

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

02 March 2023 (02.03.2023)



(10) International Publication Number

WO 2023/027910 A1

(51) International Patent Classification:

D01D 1/02 (2006.01)

D01F 2/30 (2006.01)

Published:

— with international search report (Art. 21(3))

(21) International Application Number:

PCT/US2022/040390

(22) International Filing Date:

16 August 2022 (16.08.2022)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/260,580

26 August 2021 (26.08.2021)

US

(71) Applicant: EASTMAN CHEMICAL COMPANY

[US/US]; 200 South Wilcox Drive, Kingsport, TN 37660 (US).

(72) Inventors: SHELBY, Marcus, David; 390 Whispering Haven Road, Fall Branch, TN 37656 (US). STEWART, Mark, Edward; 1104 Dover Drive, Kingsport, TN 37664 (US). MAINE, James, Collins; 407 Deerfield Circle, Church Hill, TN 37642 (US). DORTON, Tanner, Storm; 921 Fox Avenue, Big Stone Gap, VA 24219 (US). ALLEN, John, Michael; 3917 George Court, Kingsport, TN 37660 (US). LI, Yong; 1139 Cliffview Circle, Johnson City, TN 37615 (US).

(74) Agent: EVERETT, Stuart, C.; P.O. Box 511, Kingsport, TN 37660 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: DRY SPINNING OF CELLULOSE ACETATE FIBER

(57) Abstract: A dry spinning system and process are used to produce cellulose ester fibers. The process utilizes one or more of N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, or mixtures thereof as the dissolution solvent. The process minimizes or avoids discoloration of the fibers.

WO 2023/027910 A1

## DRY SPINNING OF CELLULOSE ACETATE FIBER

### FIELD OF THE INVENTION

5 [0001] The present application is generally related to the spinning of fibers. More particularly, the present application is generally related to the dry spinning of cellulose esters into fibers.

### BACKGROUND OF THE INVENTION

10 [0002] Cellulose acetate fibers are traditionally dry spun using acetone as the spinning solvent. As the market for filament has grown, there has been a need to increase spinning capacity, however, adding new production lines is quite expensive given the need for solvent recovery, capital expense, etc. A cost-effective alternative would be to use idled dry spinning capacity that is available in the acrylic and urethane fiber  
15 markets. However, those technologies involve the use of DMF (N,N-dimethylformamide) or DMAc (N,N-dimethylacetamide) as the solvent. While a very effective solvent, DMF requires much higher operating temperatures than acetone due to its higher boiling point. These higher operating temperatures, in turn, lead to degradation of the cellulose acetate and/or the DMF, which can cause unacceptable yellowness in the  
20 fiber. Thus, there is a need for dry spinning processes using DMF that result in less color formation.

### SUMMARY OF THE INVENTION

25 [0003] The disclosure provides a process for producing a cellulose ester fiber, where the process comprises dry spinning a cellulose ester dope through a spinneret to make one or more of the fibers. The cellulose ester dope comprises at least 35% by weight on a solids basis of cellulose ester dissolved or dispersed in a solvent chosen from N,N-  
30 dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, or mixtures thereof. If the solvent comprises N,N-dimethylacetamide:

- (i) the cellulose ester dope comprises not more than 50% by weight acetone, based on the total weight of the cellulose ester dope; or
- (ii) the cellulose ester dope comprises 0% by weight cellulose nanocrystals; or
- (iii) both (i) and (ii),

The combined weight of any polyurethanes, polyolefins, nylons, polyesters, and/or polyurethaneureas that might be present in the cellulose ester dope is not more than 60% by weight, based on the total solids in the cellulose ester dope.

**[0004]** The disclosure also provides a process for producing a cellulose ester fiber where the process comprises dry spinning a cellulose ester dope through a spinneret to make one or more of the fibers. The cellulose ester dope comprises a cellulose ester dissolved or dispersed in a solvent chosen from N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, or mixtures thereof. If the solvent comprises N,N-dimethylacetamide:

- (i) the cellulose ester dope comprises not more than 50% by weight acetone, based on the total weight of the cellulose ester dope; or
- (ii) the cellulose ester dope comprises 0% by weight cellulose nanocrystals; or
- (iii) both (i) and (ii);

The cellulose ester dope comprises not more than 10% by weight polyurethanes, and not more than 50% by weight acrylonitrile-vinyl acetate copolymer, both based on the total solids in the cellulose ester dope. The combined weight of any polyurethanes, polyolefins, nylons, polyesters, and/or polyurethaneureas that might be present in the cellulose ester dope is not more than 60% by weight, based on the total solids in the cellulose ester dope.

**[0005]** The disclosure also provides a cellulose ester fiber formed according to one or both of the above processes.

**[0006]** The disclosure further provides a yarn, article, woven article, nonwoven article, staple fiber, and/or knitted textile comprising the

cellulose ester fiber formed according to one or both of the above processes.

### DETAILED DESCRIPTION

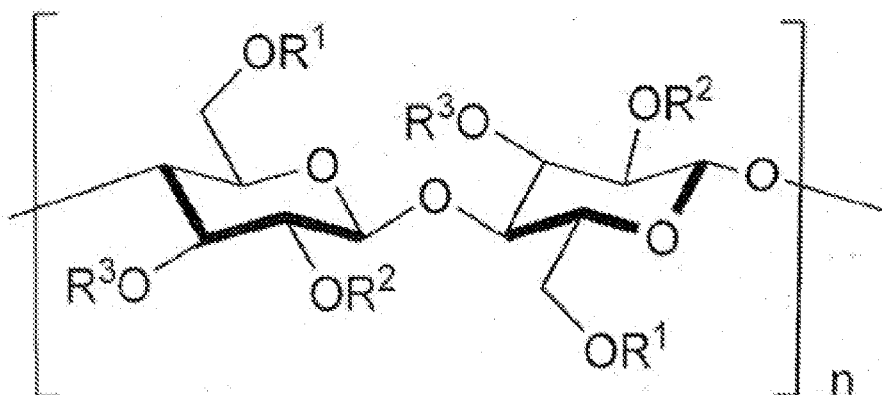
5       **[0007]**     The present application generally relates to a dry spinning process for preparing a cellulose diacetate (“CDA”) fiber and/or a cellulose triacetate (“CTA”) fiber that exhibits low color formation. Such fibers can be utilized in expanded application opportunities in downstream fiber converting and end use apparel applications. Furthermore, such cellulose ester fibers may be produced by using a dry spinning process. In this process, the cellulose ester is at least partially dissolved in a solvent (e.g., N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, and mixtures thereof), and the resulting dope is extruded through a small spinneret orifice into a spinning cabinet where the solvent is flashed off.

10       **[0008]**     At least one cellulose ester and at least one dissolution solvent may be introduced into a dope mixer so as to form the cellulose ester dope. The dope mixer can comprise any conventional device capable of mixing the cellulose ester and the dissolution solvent. Exemplary dope mixers can include a continuous stirred tank reactor (“CSTR”). While in the dope mixer, the cellulose ester and solvent can be subjected to temperature and mixing conditions that facilitate the dissolution of the cellulose ester into the dissolution solvent, thereby forming the cellulose ester dope.

15       **[0009]**     In one embodiment or in combination with any other mentioned embodiments, the cellulose ester dope can comprise a solids content of at least 15%, at least 16%, at least 17%, at least 18%, at least 19%, at least 20%, at least 21%, at least 22%, or at least 23% by weight and/or not more than 35%, not more than 34%, not more than 33%, not more than 32%, not more than 31%, not more than 30%, not more than 29%, or not more than 28% by weight, based on the total weight of the dope. For example, the cellulose ester dope can comprise a solids content in the range of 15% to 35%, 16% to 34%, 17% to 33%, 17% to 22%, 18% to

32%, 19% to 31%, 20% to 31%, 21% to 30%, 22% to 29%, or 23% to 28% by weight, based on the total weight of the dope.

**[0010]** The cellulose ester can include any cellulose ester known in the art, and particularly those that contain an acetyl group. Cellulose esters that can be used for the present invention generally comprise repeating units of the structure:



wherein  $R^1$ ,  $R^2$ , and  $R^3$  are selected independently from the group consisting of hydrogen or straight chain alkanoyls having from 2 to 10 carbon atoms. Exemplary alkanoyls include acetyl, propionyl, and/or butyryl.

**[0011]** For cellulose esters, the substitution level is usually expressed in terms of degree of substitution (“DS”), which is the average number of non-OH substituents per anhydroglucose unit (“AGU”). Generally, conventional cellulose contains three hydroxyl groups in each AGU unit that can be substituted; therefore, DS can have a value between zero and three. However, low molecular weight cellulose esters can have a total degree of substitution slightly above 3 due to end group contributions. Because DS is a statistical mean value, a value of 1 does not assure that every AGU has a single substituent. In some cases, there can be unsubstituted AGU’s, some with two and some with three substituents. The “Total DS” is defined as the average number of all of substituents per AGU and typically the value will be a non-integer. The degree of substitution per AGU can also refer to a particular substituent, such as, for example, hydroxyl, acetyl, butyryl, or propionyl.

**[0012]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester comprises a  $DS_{\text{acetyl}}$  of at least 1.5, at least 1.55, at least 1.6, at least 1.65, at least 1.7, at least 1.75, at least 1.8, at least 1.85, at least 1.9, at least 1.95, at least 2.0, at least 2.05, at least 2.1, at least 2.15, at least 2.2, at least 2.25, at least 2.3, at least 2.35, or at least 2.38 and/or not more than 2.95, not more than 2.9, not more than 2.8, not more than 2.7, not more than 2.6, not more than 2.55, not more than 2.5, or not more than 2.45. In certain embodiments, the cellulose ester may comprise a  $DS_{\text{acetyl}}$  in the range of 2.6 to 2.95, 2.7 to 2.95, 1.5 to 2.6, 1.6 to 2.6, 1.7 to 2.6, 1.8 to 2.6, 1.9 to 2.6, 2.0 to 2.6, 2.05 to 2.6, 2.1 to 2.6, 2.15 to 2.6, 2.2 to 2.6, 2.25 to 2.55, 2.3 to 2.5, or 2.38 to 2.45.

**[0013]** Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester comprises a  $DS_{\text{OH}}$  of at least 0.05, at least 0.1, at least 0.2, at least 0.3, at least 0.4, or at least 0.5 and/or not more than 1.5, not more than 1.4, not more than 1.3, not more than 1.2, not more than 1.1, or not more than 1.0. In certain embodiments, the cellulose ester comprises a  $DS_{\text{OH}}$  in the range of 0.05 to 1.5, 0.1 to 1.5, 0.2 to 1.4, 0.3 to 1.2, 0.4 to 1.1, or 0.5 to 1.0.

**[0014]** Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester comprises a  $DS_{\text{butyryl}}$  of at least 0.1, at least 0.2, or at least 0.3 and/or not more than 1.5, not more than 1.4, not more than 1.3, not more than 1.2, not more than 1.1, not more than 1.0, not more than 0.9, not more than 0.8, not more than 0.7, not more than 0.6, not more than 0.5, or not more than 0.4. In certain embodiments, the cellulose ester comprises a  $DS_{\text{butyryl}}$  in the range of 0.1 to 1.5, 0.1 to 1.2, 0.1 to 0.8, 0.1 to 0.4, 0.2 to 1.5, 0.2 to 1.2, 0.2 to 0.8, 0.2 to 0.4, 0.3 to 1.5, 0.3 to 1.2, 0.3 to 0.8, or 0.3 to 0.6.

**[0015]** Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester comprises a  $DS_{\text{propionyl}}$  of at least 0.1, at least 0.2, or at least 0.3 and/or not more than 1.5, not more than 1.4, not more than 1.3, not more than 1.2,

not more than 1.1, not more than 1.0, not more than 0.9, not more than 0.8, not more than 0.7, not more than 0.6, not more than 0.5, or not more than 0.4. In certain embodiments, the cellulose ester comprises a DS<sub>propionyl</sub> in the range of 0.1 to 1.5, 0.1 to 1.2, 0.1 to 0.8, 0.1 to 0.4, 0.2 to 1.5, 0.2 to 1.2, 0.2 to 0.8, 0.2 to 0.4, 0.3 to 1.5, 0.3 to 1.2, 0.3 to 0.8, or 0.3 to 0.6.

**[0016]** Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester comprises a Total DS of at least 1.5, at least 1.55, at least 1.6, at least 1.65, at least 1.7, at least 1.75, at least 1.8, at least 1.85, at least 1.9, at least 1.95, at least 2.0, at least 2.05, at least 2.1, at least 2.15, at least 2.2, at least 2.25, at least 2.3, at least 2.35, or at least 2.38 and/or not more than 2.95, not more than 2.9, not more than 2.85, not more than 2.8, not more than 2.75, not more than 2.7, not more than 2.65, not more than 2.6, not more than 2.55, not more than 2.5, or not more than 2.45. In certain embodiments, the cellulose ester may comprise a Total DS in the range of 1.5 to 2.95, 1.6 to 2.85, 1.7 to 2.8, 1.8 to 2.75, 1.9 to 2.7, 2.0 to 2.65, 2.05 to 2.6, 2.1 to 2.6, 2.15 to 2.6, 2.2 to 2.6, 2.25 to 2.55, 2.3 to 2.5, or 2.38 to 2.45.

**[0017]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can be a cellulose diacetate and/or cellulose triacetate. Alternatively, in certain embodiments, the cellulose ester can comprise a mixed cellulose ester, such as cellulose acetate butyrate or cellulose acetate propionate.

**[0018]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can have an acetyl content of at least 30%, at least 35%, or at least 40% by weight and/or not more than 62.5%, not more than 60%, not more than 55%, not more than 50%, or not more than 45% by weight on a combined acetic acid weight percent basis. In certain embodiments, the cellulose ester may have a degree of acetylation in the range of 30% to 62.5%, 35% to 55%, 35% to 50%, 35% to 45%,

40% to 62.5%, 40% to 60%, 40% to 55%, 40% to 50%, or 40% to 45% by weight.

**[0019]** Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester can have a hydroxyl content of at least 0.3%, at least 0.5%, at least 1%, at least 2%, at least 3%, or at least 4% by weight and/or not more than 20%, not more than 15%, not more than 10%, or not more than 5% by weight. In certain embodiments, the cellulose ester may have a hydroxyl content in the range of 0.3% to 20%, 0.5% to 20%, 2% to 15%, 3% to 10%, or 4% to 5% by weight.

**[0020]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can have a number average degree of polymerization of at least 100, at least 110, at least 120, at least 130, at least 140, at least 150, at least 160, at least 170, at least 180, at least 190, at least 200, at least 210, at least 220, at least 230, at least 240, at least 250, at least 260, or at least 265. Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester can have a number average degree of polymerization of not more than 1,000, not more than 900, not more than 800, not more than 700, not more than 600, not more than 500, not more than 400, not more than 350, not more than 325, not more than 300, not more than 290, not more than 280, not more than 270, not more than 260, not more than 250, not more than 240, not more than 230, not more than 220, not more than 210, not more than 200, not more than 190, not more than 180, not more than 170, not more than 160, not more than 150, not more than 149, not more than 148, not more than 147, not more than 146, not more than 145, not more than 144, not more than 143, not more than 142, not more than 141, not more than 140, not more than 139, not more than 138, not more than 137, not more than 136, not more than 135, not more than 134, not more than 133, not more than 132, not more than 131, not more than 130, not more than 129, not more than 128, not more than 127, not more than 126, not more than 125, not more than 124, not more than 123, not more

than 122, not more than 121, not more than 120, not more than 119, not more than 118, not more than 117, not more than 116, or not more than 115. In certain embodiments, the cellulose ester can have a number average degree of polymerization in the range of 100 to 1,000, 100 to 500, 100 to 400, 100 to 300, 100 to 250, 100 to 200, 100 to 150, 100 to 135, 100 to 200, 100 to 150, 100 to 135, 100 to 180, 100 to 150, 100 to 145, 100 to 140, 100 to 135, or 100 to 130.

**[0021]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can comprise a number average absolute molecular weight in Daltons, of at least 5,000 Daltons, at least 10,000 Daltons, at least 15,000 Daltons, at least 20,000 Daltons, or at least 25,000 Daltons and/or not more than 75,000 Daltons, not more than 70,000 Daltons, not more than 65,000 Daltons, not more than 60,000 Daltons, not more than 55,000 Daltons, not more than 50,000 Daltons, not more than 45,000 Daltons, not more than 40,000 Daltons, not more than 35,000 Daltons, or not more than 30,000 Daltons as measured by gel permeation chromatography ("GPC") according to ASTM D6474. In certain embodiments, the cellulose ester can comprise a number average absolute molecular weight in the range of 5,000 Daltons to 75,000 Daltons, 10,000 Daltons to 65,000 Daltons, or 15,000 Daltons to 35,000 Daltons as measured by GPC according to ASTM D6474.

**[0022]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can comprise a weight-average absolute molecular weight of at least 50,000 Daltons, at least 55,000 Daltons, at least 60,000 Daltons, at least 65,000 Daltons, at least 70,000 Daltons, at least 75,000 Daltons, at least 80,000 Daltons, or at least 85,000 Daltons and/or not more than 150,000 Daltons, not more than 140,000 Daltons, not more than 130,000 Daltons, not more than 120,000 Daltons, not more than 110,000 Daltons, not more than 100,000 Daltons, or not more than 95,000 Daltons as measured by GPC according to ASTM D6474. In certain embodiments, the cellulose ester can comprise a weight-average absolute molecular weight in the range of 50,000 Daltons to 150,000 Daltons,

70,000 Daltons to 120,000 Daltons, or 80,000 Daltons to 95,000 Daltons as measured by GPC according to ASTM D6474.

**[0023]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can comprise a crystallinity of at least 1%, at least 2%, at least 5%, at least 10%, at least 15%, or at least 20% as measured according to ASTM F2625. Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester can comprise a crystallinity of not more than 25%, not more than 20%, not more than 15%, not more than 10%, not more than 9%, not more than 8%, not more than 7%, not more than 6%, not more than 5%, not more than 4%, not more than 3%, not more than 2%, or not more than 1% as measured according to ASTM F2625. In certain embodiments, the cellulose ester can comprise a crystallinity of 1% to 99%, 1% to 50%, 1% to 30%, 1% to 20%, or 1% to 15% as measured according to ASTM F2625.

**[0024]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can exhibit a glass transition temperature of at least 120°C, at least 125°C, at least 130°C, at least 135°C, at least 140°C, at least 145°C, at least 150°C, at least 155°C, at least 160°C, at least 165°C, at least 170°C, or at least 175°C and/or not more than 250°C, not more than 245°C, not more than 240°C, not more than 235°C, not more than 230°C, not more than 225°C, not more than 220°C, not more than 215°C, not more than 210°C, not more than 205°C, not more than 200°C, not more than 195°C, not more than 190°C, or not more than 185°C.

**[0025]** The cellulose esters can be produced by any method known in the art. Examples of processes for producing cellulose esters are taught in Kirk-Othmer, Encyclopedia of Chemical Technology, 5th Edition, Vol. 5, Wiley-Interscience, New York (2004), pp. 394-444.

**[0026]** One method of producing cellulose esters involves esterification of the cellulose by mixing cellulose with the appropriate organic acids, acid anhydrides, and catalysts. Cellulose is then converted to a cellulose

triester. Ester hydrolysis is then performed by adding a water-acid mixture to the cellulose triester, which can then be filtered to remove any gel particles or fibers. Water is then added to the mixture to precipitate the cellulose ester. The cellulose ester can then be washed with water to remove reaction by-products followed by dewatering and drying.

**[0027]** Cellulose, the starting material for producing cellulose esters, can be obtained in different grades and sources such as from cotton linters, softwood pulp, hardwood pulp, corn fiber, and other agricultural sources, and bacterial cellulose, among others. The starting material used to produce the cellulose esters may affect the resulting hemicellulose content in the resulting cellulose esters.

**[0028]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester can comprise a hemicellulose content of at least 0.25%, at least 0.5%, at least 1%, at least 2%, at least 3%, at least 4%, at least 5%, at least 6%, or at least 7% by weight. Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester can comprise a hemicellulose content of not more than 10%, not more than 9%, not more than 8%, not more than 7%, not more than 6%, not more than 5%, not more than 4%, not more than 3%, not more than 2%, or not more than 1% by weight.

**[0029]** The dissolution solvent added to the dope mixer can include one or more solvents capable of dissolving a cellulose ester, particularly cellulose diacetate and/or cellulose triacetate. In one embodiment or in combination with any other mentioned embodiments, the dissolution solvent comprises a solvent chosen from N,N-dimethylformamide, N,N-dimethylacetamide, or dimethyl sulfoxide, or mixtures thereof.

**[0030]** In one embodiment or in combination with any other mentioned embodiments, acetone is minimized or avoided as a dissolution solvent. In certain embodiments (e.g., such as when N,N-dimethylacetamide is present in the dope), the dope comprises not more than 50%, not more than 45%, not more than 40%, not more than 35%, not more than 30%, not more than 25%, not more than 20%, not more than 15%, not more

than 10%, not more than 5%, not more than 4%, not more than 3%, not more than 2%, not more than 1%, or 0% by weight acetone, based on the total weight of the cellulose ester dope.

**[0031]** The cellulose ester may be added to the dope so that the dope comprises at least 5%, at least 8%, at least 10%, at least 12%, at least 15%, at least 18%, at least 20%, or at least 22% by weight cellulose ester, and/or not more than 35%, not more than 33%, not more than 30%, not more than 29%, not more than 25%, not more than 22%, or not more than 20% by weight cellulose ester, based on the total weight of the dope. In certain embodiments, the cellulose ester dope comprises 5% to 35%, 10% to 33%, 12% to 30%, 15% to 29%, or 25% to 29% by weight of cellulose ester, based on the total weight of the dope.

**[0032]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester is present in the dope at a level of at least 35%, at least 40%, at least 55%, at least 65%, at least 75%, at least 85%, at least 95%, at least 98%, or 100% by weight, based on total solids in the dope. In certain embodiment, the cellulose ester is present in the dope from 35% to 100%, from 45% to 100%, from 55% to 100%, from 55% to 98%, from 65% to 98%, or from 75% to 98%, based on total solids in the dope.

**[0033]** In one embodiment or in combination with any other mentioned embodiments, when the cellulose ester comprises CDA, the dope comprises at least 10%, at least 13%, at least 15%, at least 18%, at least 20%, at least 22%, or at least 24% by weight CDA, and/or not more than 35%, not more than 33%, not more than 30%, or not more than 29% by weight CDA, based on the total weight of the dope. In certain embodiments, the cellulose ester dope comprises 10% to 35%, 15% to 33%, 18% to 33%, 20% to 30%, or 24% to 29% by weight CDA, based on the total weight of the dope.

**[0034]** In one embodiment or in combination with any other mentioned embodiments, when the cellulose ester comprises CTA, the dope comprises at least 10%, at least 10%, at least 12%, at least 15%, at least

17%, at least 19%, or at least 21% by weight CTA, and/or not more than 27%, not more than 25%, not more than 24%, or not more than 22% by weight CTA, based on the total weight of the dope. In certain embodiments, the cellulose ester dope comprises 10% to 27%, 12% to 24%, or 15% to 22% by weight CTA, based on the total weight of the dope.

**[0035]** The dissolution solvent should be added in sufficient quantities so as to effectively dissolve the cellulose ester, thereby forming the cellulose ester dope. In one embodiment or in combination with any other mentioned embodiments, the cellulose ester dope can comprise at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, or at least 95%, or 99% and/or not more than 99%, not more than 95%, not more than 90%, or not more than 85% by weight of one or more dissolution solvents, based on the total weight of the dope. In certain embodiments, the cellulose ester dope comprises 65% to 99%, 70% to 95%, 75% to 95%, 80% to 95%, or 90% to 99% by weight of one or more dissolution solvents, based on the total weight of the dope.

**[0036]** The water or moisture content of the dope may be kept relatively low. In one embodiment or in combination with any other mentioned embodiments, the cellulose ester dope has a moisture content of not more than 4%, not more than 3.5%, not more than 3%, not more than 2.5%, not more than 2%, not more than 1.5%, not more than 1.4%, not more than 1.3%, not more than 1.2%, not more than 1.1%, not more than 1%, not more than 0.9%, not more than 0.8%, not more than 0.7%, or not more than 0.6% by weight, based on the total weight of the cellulose ester dope.

**[0037]** Due to the type of cellulose ester and dissolution solvents that are used, the cellulose dope may exhibit desirable operating viscosities. In one embodiment or in combination with any other mentioned embodiments, the cellulose ester dope may exhibit a viscosity of at least 10 poise, at least 20 poise, at least 30 poise, at least 40 poise, at least 50 poise, at least 60 poise, at least 70 poise, at least 80 poise, at least 90 poise, or at least 100 poise and/or not more than 3,000 poise, not more

than 2,000 poise, not more than 1,500 poise, not more than 1,000 poise, not more than 950 poise, not more than 900 poise, not more than 850 poise, not more than 800 poise, not more than 750 poise, not more than 700 poise, not more than 650 poise, not more than 600 poise, not more than 550 poise, or not more than 500 poise when measured at the spinning temperature used for manufacturing the fiber. This spinning temperature is nominally the temperature of the dope as it passes through and into the spinneret. The viscosity defined herein is the “zero” shear viscosity obtained by extrapolating to a very low shear rate when viscosity is plotted versus shear rate, or alternately by using a Brookfield viscometer at low spindle RPM. Thus, the “when measured” threshold does not in any manner reflect the use or practice of the actual cellulose ester dope.

**[0038]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester dope may exhibit a viscosity of at least 10 poise, at least 20 poise, at least 30 poise, at least 40 poise, at least 50 poise, at least 60 poise, at least 70 poise, at least 80 poise, at least 90 poise, or at least 100 poise and/or not more than 5,000 poise, not more than 4,000 poise, not more than 3,000 poise, not more than 2,000 poise, not more than 1,500 poise, not more than 1,000 poise, not more than 950 poise, not more than 900 poise, not more than 850 poise, not more than 800 poise, not more than 750 poise, not more than 700 poise, not more than 650 poise, not more than 600 poise, not more than 550 poise, or not more than 500 poise when measured at 25°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, or 110°C. It should be noted that this “when measured” standard does not require the cellulose ester dope to be utilized only at this designated temperature; rather, this temperature standard simply provides a temperature threshold at which to measure the viscosity of the cellulose ester dope. Thus, the “when measured” threshold does not in any manner reflect the use or practice of the actual cellulose ester dope. The viscosity may be measured using a Brookfield viscometer at low spindle RPM.

**[0039]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester dope may comprise some or no additives in addition to the cellulose ester. Such additives can include, but are not limited to, plasticizers, antioxidants, thermal stabilizers, pro-oxidants, inorganics, pigments, colorants, antistatic agents, optical brighteners, lubricants, fillers, or combinations thereof.

**[0040]** In one embodiment or in combination with any other mentioned embodiments, organic acids (monofunctional and/or polyfunctional) may be included to prevent color formation in the final fibers, particularly when the dope is heated to higher temperatures. Exemplary such acids include those chosen from citric acid, malic acid, maleic acid, succinic acid, lactic acid, acetic acid, tartaric acid, or propane-1,2,3-tricarboxylic acid, or mixtures thereof.

**[0041]** In one embodiment or in combination with any other mentioned embodiments, cellulose ester dope comprises at least 0.01%, at least 0.05%, at least 0.06%, at least 0.07%, at least 0.08%, at least 0.09%, at least 0.1%, at least 0.2%, or at least 0.3% by weight and/or not more than 2%, not more than 1.5%, not more than 1.4%, not more than 1.3%, not more than 1.2%, not more than 1.1%, not more than 1%, not more than 0.9%, or not more than 0.8% by weight of the polyfunctional acid, based on the weight of the dope. In certain embodiments, the cellulose ester dope comprises 0.01% to 2%, 0.01% to 1.5%, 0.05% to 1.5%, 0.08% to 1.3%, or 0.1% to 1% by weight of the polyfunctional acid, based on the total weight of the dope.

**[0042]** In one embodiment or in combination with any other mentioned embodiments (e.g., such as when N,N-dimethylacetamide is present in the dope), the dope comprises 0% by weight cellulose nanocrystals. Cellulose nanocrystals include rod-like nanoparticles (e.g., diameter under 20 nm and length under 500 nm) produced by controlled acid hydrolysis of cellulose-based materials such as plants and trees.

**[0043]** In one embodiment or in combination with any other mentioned embodiments, the dope comprises no more than 20%, no more than 15%,

no more than 10%, no more than 5%, no more than 3%, no more than 2%, no more than 1%, or 0% by weight polymers that are not cellulose esters, based on the total solids in the dope.

**[0044]** In one embodiment or in combination with any other mentioned embodiments, the combined weight of any polyurethanes, polyolefins, nylons, polyesters, and/or polyurethaneureas that might be present in cellulose ester dope is not more than 65%, not more than 60% by weight, not more than 55%, not more than 50%, not more than 45%, not more than 40%, not more than 35%, not more than 30%, not more than 25%, not more than 20%, not more than 15%, not more than 10%, not more than 5%, not more than 4%, not more than 3%, not more than 2%, not more than 1%, or 0% by weight, based on the total solids in the cellulose ester dope.

**[0045]** In one embodiment or in combination with any other mentioned embodiments, any polyurethanes that might be present in the cellulose ester dope is not present at a level of more than 10%, not more than 9%, not more than 8%, not more than 7%, not more than 6%, not more than 5%, not more than 4%, not more than 3%, not more than 2%, not more than 1%, or 0% by weight, based on the total solids in the cellulose ester dope.

**[0046]** In one embodiment or in combination with any other mentioned embodiments, any polyurethaneureas that might be present in the cellulose ester dope is not present at a level of more than 10%, not more than 9%, not more than 8%, not more than 7%, not more than 6%, not more than 5%, not more than 4%, not more than 3%, not more than 2%, not more than 1%, or 0% by weight, based on the total solids in the cellulose ester dope.

**[0047]** In one embodiment or in combination with any other mentioned embodiments, any acrylonitrile-vinyl acetate copolymer that might be present in the cellulose ester dope is not present at a level of more than 50%, not more than 45%, not more than 40%, not more than 35%, not more than 30%, not more than 25%, not more than 20%, not more than

15%, not more than 10%, not more than 5%, not more than 4%, not more than 3%, not more than 2%, not more than 1%, or 0% by weight, based on the total solids in the cellulose ester dope.

**[0048]** In one embodiment or in combination with any other mentioned  
embodiments, the dope is prepared by mixing the cellulose ester, solvent,  
and any other components at lower temperatures. In certain  
embodiments, this mixing is performed by mixing at a temperature of at  
least 45°C, at least 46°C, at least 47°C, at least 48°C, at least 49°C, at  
least 50°C, at least 51°C, at least 52°C, at least 53°C, at least 54°C, at  
least 55°C, at least 56°C, at least 57°C, at least 58°C, at least 59°C, or at  
least 60°C and/or not more than 140°C, not more than 130°C, not more  
than 120°C, not more than 110°C, not more than 105°C, not more than  
104°C, not more than 103°C, not more than 102°C, not more than 101°C,  
not more than 100°C, not more than 99°C, not more than 98°C, not more  
than 97°C, not more than 96°C, or not more than 95°C. In certain  
embodiments, this temperature is 45°C to 140°C, 45°C to 105°C, 47°C to  
103°C, or 50°C to 100°C.

**[0049]** In one embodiment or in combination with any other mentioned  
embodiments, this mixing is carried out for at least 5 minutes, at least 6  
minutes, at least 8 minutes, at least 10 minutes, at least 12 minutes, at  
least 14 minutes, or at least 15 minutes and/or not more than 48 hours, not  
more than 36 hours, not more than 24 hours, not more than 20 hours, not  
more than 16 hours, not more than 12 hours, or not more than 8 hours. In  
certain embodiments, this time is 5 minutes to 48 hours, 5 minutes to 36  
hours, 5 minutes to 24 hours, or 5 minutes to 8 hours.

**[0050]** In one embodiment or in combination with any other mentioned  
embodiments, the dope is prepared by first slurring the cellulose ester,  
solvent, and any other components and then cooling to very low  
temperatures. In certain embodiments, this temperature is at least -100°C,  
at least -75°C, at least -70°C, at least -65°C, at least -60°C, at least -55°C,  
or at least -50°C and/or not more than 5°C, not more than 4°C, not more  
than 3°C, not more than 2°C, not more than 1°C, not more than 0°C, not

more than -5°C, or not more than -10°C and storing at one of the foregoing temperatures of at least 1 hour, at least 2 hours, at least 3 hours, at least 4 hours, at least 5 hours, at least 6 hours, at least 7 hours, at least 8 hours, at least 9 hours, or at least 10 hours and/or not more than 48 hours, not more than 36 hours, not more than 30 hours, not more than 24 hours, or not more than 15 hours. In certain embodiments, this temperature is -100°C to 5°C, -75°C to 5°C, -75°C to 0°C, -65°C to 0°C, or -50°C to -5°C, and/or storage times are 1 hour to 48 hours, 3 hours to 36 hours, 5 hours to 24 hours, or 7 hours to 10 hours. In certain embodiments, the dope is warmed back up and mixed at room temperature prior to spin drying.

**[0051]** After forming the cellulose ester dope, it may be routed to an optional dope holding tank for temporary storage and/or deaeration. The dope holding tank can comprise any conventional storage tank known in the art that is capable of storing the cellulose ester dope. While stored in the holding tank, the cellulose ester dope may be subjected to conditions facilitated to maintain the physical characteristics of the dope and/or remove gas bubbles introduced during the mixing step. The temperature and pressure of the holding and/or deaeration tank may be optimized as necessary to enhance and maintain the quality of the cellulose ester dope.

**[0052]** Next, the cellulose ester dope can be pumped out of the dope holding tank into a filter, which may remove any large and undesirable particulates and gels from the cellulose ester dope prior to spinning. The filter can comprise any conventional filter apparatus and filter type known in the art. After filtering, the filtered cellulose ester dope may be pumped to a spinneret positioned near or in an evaporation chamber or cabinet.

**[0053]** The cellulose ester dope may be metered through the spinneret to thereby form one or more fibers. The shape and size of the hole or holes in the spinneret help determine the cross section of the fiber(s). The number of holes in the spinneret face determines the number of fibers simultaneously formed as dope is metered into the spinneret. As the dope passes through the holes in the spinneret face, the individual fibers form.

**[0054]** More particularly, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester dope can be spun at a rate of 10 to 1000 m/min through spinneret holes having a design known in the art (e.g., having a hole area equivalent to a circular diameter of 20 to 200 microns). In one embodiment or in combination with any other mentioned embodiments, the spinneret may be maintained at a temperature of at least 75°C, at least 80°C, at least 85°C, at least 90°C, at least 95°C, or at least 100°C and/or not more than 175°C, not more than 170°C, not more than 165°C, not more than 160°C, not more than 155°C, or not more than 150°C. In certain embodiments, the head of the spinneret may be maintained at a temperature in the range of 75°C to 175°C, 85°C to 165°C, 95°C to 160°C, or 100°C to 150°C.

**[0055]** At the spinneret, the cellulose ester dope can be extruded through a plurality of holes to form continuous cellulose ester fibers. At the spinneret, fibers may be drawn to form bundles of multiple individual fibers, or hundreds of individual fibers, or even one thousand individual fibers. Each of these bundles may include at least 10, at least 20, at least 30, at least 40, at least 50, at least 60, at least 70, at least 80, at least 90, at least 100, at least 150, at least 200, at least 250, at least 300, at least 350, or at least 400 and/or not more than 1,000, not more than 900, not more than 800, not more than 700, or not more than 600 fibers. The spinneret may be operated at any speed suitable to produce individual filament fibers, which are then assembled into bundles having desired size and shape. As used herein, the term “individual filament fiber” refers to the continuous filament that is initially produced by each hole in the face of the spinneret.

**[0056]** The fibers are extruded through the spinneret into a vertical spinning cabinet, which may have walls that are nominally 150°C to 240°C and which may contain gases inside the cabinet that are nominally 200-500°C, where the solvent is flashed off or evaporated. In certain embodiments, evaporating comprises exposing the spun fibers to temperatures of at least 100°C, at least 110°C, at least 120°C, at least

130°C, at least 140°C, at least 145°C, at least 150°C, at least 153°C, at least 155°C, at least 160°C, at least 165°C, at least 170°C, at least 175°C, at least 180°C, at least 185°C, or at least 189°C and/or not more than 500°C not more than 400°C, not more than 375°C, not more than 350°C, not more than 325°C, not more than 300°C, not more than 275°C, not more than 250°C, not more than 240°C, not more than 230°C, or not more than 220°C. In certain embodiments, this temperature is 100°C to 500°C, 110°C to 400°C, 120°C to 375°C, 130°C to 350°C, 140°C to 300°C, or 150°C to 250°C.

**[0057]** It should be noted that the cellulose ester fibers formed may be in the form of monocomponent fibers that are formed from only one material (e.g., the cellulose ester) or a uniformly blended composition and, therefore, would not be considered “bicomponent” or “multicomponent fibers,” which are characterized by internal phases or boundaries delineating different compositions within the external surface of the fiber. In one embodiment or in combination with any other mentioned embodiments, the resulting cellulose ester fibers can comprise at least 50%, at least 55%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 99%, or at least 99.9% by weight of the cellulose ester, based on the total weight of the fiber. In certain embodiments, the cellulose ester fiber can be formed entirely from the cellulose ester.

**[0058]** The individual cellulose ester fibers discharged from the spinneret, may have any suitable transverse cross-sectional shape. Exemplary cross-sectional shapes include, but are not limited to, round or other than round (non-round). In one embodiment or in combination with any other mentioned embodiments, the individual fibers discharged from the spinneret may have a substantially round cross-sectional shape. As used herein, the term “cross-section” generally refers to the transverse cross-section of the fiber measured in a direction perpendicular to the direction of elongation of the fiber. The cross-section of the fiber may be determined and measured using Quantitative Image Analysis (“QIA”).

**[0059]** The cross-sectional shape of an individual fiber may also be characterized according to its deviation from a round cross-sectional shape. In some cases, this deviation can be characterized by the shape factor of the fiber, which is determined by the following formula: Shape Factor = Perimeter /  $(4\pi \times \text{Cross-Sectional Area})^{1/2}$ . In some embodiments, the shape factor of the individual cellulose ester fibers can be from 1 to 2, 1 to 1.8, 1 to 1.7, 1 to 1.5, 1 to 1.4, 1 to 1.25, 1 to 1.15, or 1 to 1.1. The shape factor of a fiber having a perfect round cross-sectional shape is 1. The shape factor can be calculated from the cross-sectional area of the fiber, which can be measured using QIA.

**[0060]** Furthermore, in certain embodiments, the cellulose ester fibers may be in the form of solid fibers (fibers having a solid cross-sectional shape without an aperture present therein) and not in the form of hollow fibers.

**[0061]** In one embodiment or combination with any other mentioned embodiments, whereas a typical spinning cabinet for spandex fibers may have more than 30 ends (or yarns), for cellulose esters, it is desirable to have no more than 30 ends per cabinet, no more than 25 per cabinet, no more than 20 per cabinet, no more than 15 per cabinet, no more than 10 per cabinet, no more than 8 per cabinet, no more than 6 per cabinet, no more than 4 per cabinet. The reduction in the number of ends in a vertical spinning cabinet will allow sufficient solvent evaporation at lower temperature which is beneficial for preventing discoloration of fibers.

**[0062]** In one embodiment or combination with any other mentioned embodiments, it is desirable for the cellulose ester fibers to be drawn no more than 2x, no more than 1.8x, no more than 1.6x, no more than 1.4x, no more than 1.2x. Where the draw ratio is defined as the ratio of the fiber speed at the exit of the vertical spinning cabinet over the speed of the fiber at the exit of the spinneret holes.

**[0063]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarn produced therefrom may exhibit a tenacity of at least 0.2 g/denier, at least 0.3

g/denier, at least 0.4 g/denier, at least 0.5 g/denier, at least 0.6 g/denier, at least 0.7 g/denier, at least 0.8 g/denier, at least 0.9 g/denier, at least 1 g/denier, at least 1.1 g/denier, at least 1.2 g/denier, at least 1.3 g/denier, at least 1.4 g/denier, at least 1.5 g/denier, at least 1.6 g/denier, at least 1.7 g/denier, at least 1.8 g/denier, at least 1.9 g/denier, or at least 2 g/denier, and/or not more than 3.0, or not more than 2.5, not more than 2.3, not more than 2.1, not more than 2, or not more than 1.9 g/denier, as measured according to ASTM D22556.

**[0064]** Elongation, also known as elongation at break, is expressed as a percentage and it is indicative of how much a yarn or filament will stretch before it breaks. In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarn produced therefrom may exhibit an elongation at break of at least 10%, at least 15%, at least 16%, at least 17%, at least 18%, at least 19%, at least 20%, at least 21%, at least 22%, at least 23%, at least 24%, at least 25%, at least 26%, at least 27%, at least 28%, at least 29%, or at least 30% as measured according to ASTM D22556.

**[0065]** Silk factor ("SF") is an empirically determined relationship between tenacity and elongation that is used to predict the failure envelope of a given fiber. Silk Factor can be used to characterize a yarn or fiber's suitability for use in a given process and is calculated based on the following formula:

$$\text{Silk Factor} = \text{Tenacity} * \sqrt{\text{Elongation}}$$

In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarn produced therefrom may exhibit a silk factor of at least 5.0, at least 6.0, at least 7.0, or at least 7.6, where elongation is defined as a percentage and tenacity is in grams/denier.

**[0066]** As noted above, the cellulose ester fibers are formed as continuous filament fibers. Thus, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers may

have an aspect ratio (L/D) of at least 10:1, at least 20:1, at least 30:1, at least 40:1, at least 50:1, at least 100:1, at least 500:1, at least 1,000:1, or at least 10,000:1

**[0067]** The continuous filament fibers may be accumulated onto cores or tubes at a winder after evaporation or solvent flash-off and may be sent to optional downstream processes. Notably, because this disclosure is concerned with a dry spinning process, the fibers are not passed or drawn through a coagulation bath after evaporation or solvent flash-off. The fibers may be wrapped around a take-up roll, which provides tension and pulls the fibers into the downstream steps of the process, which may include, for example, one or more annealing sections, a winder, a crimper, a cutter, or a combination thereof.

**[0068]** In one embodiment or combination with any other mentioned embodiments, whereas spandex yarn bobbins are wound with significant amount of winder draw wherein the winder speed is typically 5% faster than the speed of the previous roll; for cellulose ester continuous filament fibers, it is desirable to have less than 3% winder draw, less than 2% winder draw, less than 1% winder draw, less than 0.8% winder draw, less than 0.5% winder draw.

**[0069]** The continuous filament cellulose ester fibers may be gathered into a bundle, band, or yarn. The bundle, band, or yarn may comprise a plurality of the cellulose ester fibers. Each of these bundles, bands, or yarns may include at least 20, at least 30, at least 40, at least 50, at least 60, at least 70, at least 80, at least 90, at least 100, at least 150, at least 200, at least 250, at least 300, at least 350, or at least 400 and/or not more than 1,000, not more than 900, not more than 800, not more than 700, or not more than 600 individual fibers.

**[0070]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the cellulose ester bundle, band, or yarn may be passed through a crimping zone wherein a patterned wavelike shape may be imparted to at least a portion, or substantially all, of the individual fibers. When used, the crimping zone includes at least

one crimping device for mechanically crimping the fibers. Generally, the cellulose ester fibers desirably are not crimped by thermal or chemical means (e.g., hot water baths, steam, air jets, or chemical coatings), but instead are mechanically crimped using a suitable crimper. One example of a suitable type of mechanical crimper is a “stuffing box” or “stuffer box” crimper that utilizes a plurality of rollers to generate friction, which causes the fibers to buckle and form crimps. Other types of crimpers may also be suitable. Examples of equipment suitable for imparting crimp fibers are described in, for example, U.S. Patent Nos. 9,179,709; 2,346,258; 3,353,239; 3,571,870; 3,813,740; 4,004,330; 4,095,318; 5,025,538; 7,152,288; and 7,585,442, each of which is incorporated herein by reference to the extent not inconsistent with the present disclosure.

**[0071]** In one embodiment or in combination with any other mentioned embodiments, crimping may be performed such that the cellulose ester fibers have a crimp frequency of at least 5, at least 7, at least 10, at least 12, at least 13, at least 15, or at least 17 and/or up to 30, up to 27, up to 25, up to 23, up to 20, or up to 19 crimps per inch (“CPI”), as measured according to ASTM D3937-12. In certain embodiments, the average CPI of the fibers used to make the cellulose ester bundle, band, or yarns and/or various downstream products may be in the range of 7 to 30 CPI, 10 to 30 CPI, 10 to 27 CPI, 10 to 25 CPI, 10 to 23 CPI, 10 to 20 CPI, 12 to 30 CPI, 12 to 27 CPI, 12 to 25 CPI, 12 to 23 CPI, 12 to CPI, 15 to 30, CPI, 15 to 27 CPI, 15 to 23 CPI, 15 to 20 CPI, or 15 to 19 CPI.

**[0072]** In one embodiment or in combination with any other mentioned embodiments, when crimped, the crimp amplitude of the fibers may vary and can, for example, be at least 0.85, 0.90, 0.93, 0.96, 0.98, 1.00, or 1.04 mm. Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the crimp amplitude of the fibers can be up to 1.75, up to 1.70, up to 1.65, up to 1.55, up to 1.35, up to 1.28, up to 1.24, up to 1.15, up to 1.10, up to 1.03, or up to 0.98 mm.

**[0073]** Additionally, in one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers, the cellulose ester

bundle, band, or yarn, and/or staple fibers produced therefrom may have a crimp ratio of at least 1:1. As used herein, "crimp ratio" refers to the ratio of the non-crimped tow length to the crimped tow length. In certain embodiments, the cellulose ester fibers, the cellulose ester yarns, and/or staple fibers produced therefrom may have a crimp ratio of at least 1:1, at least 1.1:1, at least 1.125:1, at least 1.15:1, or at least 1.2:1.

**[0074]** Crimp amplitude and crimp ratio are measured according to the procedure outlined in U.S. Pat. App. Pub. No. 2020/0299822, which is incorporated herein by reference to the extent not inconsistent with the present disclosure.

**[0075]** Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, one or more types of surface finish may be applied to the cellulose ester fibers and/or the bundle, band, or yarn formed therefrom. The method of application is not limited and can include the use of spraying, wick application, dipping, or use of squeeze, lick, or kiss rollers. The location for applying a finish to a fiber can vary depending on the function of the finish. For example, the lubricant finish can be applied after spinning and before crimping, or before gathering the fibers into a bundle. Cutting lubricants and/or antistatic lubricants can be applied before or after crimping and prior to drying. Suitable amounts of all finishes (whether lubricant, cutting lubricant, antistatic electricity finish, or otherwise) on the cellulose ester fibers can be at least 0.01, at least 0.02, at least 0.05, at least 0.10, at least 0.15, at least 0.20, at least 0.25, at least 0.30, at least 0.35, at least 0.40, at least 0.45, at least 0.50, at least 0.55, or at least 0.60 percent finish-on-yarn ("FOY") relative to the weight of the dried cellulose ester fiber. Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the cumulative amount of finish may be present in an amount of not more than 2.5, not more than 2.0, not more than 1.5, not more than 1.2, not more than 1.0, not more than 0.9, not more than 0.8, or not more than 0.7 percent FOY based on the total weight of the dried fiber. The amount of finish on the fibers as expressed

by weight percent may be determined by solvent extraction. As used herein “FOY” or “finish on yarn” refers to the amount of finish on the fiber or yarn less any added water.

**[0076]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers can include at least one plasticizer or, in the alternative, no plasticizer. The cellulose ester fibers may comprise less than 30, less than 12, less than 10, less than 9, less than 8, less than 7, less than 6, less than 5, less than 4, less than 3, less than 2, less than 1, less than 0.5 weight percent of at least one plasticizer, based on the total weight of the cellulose ester fiber. When present, the plasticizer may be incorporated into the fiber itself by spinning a dope containing a plasticizer, contained in a flake used to make the dope, and/or the plasticizer may be applied to the surface of the fiber or filament by any of the methods used to apply a finish. If desired, the plasticizer can be contained in the finish formulation.

**[0077]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarns formed therefrom can be biodegradable. As used herein, the term “biodegradable” generally refers to the tendency of a material to chemically decompose under certain environmental conditions. The degree of degradation can be characterized by the weight loss of a sample over a given period of exposure to certain environmental conditions. In some cases, the cellulose ester fibers and/or the yarns formed therefrom can exhibit a weight loss of at least 5%, at least 10%, at least 15%, or at least 20% after burial in soil for 60 days and/or a weight loss of at least 15%, at least 20%, at least 25%, at least 30%, or at least 35% after 15 days of exposure in a composter. However, the rate of degradation may vary depending on the particular end use of the fibers. Exemplary test conditions are provided in U.S. Pat. Nos. 5,870,988 and 6,571,802, incorporated herein by reference.

**[0078]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarns formed therefrom can be compostable. To be considered “compostable,” a material must

meet the following four criteria: (1) the material must be biodegradable; (2) the material must be disintegrable; (3) the material must not contain more than a maximum amount of heavy metals; and (4) the material must not be ecotoxic. The term “disintegrable” refers to the tendency of a material to physically decompose into smaller fragments when exposed to certain conditions. Disintegration depends both on the material itself, as well as the physical size and configuration of the article being tested. Ecotoxicity measures the impact of the material on plant life, and the heavy metal content of the material is determined according to the procedures laid out in the standard test method.

**[0079]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarns formed therefrom can be industrially compostable, home compostable, or both. In such embodiments, the cellulose ester fibers can satisfy four criteria: (1) biodegrade in that at least 90% carbon content is converted within 180 days; (2) disintegrable in that least 90% the material disintegrates within 12 weeks; (3) does not contain heavy metals beyond the thresholds established under the EN12423 standard; and (4) the disintegrated content supports future plant growth as humus; where each of these four conditions are tested per the ASTM D6400, ISO 17088, or EN 13432 method.

**[0080]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarns formed therefrom can exhibit a biodegradation of at least 70 percent in a period of not more than 50 days, when tested under aerobic composting conditions at ambient temperature ( $28^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ) according to ISO 14855-1 (2012). In some cases, the cellulose ester fibers and/or the yarns formed therefrom can exhibit a biodegradation of at least 70 percent in a period of not more than 49, not more than 48, not more than 47, not more than 46, not more than 45, not more than 44, not more than 43, not more than 42, not more than 41, not more than 40, not more than 39, not more than 38, or not more than 37 days when tested under these conditions, also called “home

composting conditions.” These conditions may not be aqueous or anaerobic.

**[0081]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the yarns formed therefrom can exhibit a biodegradation of at least 60 percent in a period of not more than 45 days, when tested under aerobic composting conditions at a temperature of 58°C ( $\pm 2^\circ\text{C}$ ) according to ISO 14855-1 (2012). In some cases, they can exhibit a biodegradation of at least 60 percent in a period of not more than 44 days when tested under these conditions, also called “industrial composting conditions.” These may not be aqueous or anaerobic conditions.

**[0082]** The resulting cellulose ester fibers may be used to produce a vast array of end products, such as tow band, staple fibers, filament yarns, spun yarns, woven articles, nonwoven articles, and/or knitted textiles.

**[0083]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers and/or the cellulose ester yarns described above may be cut into staple fibers. Any suitable type of cutting device may be used that is capable of cutting the fibers to a desired length without excessively damaging the fibers. Examples of cutting devices can include, but are not limited to, rotary cutters, guillotines, stretch breaking devices, reciprocating blades, or combinations thereof. Once cut, the cellulose ester staple fibers may be baled or otherwise bagged or packaged for subsequent transportation, storage, and/or use. In one embodiment or in combination with any other mentioned embodiments, the d50 length of the staple fibers may be at least 5, at least 10, at least 20, at least 30, at least 40, or at least 50 mm and/or not more than 150, not more than 140, not more than 130, not more than 125, not more than 120, not more than 115, not more than 110, not more than 105, not more than 100, or not more than 95 mm.

**[0084]** Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the denier per filament (weight in g of 9000 m fiber length), or “DPF,” of the cellulose

ester fibers (whether cellulose ester staple fibers or cellulose ester continuous fibers) may be within a range of 0.5 to less than 20. The particular method for measurement is not limited and include the ASTM 1577-07 method using the FAVIMAT vibroscope procedure if filaments can be obtained from which the staple fibers are cut, a microbalance weight measurement of a sample of known length, or a width analysis using any convenient optical microscopy or analyzer. The DPF can also be correlated to the maximum width of a fiber.

**[0085]** In one embodiment or in combination with any other mentioned embodiments, the staple fibers can be formed into a cellulose ester spun yarn. Spun yarns are continuous strands comprising short staple fibers which are mechanically entangled by a staple yarn spinning process. Staple yarn spinning processes can be, but are not limited to, ring spinning, open-end spinning, air jet spinning, compact spinning, siro spinning, vortex spinning, worsted spinning, semi-worsted spinning, woolen spinning, and wet spinning with flax.

**[0086]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester fibers may be formed into a nonwoven article, such as a nonwoven textile. Exemplary nonwoven articles can include wet-laid nonwoven articles, air-laid non-woven articles, carded articles, and/or dry-laid non-woven articles.

**[0087]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester yarns may be formed into a woven article, such as a woven textile. Woven textiles can be formed on a loom by interlacing at least two yarns, a warp yarn, and a weft yarn, wherein the warp yarn strands are oriented in parallel and the weft yarns are interlaced at an angle to the orientation of the warp yarns in an alternating pattern over and under the warp yarns.

**[0088]** In one embodiment or in combination with any other mentioned embodiments, the cellulose ester yarns may be formed into a knitted article, such as a knitted textile. Such knitted textiles may be formed by interlocking loops of yarn.

**[0089]** In one embodiment or in combination with any other mentioned embodiments, the end products described herein, including the staple fibers, yarns, nonwoven articles, knitted articles, and the woven articles, may comprise, consist essentially of, or consist of the cellulose ester fibers. The end products described herein, including the staple fibers, yarns, nonwoven articles, knitted articles, and the woven articles, may comprise at least 0.25, at least 0.5, at least 0.75, at least 1, at least 2, at least 3, at least 4, at least 5, at least 6, at least 7, at least 8, at least 9, at least 10, at least 12, at least 15, at least 18, at least 20, at least 25, at least 30, at least 35, at least 40, at least 45, at least 50, at least 55, at least 60, at least 65, at least 70, at least 75, at least 80, at least 85, at least 90, at least 95, at least 99, or at least 99.9 weight percent of one or more cellulose ester fibers, based on the total weight of the article.

Additionally or alternatively, in one embodiment or in combination with any other mentioned embodiments, the end products described herein, including the staple fibers, yarns, nonwoven articles, knitted articles, and the woven articles, may comprise not more than 99, not more than 95, not more than 90, not more than 85, not more than 80, not more than 75, not more than 70, not more than 65, not more than 60, not more than 55, not more than 50, not more than 45, not more than 40, not more than 35, not more than 30, not more than 25, not more than 20, not more than 15, not more than 10, not more than 9, not more than 8, not more than 7, not more than 6, or not more than 5 weight percent of one or more cellulose ester fibers, based on the total weight of the article. In certain embodiments, the end products may be formed entirely from the cellulose ester fibers or comprise in the range of 0.25 to 50, 1 to 99, 1 to 50, 50 to 99, 1 to 20, or 0.25 to 5 weight percent of one or more cellulose ester fibers, based on the total weight of the article.

**[0090]** Additional advantages of the various embodiments will be apparent to those skilled in the art upon review of the disclosure herein and the working examples below. It will be appreciated that the various embodiments described herein are not necessarily mutually exclusive

unless otherwise indicated herein. For example, a feature described or depicted in one embodiment may also be included in other embodiments but is not necessarily included. Thus, the present disclosure encompasses a variety of combinations and/or integrations of the specific embodiments described herein.

## DEFINITIONS

**[0091]** It should be understood that the following is not intended to be an exclusive list of defined terms. Other definitions may be provided in the foregoing description, such as, for example, when accompanying the use of a defined term in context.

**[0092]** As used herein, the terms “a,” “an,” and “the” mean one or more.

**[0093]** As used herein, the term “and/or,” when used in a list of two or more items, means that any one of the listed items can be employed by itself or any combination of two or more of the listed items can be employed. For example, if a composition is described as containing components A, B, and/or C, the composition can contain A alone; B alone; C alone; A and B in combination; A and C in combination, B and C in combination; or A, B, and C in combination.

**[0094]** As used herein, the terms “comprising,” “comprises,” “comprise,” “contain,” “containing,” and “contains” are open-ended transition terms used to transition from a subject recited before the term to one or more elements recited after the term, where the element or elements listed after the transition term are not necessarily the only elements that make up the subject.

**[0095]** As used herein, the terms “having,” “has,” and “have” have the same open-ended meaning as “comprising,” “comprises,” and “comprise” provided above.

**[0096]** As used herein, the terms “including,” “include,” and “included” have the same open-ended meaning as “comprising,” “comprises,” and “comprise” provided above.

## NUMERICAL RANGES

[0097] The present description uses numerical ranges to quantify certain parameters relating to the invention. It should be understood that when numerical ranges are provided, such ranges are to be construed as providing literal support for claim limitations that only recite the lower value of the range as well as claim limitations that only recite the upper value of the range. For example, a disclosed numerical range of 10 to 100 provides literal support for a claim reciting “greater than 10” (with no upper bounds) and a claim reciting “less than 100” (with no lower bounds).

[0098] Additionally, it should be understood that a listing of numerical values following a descriptor, such as “at least” and “not more than,” provides literal support for a range based on all of the numerical values following that descriptor. For example, a statement specifying “at least 2, 5, or 10 and/or not more than 100, 50, or 25” would provide literal support for ranges of “at least 25,” “not more than 50,” and “at least 10 and not more than 25.”

## EXAMPLES

[0099] The following examples set forth methods in accordance with the disclosure. It is to be understood, however, that these examples are provided by way of illustration, and nothing therein should be taken as a limitation upon the overall scope.

## MATERIALS AND METHODS

[0100] Dopes were prepared by using fresh bottles of reagent grade DMF in order to minimize any contamination or residual water. Each dope contained 25 grams of Eastman CA 394-60 cellulose acetate (CDA) and 75 grams of DMF solvent. For the case of “hot mixing,” the DMF was first heated to the desired mixing temperature (typically 90°C) in a jar for 15 minutes prior to the addition of the CDA powder. The jar had a lid which minimized entry of atmospheric air. Mixing commenced for 1 hour using a

mechanical stirrer after which the sample was removed, cooled to room temperature, and tested for color and haze.

**[0101]** For the “cold mix” samples, the CDA was slurried with DMF at room temperature, and the jar was then sealed and inserted in a cooler full of dry ice where it was stored for 4 hours and then allowed to warm up to room temperature where it was then rolled overnight at room temperature to finish homogenization of the mixing. A few additional samples were run where the sample was inserted into a standard laboratory freezer, rather than dry ice, but the procedure was otherwise the same.

**[0102]** Moisture content of the starting CDA was measured using a Sartorius Mark 3 analyzer (Goettingen, Germany). As-received samples had a moisture content of 1.3 wt%. Wet CDA samples having a moisture level of 3.5 wt% were obtained from an open bag that had been in the lab for a number of months. Dried samples having a moisture level of 0.1 wt% were obtained by drying the wet sample at 60°C in a vacuum oven.

**[0103]** Color and haze were determined on dope samples using Hunter Labs Ultrascan Pro (Reston, VA) system by pouring the dope into a 20mm cuvette. This cuvette was then inserted into the chamber for optical testing. Values were typically measured after initial dope mixing, and then again after 2 hrs of storage at 120°C (to simulate the temperature of dry spinning). Color is reported in terms of L\* (a gray scale indicator), a\* (red to green scale), and b\* (blue to yellow). A high value of b\* is indicative of a more yellow sample. Some samples showed very low L\*, which meant they were very dark.

**[0104]** Film casting of the samples was performed to simulate fiber spinning, in order to more readily obtain color measurements. Dopes were cooled to 90°C after the 120°C storage, and then cast on glass plates (also heated to 90°C) using a doctor blade. Nominal thickness of the final films ranged from 40 um to 70 um. Films were annealed at 180°C for 20 minutes to remove solvent (some samples were annealed for less time to better simulate cabinet conditions). Color and haze were also measured

on the film samples using the same instrument in transmission mode (no correction was made for differences in thickness).

**[0105]** Absolute molecular weights were measured on the cast films using GPC by dispersing the sample into NMP solvent. The GPC column was calibrated using absolute Mw standards.

## EXAMPLES 1-7

### Effect of Moisture and Temperature on Dope Formation

**[0106]** A comparison was made of wet and dry samples that were produced using "hot mixing" and "cold mixing" methods. Color and haze were determined on the dopes after mixing, as well as after 2 hrs at 120°C (See Table I). Sample #1 had the least yellowing (lowest b\*) and was produced using the wetter cellulosic sample and with the cold mixing process. Next best was #4, which was produced by hot mixing with the dry sample. It is interesting that "cold and wet" or "hot and dry" produced the lowest yellowness. All of the other combinations were worse and roughly the same relative to each other.

Table I. Effect of Moisture and Mixing Temperature

| Ex. # | Temp | % H <sub>2</sub> O | As Mixed Color |       |       |      | Color after 120C/2hrs |      |       |      | thick (μm) | Film  |       |      |      |
|-------|------|--------------------|----------------|-------|-------|------|-----------------------|------|-------|------|------------|-------|-------|------|------|
|       |      |                    | L*             | a*    | b*    | Haze | L*                    | a*   | b*    | Haze |            | L*    | a*    | b*   | Haze |
| 1     | -75C | 3.5                | 92.51          | -0.44 | 8.23  | 7.8  | 86.50                 | 2.46 | 22.75 | 7.1  | 70         | 96.43 | -0.01 | 1.80 | 3.2  |
| 2     | -75C | 0.1                | 92.35          | -0.44 | 9.33  | 8.1  | 78.21                 | 7.10 | 33.61 | 8.0  | 84         | 96.65 | -0.05 | 1.61 | 1.5  |
| 3     | 90C  | 3.5                | 92.10          | -0.50 | 10.90 | 10.6 | 80.00                 | 6.42 | 31.68 | 7.8  | 45         | 96.91 | -0.01 | 0.83 | 1.3  |
| 4     | 90C  | 0.1                | 91.62          | -0.39 | 12.73 | 7.9  | 83.27                 | 4.46 | 28.16 | 7.3  | 50         | 96.80 | -0.02 | 1.16 | 0.3  |
| 5     | 50C  | 3.5                | 93.30          | -0.42 | 7.00  | 7.0  | 79.11                 | 6.39 | 32.91 | 7.5  | NT         | NT    | NT    | NT   | NT   |

**[0107]** Film haze values are also shown with all having low color relative to the dopes. The slight difference in values between film samples is primarily attributed to the differences in film thickness.

**[0108]** Sample #5 was mixed at 50°C instead of 90°C to determine a practical lower temperature limit for hot mixing. This sample took about twice as long to go into solution relative to 90°C. Another sample (#6) was mixed at room temperature but did not go into solution even after 3 hours.

However a dope sample (#7) that was stored in a freezer at -10°C produced a good quality dope.

## EXAMPLES 10-16

### Additive Effects via Cold Mixing

**[0109]** In this example, dopes were prepared using the cold mixing process similar to Example 1 above, except an additional amount of a stabilizing additive (either 0.5 or 1 wt%) was also included. Starting moisture was 1.3 wt% for all of the CDA samples. Additives represented a range of possible stabilizing agents representing acids, buffers, antioxidants, etc. As observed and shown in Table II, the addition of citric acid had the most noticeable effect on b\* and dramatically reduced color formation. The mixtures of citric acid and potassium citrate (#12 and #13) were next best having intermediate levels of color formation. Samples #13, #14, and #15 still had some undissolved solids as the additives did not go completely in solution. The acetate salts added as a buffer fared the worst as these had the highest color generation (worse than having no additive at all). Note that #15 had a low b\*, but this sample turned black during heating as denoted by the very low L\*.

Table II. Cold Mixed Dopes Using Dry Ice

| Sample # | Additive                    | As Mixed Color |       |       |      | 120C/2hrs Color |       |       |      |
|----------|-----------------------------|----------------|-------|-------|------|-----------------|-------|-------|------|
|          |                             | L*             | a*    | b*    | Haze | L*              | a*    | b*    | Haze |
| 10       | 0.5% citric acid            | 92.42          | -0.55 | 6.81  | 8.1  | 92.04           | -0.93 | 13.11 | 8.5  |
| 11       | 1.0% citric acid            | 93.26          | -0.52 | 6.80  | 10.5 | 91.84           | -0.88 | 12.80 | 9.0  |
| 12       | 0.5% potassium acid citrate | 92.37          | -0.42 | 8.63  | 12.0 | 85.64           | 2.47  | 23.95 | 9.0  |
| 13       | 1.0% potassium acid citrate | 87.73          | -0.49 | 6.82  | 28.1 | 90.53           | -0.61 | 16.50 | 13.8 |
| 14       | 0.5% dovaphos 9228T         | 58.19          | 1.52  | 12.90 | 98.2 | 86.97           | 0.75  | 17.74 | 9.6  |
| 15       | 1.0% sodium acetate         | 75.86          | -0.37 | 15.10 | 21.7 | 4.89            | 22.65 | 7.15  | 8.4  |
| 16       | 1.0% magnesium acetate      | 91.11          | -0.98 | 13.56 | 9.6  | 18.24           | 29.91 | 29.82 | 44.0 |

**EXAMPLES 20-37****Additive Effects via Hot Mixing at 90°C**

**[0110]** These examples are similar to #10 above except the samples were mixed at 90°C. In addition, the additive level was reduced to 0.15 wt% for all of the additives (except for #30 through #32 which used 0.5wt%) to help minimize undissolved particulates. All samples had 1.3wt% starting moisture except for #31, which had 0.1% moisture. As with the cold mixing, the various salts and buffers tended to make color worse. The monofunctional acetic acid also had the same effect. The only samples with lower color contained the polyfunctional citric acid. Succinic acid (#32) did not produce good color in the film even though it is polyfunctional like citric acid.

**[0111]** Note that the 0.15 wt% level is on the lower end of what is effective for reducing color. A more ideal target based on the data, would be around 0.3 to 0.7 wt%. At higher levels of 1% as per previous examples, there is no significant improvement in color over the 0.5% loading.

**[0112]** Sample #31 also included a comparison with a highly dried sample at 0.5% citric acid to see if moisture made a difference. Comparing this to #10, #11 and #20 suggests that moisture is not as critical with regards to citric acid as the amount seems to be the more important variable

**[0113]** Samples #32 through 37 compared other polyfunctional acids with the thought that these could help color stabilization as well. It was observed that citric acid was much better than controlling color than either succinic, malic or tartaric acid.

Table III. Hot Mixed Dopes at 90°C

| Sample # | Additive                     | As Mixed Color |       |       |      | 120C/2hrs Color |       |       |      |
|----------|------------------------------|----------------|-------|-------|------|-----------------|-------|-------|------|
|          |                              | L*             | a*    | b*    | Haze | L*              | a*    | b*    | Haze |
| 20       | 0.15% citric acid            | 92.96          | -0.67 | 7.60  | 9.5  | 89.31           | -0.60 | 19.11 | 13.8 |
| 21       | 0.15% tri-phenyl phosphate   | 92.07          | -0.46 | 11.13 | 7.0  | 79.96           | 5.09  | 31.98 | 9.4  |
| 22       | 0.15% tri-phenyl phosphite   | 92.78          | -0.66 | 9.47  | 8.2  | 88.85           | 0.01  | 21.22 | 8.7  |
| 23       | 0.15% potassium acid citrate | 92.70          | -0.59 | 8.93  | 11.1 | 88.36           | 0.00  | 21.00 | 12.4 |
| 24       | 0.15% irganox 1010           | NA             | NA    | NA    | NA   | 88.10           | 0.81  | 20.10 | 11.4 |
| 25       | 0.15% dovaphos 9228T         | 91.17          | -0.21 | 12.55 | 9.6  | 79.51           | 5.17  | 36.21 | 7.8  |
| 26       | 0.15% sodium bicarbonate     | 88.38          | 0.25  | 16.83 | 29.6 | 13.88           | 30.42 | 22.12 | 22.8 |
| 27       | 0.15% sodium acetate         | 73.20          | 8.20  | 49.40 | 9.9  | 10.60           | 29.80 | 17.30 | 8.3  |
| 28       | 0.15% magnesium acetate      | 87.90          | -0.17 | 22.09 | 12.2 | 36.40           | 28.26 | 54.80 | 13.3 |
| 29       | 0.15% vikoflex               | 91.06          | -0.21 | 13.35 | 8.8  | 73.54           | 9.09  | 41.75 | 10.5 |
| 30       | 0.5wt% acetic acid           | 77.50          | 0.06  | 14.09 | 31.5 | 79.40           | 5.37  | 38.60 | 9.2  |
| 31       | 0.5% citric acid (dried CA)  | 83.70          | -0.64 | 7.27  | 24.7 | 92.60           | -1.09 | 12.04 | 7.5  |
| 32       | 0.5% succinic acid           | 89.33          | -0.63 | 11.34 | 12.6 | 82.78           | 2.08  | 41.70 | 8.6  |
| 33       | .05% Citric                  | 93.84          | -0.57 | 6.50  | 7.4  | 91.07           | -0.41 | 15.15 | 7.7  |
| 34       | .5% Malic                    | 82.73          | -0.78 | 7.28  | 27.4 | 86.86           | 0.80  | 26.58 | 10.0 |
| 35       | .5% Tartaric                 | 80.51          | -0.81 | 7.47  | 29.8 | 85.40           | 1.73  | 31.31 | 7.4  |
| 36       | .025% Malic                  | 92.71          | -0.79 | 10.52 | 7.6  | 89.24           | 0.28  | 20.02 | 7.9  |
| 37       | .025% Tartaric               | 92.09          | -1.03 | 12.16 | 8.6  | 85.05           | 1.45  | 29.43 | 8.7  |

**EXAMPLES 40 - 48****Effect of Acids on Film Casting Color**

[0114] In this example, samples of film were cast and annealed for various times. In sample #40 and #41, the films were cast from the same dope (#10). In #40, the film was cast and annealed at 180C for 20 minutes in a hot air oven to dry the film (see Table IV). Note that the citric acid film was very yellow after 20 minutes as this is above its melting and degradation is likely occurring due to oxygen exposure. In a typical dry spinning cabinet, the temperature exposure will only occur for just a few seconds (and likely with a nitrogen blanket). So to better reflect spinning conditions, a second film (#41) was cast and dried for 4 minutes at 180C, which was the minimum time needed to dry the film. As observed, the color dropped significantly and resulted in much better color than the other samples. Samples were also completely dry and free of any DMF odor. Lastly, sample #47 was cast from the same dope but

annealed at 150C for 20minutes. This sample also had excellent color similar to that at 180C for 4 minutes. In the remaining examples, samples of other acids were also cast into film and annealed using the 4min protocol at 180C. Dopes containing citric acid had lower yellowness than the control at all levels of citric acid addition. In contrast, malic and tartaric at 0.5% were slightly more yellow than the control.

Table IV. Film Haze and Annealing Time

| Sample # | Additive         | Dry time/180C | Film |       |       |       | Haze 65/10 |
|----------|------------------|---------------|------|-------|-------|-------|------------|
|          |                  |               | μm   | L*    | a*    | b*    |            |
| 40       | 0.5% citric acid | 20 min        | 60   | 90.30 | 0.46  | 18.51 | 2.7        |
| 41       | 0.5% citric acid | 4 min         | 65   | 97.06 | -0.02 | 0.46  | 2.7        |
| 43       | Control          | 4 min         | 60   | 96.95 | -0.01 | 0.76  | 0.4        |
| 44       | .5% Tartaric     | 4 min         | 60   | 96.90 | 0.01  | 1.04  | 0.7        |
| 45       | .5% Malic        | 4 min         | 60   | 96.97 | -0.04 | 0.85  | 0.8        |
| 46       | .5% Citric       | 4 min         | 60   | 97.06 | 0.00  | 0.51  | 0.3        |
| 47       | .5% Citric       | 20min/150C    | 66   | 97.01 | 0.02  | 0.46  | 0.9        |
| 48       | .05% Citric      | 4 min         | 60   | 97.12 | 0.00  | 0.38  | 0.4        |

## CLAIMS NOT LIMITED TO DISCLOSED EMBODIMENTS

**[0115]** The preferred forms of the invention described above are to be used as illustration only and should not be used in a limiting sense to interpret the scope of the present invention. Modifications to the exemplary embodiments, set forth above, could be readily made by those skilled in the art without departing from the spirit of the present invention.

**[0116]** The inventors hereby state their intent to rely on the Doctrine of Equivalents to determine and assess the reasonably fair scope of the present invention as it pertains to any apparatus not materially departing from but outside the literal scope of the invention as set forth in the following claims.

What is claimed is:

1. A process for producing a cellulose ester fiber, said process comprising dry spinning a cellulose ester dope through a spinneret to make one or more of said fibers, wherein said cellulose ester dope comprises dissolved and/or dispersed solids (hereinafter "solids") and solvent, at least 35 wt.% of said solids comprises cellulose ester, and said solvent comprises N,N-dimethylformamide, N,N-dimethylacetamide, or dimethyl sulfoxide, or mixtures thereof, provided that if said solvent comprises N,N-dimethylacetamide:
  - (i) said cellulose ester dope comprises not more than 50% by weight acetone, based on the total weight of the cellulose ester dope; or
  - (ii) said cellulose ester dope comprises 0% by weight cellulose nanocrystals based on the total weight of the cellulose ester dope; or
  - (iii) both (i) and (ii),wherein the combined weight of a polyurethane, polyolefin, nylon, polyester, and/or polyurethaneurea, if present in said cellulose ester dope, is not more than 60% by weight, based on the total solids in said cellulose ester dope.
2. The process of claim 1, wherein said cellulose ester dope comprises not more than 10% by weight polyurethanes or polyurethaneureas, based on the total solids in the cellulose ester dope.
3. The process of claim 1 or 2, wherein said cellulose ester dope comprises not more than 50% by weight acrylonitrile-vinyl acetate copolymer, based on the total solids in the cellulose ester dope.
4. The process according to any one of the preceding claims, wherein said cellulose ester fiber comprises at least 50% by weight cellulose ester obtained from said cellulose ester dope.

5. The process according to any one of the preceding claims, wherein said cellulose ester has a  $DS_{\text{acetyl}}$  of at least 1.5 and/or not more than 2.95.
- 5 6. The process according to any one of the preceding claims, wherein said cellulose ester has a glass transition temperature of at least 120°C and/or not more than 250°C.
- 10 7. The process according to any one of the preceding claims, wherein said dry spinning comprises:  
spinning said cellulose ester dope so as to produce spun fibers containing said solvent; and  
evaporating said solvent from said spun fibers.
- 15 8. The process according to any one of the preceding claims, wherein said cellulose ester dope comprises a polyfunctional acid.
- 20 9. The process according to any one of the preceding claims, wherein said cellulose ester dope has a moisture content of not more than 4% by weight, based on the total weight of the cellulose ester dope.
- 25 10. The process according to any one of the preceding claims, further comprising preparing said cellulose ester dope by slurring the cellulose ester and said solvent and subsequently cooling said dope to a temperature of at least -100°C and/or not more than 5°C and storing at one of the foregoing temperatures for at least 1 hour.
- 30 11. The process according to any one of the preceding claims, wherein said cellulose ester dope of any one of claims 1-8 wherein the  $b^*$  value is not more than 0.75.

- 5
12. A cellulose ester fiber formed according to any one of the preceding claims.
13. A yarn comprising said cellulose ester fiber formed according to claim 12.
14. An article comprising said cellulose ester fiber formed according to claim 12.
- 10
15. A woven article comprising said cellulose ester fiber formed according to claim 12.
- 15
16. A nonwoven article comprising said cellulose ester fiber formed according to claim 12.
17. A staple fiber comprising said cellulose ester fiber formed according to claim 12.
- 20
18. A knitted textile comprising said cellulose ester fiber formed according to claim 12.
19. The process of claim 7, wherein evaporating said solvent from said spun fibers takes place in a spinning cabinet.
- 25
20. The process of claim 16, wherein said spun fibers in said spinning cabinet are drawn to a draw ratio of no more than 2x.

# INTERNATIONAL SEARCH REPORT

International application No  
**PCT/US2022/040390**

**A. CLASSIFICATION OF SUBJECT MATTER**  
**INV. D01D1/02 D01F2/30**  
**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
**D01D D01F**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**EPO-Internal, WPI Data**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                             | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| <b>X</b>  | <b>CN 103 014 893 A (UNIV SICHUAN)</b><br><b>3 April 2013 (2013-04-03)</b><br><b>abstract; claims 1-3; examples 1,2,4,5,6</b><br>-----                                                         | <b>1-20</b>           |
| <b>A</b>  | <b>KR 2013 0047258 A (SAMSUNG FINE CHEMICALS</b><br><b>CO LTD [KR]) 8 May 2013 (2013-05-08)</b><br><b>paragraphs [0045], [0046], [0056] -</b><br><b>[0059]; claims 1-8; example 1</b><br>----- | <b>1-20</b>           |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* 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 application or patent 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 when the document is taken alone

"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

Date of the actual completion of the international search

**22 November 2022**

Date of mailing of the international search report

**02/12/2022**

Name and mailing address of the ISA/  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

**Malik, Jan**

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

**PCT/US2022/040390**

| Patent document<br>cited in search report |          | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|----------|---------------------|----------------------------|---------------------|
| <b>CN 103014893</b>                       | <b>A</b> | <b>03-04-2013</b>   | <b>NONE</b>                |                     |
| -----                                     |          |                     |                            |                     |
| <b>KR 20130047258</b>                     | <b>A</b> | <b>08-05-2013</b>   | <b>NONE</b>                |                     |
| -----                                     |          |                     |                            |                     |