARTICLES FROM SOLUTIONS CAPABLE OF INCREASED PRODUCTION SPEEDS (57) Abstract An improved extrudable solution such as a cellulose acetate/acetone spinning solution is provided containing cellulose ester, solvent, metal oxide precursor, acid, and water. The solution is extruded such as by spinning and produces a shaped article such as a cellulose acetate fiber containing metal oxide interpenetrating networks.		

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- 1 -

5 Cellulose Ester Shaped Articles from
 Solutions Capable of Increased Production Speeds

Field of the Invention

10 The present invention relates to shaped articles
 such as fibers and films of cellulose esters. The
 present invention also relates to a production solution
 capable of producing the shaped articles at increased
 production speeds. The present invention also relates
15 to a process for producing these shaped articles from
 the production solution.

Background of the Invention

 Shaped articles such as fibers and films of
 cellulose esters produced by the extrusion of a
20 cellulose ester production solution are well known.
 Cellulose esters are produced from a cellulosic
 feedstock such as wood pulp or cotton linters. The
 cellulose ester is precipitated after acetylation and
 hydrolysis, is then washed and dried, and then
25 redissolved in cellulose ester solvents such as aqueous
 acetone, or methylene chloride/alcohol. This solution
 is then filtered to form a production solution. The
 shaped articles are then produced from this production
 solution or extrudable solution by solvent evaporation
30 techniques such as dry spinning to form fibers.

 High production speeds are very desirable in that
 more shaped product can be formed during a set period of
 time than at lower production speeds. This is
 particularly important for the production of cellulose
35 acetate fiber from a cellulose acetate/acetone dope
 solution by the dry spinning technique. Spinning speeds
 seem to be limited by the residence time required to

- 2 -

remove the solvent from the wet filaments through diffusion and evaporation, and by reduced strength of the spinline while large quantities of solvent are present. Spinning speeds are also limited by the presence of non-uniformities in the dope such as particles, rheological inhomogeneities etc. which interact with the bulk rheological properties of the dope and with the spinning conditions. Spinning speeds can be increased by incorporating appropriate additives or diluents to drop the viscosity of the cellulose acetate/acetone solution. For example U.S. 3,272,638 discloses the addition of sugar to the spinning solution to increase the spinning rate, and U.S. 4,418,026 discloses the addition of poly(ethylene) glycol to the spinning solution to improve the spinnability. The methods of increasing the dry spinning spinnability of cellulose acetate/acetone solution by changing the viscosity of the spinning solution is limited by the thread spinline or threadline strength of the spinning medium. U.S. 3,952,081 discloses an alternative method of increasing the spinning speed of cellulose acetate fibers that entails partially avoiding the dry spinning process by extruding a solution of cellulose acetate at elevated temperature and at elevated pressure precipitating out insoluble cellulose acetate to form the cellulose acetate filamentary material. Although this method may improve the spinning speed, different equipment would be needed since dry spinning at mild conditions is the current method of producing cellulose acetate fibers.

It would be very desirable to be able to further increase the production speed of cellulose ester shaped articles by solvent evaporation techniques at mild conditions. It would be particularly desirable to be able to increase the dry spinning speed of a cellulose

- 3 -

ester fiber beyond the speeds currently available limited by the current spinline strength.

Summary of the Invention

5 The extrudable solution of the present invention comprises a homogenous mixture of cellulose ester, solvent, metal oxide precursor, acid, and water. This extrudable solution can be extruded such as by dry casting or by dry spinning at significantly increased
10 speeds producing a shaped article containing metal oxide interpenetrating networks.

Detailed Description of the Invention

15 Applicants have unexpectedly discovered that by incorporating an amount of acid, water, and metal oxide precursor into an extrudable solution such as cellulose acetate/acetone spinning solution that the production speed is significantly increased without aggravating the tensile properties of the resulting materials. This
20 increased speed is believed to be the result of a reduction in viscosity of the production spinning solution, (below normal lower limits) while maintaining or increasing the concentration of cellulose esters and other non-volatiles in the spinning solution. Lower
25 viscosity and higher solids allow higher production rates without the need to alter equipment or production parameters. The present invention, while increasing production speeds, permits the use of the same gear pump speeds, piping configuration, acetone recovery, and
30 filtration equipment as used in the existing plant. The addition of the metal oxide precursor not only has a dilution effect on the spinning solution but it is believed that it also enhances the threadline strength through the in-situ polymerization of the metal oxide

- 4 -

precursor in the solution as it is extruded forming metal oxide interpenetrating networks.

The shaped articles produced according to the present invention are generally films and fibers such as reinforced films, yarn filaments, and cellulose acetate fibers for use in felt tip pens and air filters such as cigarette filters, etc.

The extrudable solution according to the present invention comprises a homogeneous mixture of:

- 10 (a) 10 to 40 weight percent cellulose ester based on the totals of (a), (b), and (c);
- (b) 40 to 90 weight percent cellulose ester solvent based on the totals of (a), (b), and (c);
- 15 (c) up to 30 weight percent metal oxide precursor, based on the totals of (a), (b), and (c), of the formula MX_n or MRX_{n-1} wherein M is silicon, titanium, boron, aluminum, zirconium, tin, germanium, tantalum, phosphorus, lead, arsenic, lanthanum, iron indium, copper, yttrium, barium, magnesium or mixtures thereof; R is alkyl or aryl of 1 to 20 carbon atoms; X is halogen, alkoxy, aryloxy, carboxy, or an $-NR'_2$ group in which R' is hydrogen, alkyl, or aryl; and n is the valence of the metal;
- 20 (d) acid, the molar ratio of acid expressed as hydronium ions H_3O^+ to mole metal oxide precursor being between 0.0005 and 0.02; and
- 25 (e) water, the molar ratio of water to metal oxide precursor being between 1 and 20;
- 30

wherein said solution has a zero-shear viscosity at 29°C between 100 and 10,000 poise (10 and 1000 Pa.s).

- 5 -

The process of producing the extrudable solution entails forming a mixture of (a) and (b); adding (c); and adding (d) and (e) as acid in aqueous solution.

This process comprises:

- 5 (i) forming a mixture of cellulose ester (a) and cellulose ester solvent (b);
- (ii) adding a metal oxide precursor (c) to form a homogeneous mixture of 10 to 40 weight percent (a), 40 to 90 weight
- 10 percent (b) and up to 30 weight (c) wherein said metal oxide precursor (c) is of the formula MX_n or MRX_{n-1} wherein M is silicon, titanium, boron, aluminum, zirconium, tin, germanium, tantalum,
- 15 phosphorus, lead, arsenic, lanthanum, iron, indium, copper, yttrium, barium, magnesium or mixtures thereof; R is alkyl or aryl of 1 to 20 carbon atoms; X is halogen, alkoxy, aryloxy, carboxy, or an
- 20 $-NR'_2$ group in which R' is hydrogen, alkyl, or aryl; and n is the valence of the metal; and
- (iii) adding an aqueous acid, the molar ratio of acid expressed as hydronium ions H_3O^+ to mole
- 25 metal oxide precursor being between 0.0005 and 0.02 and the molar ratio of water to metal oxide precursor being between 1 and 20;

 wherein said extrudable solution has a zero-shear viscosity at 29°C between and 100 and 10,000 poise (10

30 and 1000 Pa.s).

The process for producing the shaped articles such as cellulose acetate fiber comprises:

- (I) homogeneously mixing (a), (b), (c), (d), and (e) above to form a solution;
- 35 (II) filtering to form a spinning solution; and

- 6 -

(III) spinning said spinning solution at 200-1500 m/min at 25-60°C through spinneret holes having a hole area equivalent to a circular diameter of 25-100 microns and length to diameter ratio between 0.5 and 3, forming filaments with dry linear densities of 0.5 to 8 denier per filament and a total product denier of 10,000 to 50,000 denier.

The process of the present invention results in shaped articles such as cellulose ester fibers containing metal oxide interpenetrating networks. The cellulose esters in the extrudable solution of the present invention are cellulose acetates that preferably have a degree of substitution of 2 to 3 of acetyl and an inherent viscosity in acetone of 1.2 to 1.7 dl/gram. These cellulose acetates more preferably have a degree of substitution of 2.5 and an inherent viscosity of 1.5 dl/gram.

The extrudable solution according to the present invention contains 10 to 40 weight percent cellulose ester and 40 to 90 weight percent cellulose ester solvent. An amount much below 10 percent cellulose ester is ineffective in spinning and an amount over 40 weight percent cellulose ester is too viscous to extrude, spin, filter, and convey. This solution also contains up to 30 weight percent of the metal oxide precursor but preferably at least 1 percent. An amount of metal oxide precursor below 1 percent does not impart a significant increase in spinning speed where as an amount much over 30 weight percent is not economical and can cause an inhomogeneous spinning solution. The extrudable solution preferably contains 20 to 30 weight percent cellulose ester, 45 to 75 weight percent cellulose ester solvent, and 5 to 25 weight percent metal oxide precursor. The extrudable solution

- 7 -

according to the present invention more preferably contains 25 weight percent cellulose ester, 55 to 65 weight percent cellulose ester solvent, and 10 to 20 weight percent metal oxide precursor.

5 The cellulose ester solvents are preferably selected from polar solvents such as acetic acid, tetrahydrofuran, methylene chloride, and acetone. The most preferred cellulose ester/solvent mixtures are cellulose triacetate/methylene chloride/methanol, and
10 cellulose acetate/acetone/water.

 The metal oxide precursor is an energy rich metal organic precursor. It hydrolyzes with water such that the organic portion forms the more thermodynamically stable protonated species, such as an organic alcohol.
15 The multivalent metal forms an extensive metal oxide network such as a silicon oxide network in which each silicon atom is bonded to four oxygen atoms. The degree of interpenetration of the metal oxide network into the cellulose ester matrix is a function of the degree of
20 mixing and the reaction rate. The rate of conversion is increased by the addition of an appropriate level of acid catalyst, the proton of which being the major catalytic agent. The use of a metal oxide precursor is disclosed in U.S. Patent No. 5,010,128 the disclosure of
25 which is incorporated herein by reference. The metal oxide precursor is generally of the formula MX_n or MRX_{n-1} wherein M is silicon, titanium, boron, aluminum, zirconium, tin, germanium, tantalum, phosphorus, lead, arsenic, lanthanum, iron, indium, copper, yttrium,
30 barium, magnesium or mixtures thereof; R is alkyl or aryl of 1 to 20 carbon atoms; X is halogen, alkoxy, aryloxy, carboxy, or an $-NR'_2$ group in which R' is hydrogen, alkyl, or aryl; and n is the valence of the metal. The metal oxide precursor is preferably a
35 silicon, titanium, zirconium, or aluminum oxide

- 8 -

precursor with silicon oxide precursor being most preferred. The metal oxide precursor is preferably a metal alkoxide. The metal alkoxide can also contain an aryl group. The alkyl group of the metal alkoxide is preferably selected from, methyl, ethyl, and propyl. The more preferred metal alkoxides are selected from tetraethoxysilane, tetramethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, aminopropyltriethoxysilane, and propyltriethoxysilane.

10 The amount of acid incorporated in the extrudable solution of the present invention is a ratio depending upon the content of metal oxide precursor. The molar ratio of acid is expressed as moles of H_3O^+ to moles of metal oxide precursor and is between 0.0005 and 0.02 more preferably between 0.001 and 0.01 with between 0.002 and 0.008 being most preferred. The amount of water used in the solution of the present invention is preferably expressed as a molar ratio depending upon the amount of metal oxide precursor present. This molar ratio of water to metal oxide precursor is between 1 and 20 preferably between 1 and 10 with between 2 and 4 being most preferred. The total amount of water present in the solution can also be expressed as a percentage based on the total and is up to 10 weight percent preferably 1 to 10 weight percent with 2 to 8 weight percent being most preferred. At least a portion of the water needed in the present invention can be added with the undried cellulose ester and solvent, the remainder of the water being added with the acid. Water is required by the present invention and water by itself lowers the viscosity, but also reduces the strength of the undried extruded material.

35 The extrudable solution of the present invention can have a viscosity that is below the normal lower limits at which unmodified parent solution can be

- 9 -

extruded or spun without breaks in the extruded material or premature fusing of filaments spun from spinnerets of high hole density. It is believed that the lower viscosity permits the increased production speed at the same or higher polymer concentration and the increased strength of the extruded material results from the interpenetrating networks formed around the cellulose ester molecules during extrusion. This extrudable solution generally has a zero shear viscosity at 29°C between 100 and 10,000 poise (10 and 1000 Pa.s). The extrudable solution is preferably a spinning solution that has a zero shear viscosity at 29°C between 200 and 4,000 poise (20 and 400 Pa.s) more preferably between 300 and 3,000 poise (30 and 300 Pa.s). This viscosity is most preferably between 800 and 1,200 poise (80 and 120 Pa.s) when using 2 jets in the heating cabinet and between 1,800 and 2,500 poise (180 and 250 Pa.s) when using 1 jet in the heating cabinet.

The extrudable solution of the present invention is prepared by adding the materials and sufficiently mixing the materials to produce a homogenous mixture. Any method of mixing is considered to be useful, however mixing cellulose ester/solvent first and then adding metal oxide precursor and aqueous acid is more preferred. The extrudable solution also contain the conventional additives including pigments such as TiO_2 .

The process of extruding or spinning the solution of the present invention is conducted at a speed of 200 to 1,500 meter/min preferably 500 to 1,000 meter/min with 620 meter/min being more preferred due to the limits of currently available baling equipment. The spinning of the solution of the present invention is conducted at a temperature of 25 to 60°C preferably 45 to 55°C with 53°C being most preferred due to the boiling point of the solvent at atmospheric pressure.

- 10 -

The spinning solution of the present invention can be spun through holes in spinnerets of various shapes. These spinneret holes have a preferred area equivalent to a circular diameter of 25 to 100 μm . This means that
5 the area covered by a cross-section of the hole is equivalent to the area of a circular hole having a diameter of 25 to 100 μm . This diameter is more preferably 30 to 70 μm . These holes also have a preferred length-to-diameter ratio of 0.5 to 3 more
10 preferably 0.5 to 1.

After the fibers are spun the fibers are treated as conventional fibers. The fibers can be lubricated, dried and subjected to standard post processing.

The extrudable solution of the present invention is
15 particularly useful in spinning cellulose acetate/acetone solutions to produce cellulose acetate fibers containing metal oxide interpenetrating networks. These metal oxide interpenetrating networks are formed from the metal oxide precursors.

20 The resulting fibers of the present invention have an increased elongation when compared to normal unmodified fibers. This elongation is at least 15 percent, more preferably at least 20 percent with 25 to 30 percent being most preferred. Percent elongation is
25 based on the length of acetate yarn fibers.

The following examples are intended to illustrate the present invention but are not intended to limit the reasonable scope thereof.

- 11 -

EXAMPLES

Maximum takeup speed is determined by a takeup roll with 3.1 in. (7.87 cm) diameter positioned at 32 in. (81 cm) below the spinning capillary.

5 Tenacity of the spun fiber is determined by ASTM Method D3822-90 with 1 in. (2.54 cm) gauge length and 0.4 in./min (1 cm/min) extension rate.

10 Elongation of the spun fiber is determined by ASTM Method D3822-90 with 1 in. (2.54 cm) gauge length and 0.4 in./min (1cm/min) extension rate.

Example 1 (Control)

A spinning solution having an inherent viscosity of 1.52 dl/gram containing approximately 26 grams of undried cellulose acetate (degree of substitution 2.50) and 74 grams of acetone was mixed by rolling the jar on a roll mixer for several days or until a homogeneous solution was obtained. The solution prepared thereby was spun at 29°C on a capillary rheometer with a capillary of 0.027 in. (0.69 mm) diameter and 0.135 in. (3.4 mm) length. The shear rate inside the capillary was 750 sec⁻¹. The maximum takeup speed of the unmodified spinning solution was 75 ft/min (381 m/s). The tenacity was 0.91 g/denier and the elongation was 16.8 %. Viscosity of this solution was 154 poise (15.4 Pa.s) at 750 sec⁻¹.

Example 2

A spinning solution containing approximately 26 grams of cellulose acetate in 74 grams of acetone as prepared in Example 1, was mixed with 26 grams of tetraethoxysilane containing 4.5 milliliters of a 0.1 N hydrochloric acid solution. The final solution was mixed by rolling the jar on a roll-mixer for at least one day. The solution prepared thereby was spun at 29°C

- 12 -

on a capillary rheometer with a capillary of 0.027 inch (0.69 mm) diameter and 0.135 inch (3.4 mm) length. The shear rate inside the capillary was 750 sec^{-1} . The maximum takeup speed of the spinning solution modified with tetraethoxysilane was 250 ft/min (1270 m/s) which is a 230 % increase from the spinning speed of unmodified parent spinning solution which was 75 ft/min (381 m/s). The tenacity of the fiber from this modified solution was 0.88 g/denier, comparable to 0.91 g/denier for the unmodified parent solution. The elongation of the fiber from the modified solution was 24.5 % while that for the parent solution was 16.8 %. Viscosity of this spinning solution was 88 poise (8.8 Pa.s) at 750 sec^{-1} .

Example 3

A spinning solution containing approximately 26 grams of cellulose acetate in 74 grams of acetone as prepared in Example 1 was mixed with 1.4 grams of tetraethoxysilane containing 0.5 milliliter of a 0.1 N hydrochloric acid solution. The final solution was mixed by rolling the jar on a roll-mixer for at least one day. The solution prepared thereby was spun at the same conditions as in Example 1. The maximum takeup speed of this modified spinning solution was 80 ft/min (406 m/s) which is a 7 % increase from the spinning speed of unmodified parent spinning solution. The tenacity of the fiber from this solution was 0.80 g/denier and elongation was 17.5 %. Viscosity of this spinning solution was 146 poise (14.6 Pa.s) at 750 sec^{-1} .

- 13 -

Example 4

A spinning solution containing approximately 26 grams of cellulose acetate in 74 grams of acetone as prepared in Example 1 was mixed with 26 grams of tetramethoxysilane containing 4.5 milliliters of a 0.1 N hydrochloric acid solution. The final solution was mixed by rolling the jar on a roll-mixer for at least one day. The solution prepared thereby was spun at the same conditions as in Example 1. The maximum takeup speed of this modified spinning solution was 185 ft/min (940 m/s) which is a 147 % increase from the spinning speed of unmodified parent spinning solution. The tenacity of the fiber from this solution was 0.83 g/denier and elongation was 18.3 %. Viscosity of this spinning solution was 95 poise (9.5 Pa.s) at 750 sec⁻¹.

Example 5

A spinning solution containing approximately 26 grams of cellulose acetate in 74 grams of acetone as prepared in Example 1 was mixed with 26 grams of phenyltriethoxysilane containing 4.5 milliliters of a 0.1 N. hydrochloric acid solution. The final solution was mixed by rolling the jar on a roll-mixer for at least one day. The solution prepared thereby was spun at the same conditions as in Example 1. The maximum takeup speed of this modified spinning solution was 180 ft/min (914 m/s) which is a 140 % increase from the spinning speed of unmodified parent spinning solution. The tenacity of the fiber from this solution was 0.89 g/denier and the elongation was 17.9 %. Viscosity of this spinning solution was 95 poise (9.5 Pa.s) at 750 sec⁻¹.

- 14 -

Example 6 (Comparative - no acid)

A spinning solution containing approximately 26 grams of cellulose acetate in 74 grams of acetone as prepared in Example 1 was mixed with 2.9 grams of tetraethoxysilane only. The solution was mixed by rolling the jar on a roll-mixer for at least one day. The solution prepared thereby would not spin at the same spinning condition as in Example 1.

10 Example 7 (Comparative - no tetraethoxysilane)

A spinning solution containing approximately 26 grams of cellulose acetate in 74 grams of acetone as prepared in Example 1 was mixed with 4.5 milliliters of a 0.1 N hydrochloric acid solution. The solution was mixed on a roll-mixer for at least one day. The solution prepared thereby was spun at the same condition as in Example 1. The maximum takeup speed was 70 ft/min (356 m/s) which is 7% decrease from the spinning speed of unmodified parent spinning solution.

20

Example 8 (Comparative - prepolymerized silicon oxide)

A spinning solution containing 26 grams of cellulose acetate and 74 grams of acetone as prepared in Example 1 was homogeneously mixed with 20 grams of polyphenylpropyl silsesquioxane (obtained from Hüls Chemical) containing 73 mole % phenylsilicon oxide and 27 mole % propylsilicon oxide. The solution prepared thereby did not improve the spinning speed from that of the unmodified solution described in Example 1. The tenacity of the fiber spun from this solution was 0.64 g/denier and the elongation was 12.33 g/denier.

- 15 -

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and
5 scope of the invention.

- 16 -

Claims

1. An extrudable solution comprising a homogeneous mixture of

- 5 (a) 10 to 40 weight percent based on the totals of (a), (b), and (c), cellulose ester;
- (b) 40 to 90 weight percent based on the totals of (a), (b), and (c), cellulose ester solvent;
- 10 (c) up to 30 weight percent based on the total of (a), (b), and (c), metal oxide precursor of the formula MX_n or MRX_{n-1} wherein M is silicon, titanium, boron, aluminum, zirconium, tin, germanium, tantalum, phosphorus, lead, arsenic, lanthanum, iron, indium, copper, yttrium, barium, magnesium or mixtures thereof; R is alkyl or aryl of 1 to 20 carbon atoms; X is halogen, alkoxy, aryloxy, carboxy, or an $-NR'_2$ group in which R' is hydrogen, alkyl, or aryl; and n is the valence of the metal;
- 15 (d) acid, the molar ratio of acid expressed as hydronium ions H_3O^+ to mole metal oxide precursor being between 0.0005 and 0.02; and
- 20 (e) water, the molar ratio of water to metal oxide precursor being between 1 and 20;
- 25 wherein said solution has a zero-shear viscosity at 29°C between 100 and 10,000 poise (10 and 1000 Pa.s).

2. The composition according to Claim 1 wherein

30 said homogeneous mixture contains between 20 to 30 weight percent cellulose acetate, 45 to 75 weight percent acetone, and 5 to 25 weight percent metal oxide precursor.

- 17 -

3. The composition according to Claim 1 wherein the metal of said metal oxide precursor is selected from silicon, titanium, zirconium and aluminum.

5 4. The composition according to Claim 3 wherein said metal is silicon.

5. The composition according to Claim 1 wherein said metal oxide precursor is a metal alkoxide.

10

6. The composition according to Claim 5 wherein at least one group in said metal alkoxide is selected from methyl, ethyl and propyl.

15 7. The composition according to Claim 5 wherein said metal alkoxide is selected from tetraethoxysilane, tetramethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, aminopropyltriethoxysilane and propyltriethoxysilane.

20

8. The composition according to Claim 1 wherein said solution is a spinning solution that has a zero-shear viscosity at 29°C between 300 and 3000 poise (30 and 300 Pa.s)

25

9. A process of producing an extrudable solution comprising;

- (i) forming a mixture of cellulose ester (a) and cellulose ester solvent (b);
- 30 (ii) adding a metal oxide precursor (c) to form a homogeneous mixture of 10 to 40 weight percent (a) 40 to 90 weight percent (b) and up to 30 weight percent (c) wherein said metal oxide precursor (c) is of the formula MX_n or MRX_{n-1}
- 35 wherein M is silicon, titanium, boron,

- 18 -

- aluminum, zirconium, tin, germanium, tantalum, phosphorus, lead, arsenic, lanthanum, iron, indium, copper, yttrium, barium, magnesium or mixtures thereof; R is alkyl or aryl of 1 to 20 carbon atoms; X is halogen, alkoxy, aryloxy, carboxy, or an $-NR'_2$ group in which R' is hydrogen, alkyl, or aryl; and n is the valence of the metal ; and
- (iii) adding an aqueous acid solution, the molar ratio of acid expressed as hydronium ions H_3O^+ to mole metal oxide precursor being between 0.0005 and 0.02 and the molar ratio of water to metal oxide precursor being between 1 and 20;
- wherein said extrudable solution has a zero-shear viscosity at 29°C between and 100 and 10,000 poise (10 and 100 Pa.s).

10. The process according to Claim 9 further comprising filtering the extrudable solution.

11. An article of manufacture comprising cellulose ester fibers containing metal oxide interpenetrating networks.

12. The article of manufacture according to Claim 11 wherein said cellulose ester fibers are cellulose acetate fibers.

- 19 -

13. The article of manufacture according to Claim 12 wherein said metal oxide interpenetrating networks are prepared from metal oxide precursors selected from tetraethoxysilane, tetramethoxysilane, phenyltriethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, aminopropyltriethoxysilane and propyltriethoxysilane.

14. The article of manufacture according to Claim 12 wherein said fibers have an elongation of at least 15%.

15. A process for the production of cellulose acetate fibers comprising:

- (I) homogeneously mixing to form a solution
- (a) 10 to 40 weight percent based on the totals of (a), (b), and (c), cellulose acetate;
 - (b) 40 to 90 weight percent based on the totals of (a), (b), and (c), acetone;
 - (c) up to 30 weight percent based on the totals of (a), (b), and (c), metal oxide precursor of the formula MX_n or MRX_{n-1} wherein M is silicon, titanium, boron, aluminum, zirconium, tin, germanium, tantalum, phosphorus, lead, arsenic, lanthanum, iron, indium, copper, yttrium, barium, magnesium or mixtures thereof; R is alkyl or aryl of 1 to 20 carbon atoms; X is halogen, alkoxy, aryloxy, carboxy, or an $-NR'_2$ group in which R' is hydrogen, alkyl, or aryl; and n is the valence of the metal;

- 20 -

- (d) acid, the molar ratio of acid expressed as hydronium ions H_3O^+ to mole metal oxide precursor being between 0.0005 and 0.02; and
- 5 (e) water, the molar ratio of water to metal oxide precursor being between 1 and 20 wherein said solution has a zero-shear viscosity at 29°C between 200 and 4,000 poise (20 and 400 Pa.s);
- 10 (II) filtering to form a spinning solution; and
(III) spinning said spinning solution at a solution temperature of 25-60°C at 200-1,500 meter/min through spinneret holes having a hole area equivalent to a circular diameter of 25-100 μm
- 15 and length to diameter ratio of 0.5 to 3, forming filaments with dry linear densities of 0.5 to 8 denier per filament and a total product denier of from 10,000 to 50,000 denier.

20

16. The process according to Claim 15 wherein the solution temperature is 45-55°C and the spinning speed is 500-1000 meter/min.

- 25 17. The process according to Claim 15 wherein said spinning solution contains 20 to 30 weight percent cellulose acetate, 45 to 75 weight percent acetone, and 10 to 30 weight percent metal oxide precursor.

- 30 18. The process according to Claim 15 wherein said metal oxide precursor is a metal alkoxide selected from tetraethoxysilane, tetramethoxysilane, phenyltriethoxysilane, methyltriethoxysilane, aminopropyltriethoxysilane and propyltriethoxysilane.

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INTERNATIONAL SEARCH REPORT

PCT/US 92/11208

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D01F2/30; D01F1/10; C08K5/05; C08K3/22 //C08L1:12		
II. FIELDS SEARCHED		
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Classification System	Classification Symbols	
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	WO,A,9 109 080 (EASTMAN KODAK COMPANY) 27 June 1991 see the whole document ---	1-18
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 56 (C-214)14 March 1984 & JP,A,58 213 620 (ASAHI GLASS KK) 12 December 1983 see abstract ---	1-18
P,A	DATABASE WPIL Section Ch, Week 9244, Derwent Publications Ltd., London, GB; Class A, AN 92-360917 & JP,A,4 261 437 (MITSUBISHI RAYON CO., LTD.) 17 September 1992 see abstract --- -/--	1-18
¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 15 APRIL 1993		Date of Mailing of this International Search Report 17.05.93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer TARRIDA TORRELL J.B.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
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The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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