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CELLULOSE ACETATE SPINNING SOLUTIONS CONTAINING ZIRCONIUM ADDITIVES

John E. Kiefer and George P. Touey, Kingsport, Tenn., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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This invention concerns a new spinning solution and the process of spinning such solution into fine denier filaments. More particularly, this invention concerns the incorporation of relatively small amounts of certain zirconium compounds into cellulose acetate spinning solutions whereby the viscosity of the cellulose acetate solution is increased in a manner that facilitates the spinning of fine denier filaments therefrom.

This application is related to and is a continuation in part of our companion copending applications Serial Numbers 848,187 and 848,188.

As set forth in our companion applications, in the production of cellulose acetate yarn, cellulose acetate is dissolved in acetone or the like solvent. The spinning dope is put under pressure and forced through small holes or orifices in a spinneret. The fine strands of dope are continuously pulled from the spinneret through a spinning cabinet where the solvent is evaporated by means of hot air. The denier of the resulting filaments can be defined by the factors of dope solids, draft, dope density, and orifice diameter as follows:

$$\text{Denier per filament} = \frac{K\,(\text{dope percent solids})}{(\text{orifice diameter})^2\,(\text{dope density})} \Big/ \text{spinning draft}$$

The spinning draft is defined as the linear speed of yarn take-up divided by the linear extrusion speed of the spinning solution at the orifice. In many instances spinning draft is limited to about 1.8. Excessive draft can result in many broken filaments and filaments with reduced physical properties.

The above relationship suggests changing the orifice diameter as a means of varying the denier of cellulose acetate filaments. However, when spinnerets with orifices with diameters less than about 0.035 mm. are used, mechanical difficulties may arise in the spinning operation. The acetate spinning dope does not flow through the smaller holes at an even rate and the holes tend to become clogged.

The denier of cellulose acetate filaments can also be varied by varying the solids content of the spinning dope. It is apparent that lowering the solids concentration of a dope will decrease the denier of the resulting filament, assuming the extrusion rate and the take-up rate are held constant. However, when the solids content of cellulose acetate is decreased, the dope viscosity also decreases. This produces difficulties in controlling the proper flow rate of the dope through the spinneret. Also, dopes with low viscosity may tend to stick to the metal spinneret and are, therefore, difficult to pull into filaments. One method of eliminating this problem is to use a cellulose acetate with a higher intrinsic viscosity than is normally used for cellulose acetate yarn. The higher cost of producing a high intrinsic viscosity ester has tended to make this approach unattractive.

In recent years there has developed a market for fine

denier filaments. One particular use therefor is the manufacture of tobacco smoke filters from such fine denier cellulose acetate filaments. It is apparent, therefore, that the development of simple, less expensive procedure for making such cellulose acetate filaments represents a highly desirable result.

After extensive investigation we have discovered a relatively simple way by which such fine denier filaments may be produced without involving the change of presently used spinning equipment or other material changes in existing processes for producing cellulose acetate filaments.

This invention has for one object to provide a cellulose acetate spinning solution of increased viscosity but with relatively low solids content. Still another object is to provide a way of improving cellulose acetate spinning solutions whereby they may be more readily spun into fine denier filaments. A particular object is to provide a cellulose acetate spinning solution which has a relatively small amount of certain zirconium compounds therein. Still a further object is to provide a method for spinning cellulose acetate filaments of relatively small deniers such as deniers of the order of 0.2–2 denier per filament. Other objects will appear hereinafter.

In the broader aspects of our invention we have found that commercial yarn grade cellulose acetate spinning dope diluted with acetone or equivalent solvents to a low solids content (15–23%), which concentration is not normally suitable for spinning, can be made suitable for spinning by the addition of 0.02 to 1.5% (based on the cellulose acetate) of zirconium chelate esters. Such zirconium compounds apparently partially affect the cellulose acetate in some manner which results in a large increase in the viscosity of the cellulose acetate spinning dope. The large increase in dope viscosity, on addition of very small amounts of zirconium chelates, was quite unexpected.

Therefore, the present invention may be accomplished by adding 0.01 to 1.00% (based on the cellulose acetate) of a zirconium chelate to a low solids cellulose acetate spinning dope, then spinning the dope into fibers using conventional cellulose acetate spinning equipment.

The zirconium chelates useful in carrying out this invention are those chelates which are acetone soluble, are fairly resistant to hydrolysis (most cellulose acetate spinning dopes contain some water) and which react with the free hydroxyl groups of the cellulose acetate. They have the following composition.

$$(RO)_xZr(R')_{4-x}$$

where x=0, 1, 2, or 3 and R represents an alkyl or aryl hydrocarbon such as the ethyl, propyl, butyl, 2-ethylhexyl, or phenyl group. R' represents an oxy compound capable of chelating with zirconium such as dihydroxy, diketo, hydroxyketo compounds, hydroxycarboxylic acids and their esters, and ketocarboxylic acids and their esters. Examples of the oxy chelating compounds useful in carrying out this invention are acetyl acetone, ethyl acetoacetate, diacetone alcohol, 1,3-octylene glycol, and ethyl lactate.

The cellulose acetate which can be used in carrying out this invention comprises yarn grade acetone soluble cellulose acetate with an acetyl content of 37–42%. The cellulose acetate spinning dopes which are preferred for use in carrying out this invention consist of 10 to 23%

cellulose acetate, 76 to 89% acetone, .5 to 3% water and 0.01 to 0.50% (based on the cellulose acetate) of the zirconium chelate.

A further understanding of our invention will be apparent from the several examples which follow for illustrating certain of our preferred embodiments.

EXAMPLE I

A cellulose acetate dope was prepared consisting of 20% cellulose acetate and 80% acetone. The dope was divided into 1 kg. samples. One sample was used as a control. Zirconium chelate additive compounds of the present invention were added to the other samples. Each dope was then mixed 30 minutes. The viscosity of the dopes was measured with a Brookfield viscometer. The dopes were stored at room temperature and the viscosity was redetermined at intervals. The results shown on Table 1 illustrate how zirconium complexes affected the viscosities of these dopes. The data indicates that the zirconium chelate increases the viscosity of the cellulose acetate very rapidly. Following this initial increase of viscosity, no further change in the dope is apparent.

EXAMPLE II

A cellulose acetate spinning dope consisting of 20% cellulose acetate, 78% acetone and 2% water was divided into two portions. One portion was spun using a conventional cellulose acetate spinning cabinet. A spinneret with orifices with a 0.035 mm. diameter was used. The spinning draft was maintained at 1.5. The dope stuck to the face of the spinneret, stopping up the orifices. No filaments with satisfactory tensile properties were obtained.

To the second portion of the dope was added four-tenths percent (based on the cellulose acetate weight) zirconium ethyl acetoacetate chelate,

$$Zr(OC_3H_7)_2(CH_3COCH_2COOC_2H_5)_2$$

with suitable mixing. On mixing, the viscosity of the dope increased from 12,100 cps. to 48,300 cps. This dope was spun into yarn using a conventional cellulose acetate spinning cabinet. A spinneret with orifices with a 0.035-mm. diameter was used. The 1.02 denier per filament yarn obtained had a tensile strength of 1.32 grams per denier and an elongation of 24%.

EXAMPLE III

A cellulose acetate spinning dope consisting of 15% cellulose acetate, 83% acetone, 2% water had a viscosity of 6,320 cps. The dope could not be spun into filaments using conventional techniques. Five-tenths percent (based on the cellulose acetate weight) zirconium tetrakis acetylacetonate (prepared by the method described by W. B. Blumenthal, "The Chemical Behavior of Zirconium," D. Van Nostrand Co., Princeton, New Jersey, 1958, p. 367), was added to the dope. The viscosity increased to 38,500 cps. The dope was then spun into yarn using a conventional spinning cabinet. A spinneret with 0.035-mm. orifices and a spinning draft of 1.5 was used. Seventy-six hundredths denier per filament yarn was obtained. It had a tensile strength of 1.21 grams per denier and an elongation of 24%.

The data appearing in the following table will further illustrate the feature of increasing the viscosity and the constant nature thereof.

Table 1

Viscosity Modifier	Concentration (Based on Cellulose Acetate Weight)	Viscosity, Cps. After—		
		30 Min.	1 Day	30 Days
No additive (control)		12,100	12,300	12,400
Zirconium ethyl acetoacetate	0.2	26,400	26,900	27,100
$Zr(OC_4H_9)_2(CH_3COCH_2COOC_2H_5)$				
Zirconium tetrakis acetylacetonate	0.2	19,700	20,200	20,100
Do	0.3	29,000	29,700	30,200
Do	0.4	46,400	47,400	46,900

While we prefer to operate with acetone solutions of cellulose acetate, since as is well known acetone is the common readily available commercial solvent frequently used for dissolving cellulose acetate as illustrated above, our invention will function when other solvents are used for the cellulose acetate. Accordingly, our invention is not limited to the particular cellulose acetate acetone solutions described above.

Fine denier filaments produced in accordance with this invention have utility for various purposes such as in the production of cigarette filters.

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 scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A spinning solution consisting essentially of cellulose acetate, solvent therefore and an amount of zirconium chelate compound of 0.02 to 1.5% based on the weight of the cellulose acetate, said chelate compound falling under the empirical formula:

$$(RO)_xZr(R^1)_{4-x}$$

wherein x represents a figure from the group consisting of 0, 1, 2 and 3, R represents a group from the class consisting of ethyl, propyl, butyl, 2-ethylhexyl and phenyl and R^1 represents an oxy-compound capable of chelating with zirconium from the group consisting of dihydroxy, diketo, hydroxy keto, hydroxy carboxylic acids and their esters and keto carboxylic acids and their esters.

2. The method for producing a cellulose acetate spinning solution of higher viscosity which comprises adding 0.02 to 1.5%, based on the weight of the cellulose acetate, a zirconium material chelated with a material from the group consisting of octylene glycol, ethyl acetoacetate, diacetone alcohol and ethyl lactate, to a solution which contains as essential ingredients cellulose acetate and acetone.

3. The method of making fine denier filaments which comprises forming a spinning solution containing cellulose acetate 15–23%, 0.02 to 1.5% based on the weight of the cellulose acetate of a zirconium chelate having the properties of dissolving in the spinning solution solvent, causing an increase in viscosity of the spinning solution as well as being resistant to hydrolysis and wherein the zirconium chelate consists of zirconium chealted with a material from the group consisting of octylene glycol, ethyl acetoacetate, diacetone alcohol and ethyl lactate.

4. The method in accordance with claim 3 wherein the solution is forced through spinneret holes of a diameter not substantially greater than 0.035 mm. and withdrawing the filaments formed at a draft not greater than about 1.8 and into an atmosphere which evaporates the solvent.

5. The method in accordance with claim 3 wherein the amount of the zirconium chelate is less than 1.00%.

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