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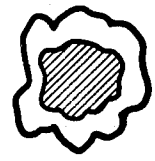
METHOD OF SPINNING VISCOSE

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Fig. 2



Fig. 1



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METHOD OF SPINNING VISCOSE

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This invention relates particularly to improvements in the spinning of filaments from unripened viscose.

It is customary in the art of spinning regenerated cellulose filaments and yarns to utilize viscose which has been ripened, i. e. aged for a certain period of time, in order to produce optimum properties in filaments and yarns, particularly when using coagulating baths which comprise sulfuric acid and sodium sulfate, which baths, according to modern practice, also preferably contain one or more salts of divalent metals, e. g. sulfates of zinc, ferrous iron, nickel, manganese, chromium and magnesium; zinc sulfate particularly is widely used in sulfuric acid-sodium sulfate spinning baths. Unless the viscose is ripened sufficiently, the filaments and yarns produced are of poor quality and unsuitable for use in the textile industry. For example, when an unripened (i. e. green) viscose prepared from sodium cellulose xanthate (commonly termed "cellulose xanthate" herein), which is produced by combining alkali cellulose with 35% carbon disulfide based on the weight of bone dry cellulose in the alkali cellulose and which has a salt index of 8.0 to 10.0, a xanthate sulfur concentration of 1.4% and a sodium trithiocarbonate content of 0.75%, is spun into baths containing an appreciable ferrous and/or zinc sulfate content, thin skinned yarns with inferior properties are obtained. However, when the salt index and xanthate sulfur concentration are reduced through ripening to 5.0% and 1.1%, respectively (the ripening step being accompanied by an increase in sodium trithiocarbonate content of from about 0.75% to about 1.3%), yarns having thick skins and excellent physical properties are obtained. The importance of skin thickness will be appreciated from the fact that, in general, when the skin represents a relatively large proportion of the cross-section of the filament, the filament and yarn properties are acceptable. In good yarn, particularly in high tenacity yarn for tire cord, the skin constitutes ordinarily 50% or more of the cross-section of the filament.

The level of properties for commercial regenerated cellulose yarns spun from the usual viscoses is at a maximum when the viscose is at a salt index of about 5.0, and when the viscose is ripened further, the level of properties falls off sharply.

It is desirable to use viscose having as high a salt index (and as high a xanthate sulfur concentration since this is directly proportional to the

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salt index) as is consistent with optimum yarn properties when using the spinning baths known to the art, particularly since the diminution in the ripening time or the elimination of ripening would effect a substantial economy. However, in viscose as it is normally prepared, the ripening step has been considered necessary in order to reduce the xanthate sulfate concentration (salt index) to an optimum value for spinning. The accompanying increase in sodium trithiocarbonate, which is generated during the xanthating and ripening step, has been considered a necessary evil since the sodium trithiocarbonate may cause excessive gassing and the development of defects in the filaments and yarns. It has now been discovered, contrary to the generally held views, that if additional sodium trithiocarbonate is incorporated into unripened viscose, said unripened viscose can be spun with little or no ripening (e. g. at a high salt index and xanthate sulfur concentration) to produce thick skinned filaments of excellent quality, particularly if a spinning bath containing zinc sulfate is used. The use of added sodium trithiocarbonate is of advantage also even where the viscose is subjected to a substantial degree of ripening.

An object of this invention is to improve the production of various articles from viscose. Another object of this invention is to utilize viscose having a high salt index for the production of shaped articles, particularly filaments and yarns acceptable for use in the textile industry. Still another object is concerned with the utilization of substantially unripened viscose for the production of filaments and yarns and other products. Further objects of the invention are improvements in the manufacture of viscose and in the spinning of viscoses into filaments and yarns and a novel and simple process for producing thick skinned regenerated cellulose filaments. A still further object is to eliminate the time-consuming step of ripening the viscose in the manufacture of various products and particularly of regenerated cellulose filaments. Other objects of the invention will appear hereinafter.

The objects of the invention are accomplished in general by making up a viscose containing dissolved therein an added amount of an alkali metal trithiocarbonate, extruding the viscose, preferably without substantial ripening, into a sulfuric acid-sodium sulfate bath preferably containing zinc sulfate or other sulfate of a divalent metal, stretching the filaments if desired, preferably in a two-bath system in which all or a

major part of the stretching occurs in the second bath, and collecting the yarn in any suitable fashion.

In the drawings:

Figure 1 illustrates diagrammatically a magnified cross-section of a filament produced in accordance with the present invention which has been dyed and reswollen in water, the central shaded portion representing the core and the unshaded outer portion representing the skin, and

Figure 2 shows, by comparison, a similarly magnified cross-section of a dyed and water-reswollen filament produced from unripened viscose which has not been modified in accordance with the present invention and in which the shaded portion illustrates the core and the unshaded portion the skin of the filament.

The following examples illustrate various methods of applying the principles of the invention. In the examples and elsewhere throughout the specification, parts, proportions and percentages are by weight unless otherwise specified.

EXAMPLE I

Cotton linters viscose containing 7% cellulose, 6% total caustic (sodium hydroxide), this viscose being commonly called 7–6 viscose, and added sodium trithiocarbonate is prepared in the following manner. Alkali cellulose aged to give the desired viscosity (40 to 60 poises) is xanthated for two and one half hours, using 35% carbon disulfide, based on the bone dry cellulose in the alkali cellulose. The xanthate crumbs are dissolved in an aqueous solution of caustic containing added sodium trithiocarbonate in the amount of 1.44%, based on the weight of the viscose, the total alkali present in the finished viscose being 6%, calculated as NaOH. The sodium trithiocarbonate is prepared by reacting carbon disulfide with sodium hydroxide. In this reaction, one mol of sodium carbonate for every two mols of sodium trithiocarbonate is formed. The sodium trithiocarbonate normally found in viscose is formed by this same reaction. Consequently, the ratio of carbonate to trithiocarbonate in the viscose described herein has not been disturbed. After mixing for one to one and a half hours at 0° C., the freshly prepared viscose is filtered while it is cold, deaerated and then, to prevent ripening, kept at 0° C. until spun. The viscose is spun into filaments by extruding through a 100-hold spinneret having holes of 0.0025 inch diameter into primary coagulating and regenerating baths having a temperature of 50° C. and respectively comprising (1) 6% sulfuric acid, 14% sodium sulfate and 15% zinc sulfate and (2) 9% sulfuric acid, 22% sodium sulfate, 1% zinc sulfate and 5% ferrous sulfate. The bundle of filaments is given a bath travel of 28 inches by using a roller guide and is passed from the bath to a feed wheel rotating at a peripheral speed of 485 inches per minute. The filaments are then carried through a hot water bath and wound upon a bobbin at such a speed as to give 80% stretch beyond the feed wheel. The resulting regenerated gel yarn is washed free of acid and salt, processed for further purification and is then collected and dried on a bobbin. The dried yarn is twisted four turns per inch and tested after conditioning at 21° C. and 60% relative humidity for forty-eight hours.

The properties of the yarn prepared from the viscose, modified as described in this example, and yarn similarly prepared respectively from green, unmodified viscose and ripened, unmodified (control) viscose are listed in the first, second and third columns respectively in the accompanying Table I. It will be seen in the table of properties that the level of properties is lowest for the yarns from unripened, unmodified viscose and is highest for the yarns from unripened, sodium trithiocarbonate modified viscose. The properties for the yarns from ripened, control viscose (index 5.0) are intermediate. In addition to improved yarn properties, other advantages to the use of the modified, green viscose are the elimination of the ripening step and improvement (i. e. reduction) in wet contraction as compared with yarn made from ripened viscose; wet contraction signifies shrinkage or loss in length resulting from the wetting of dry yarns and filaments and drying the wetted yarns and filaments without tension, this shrinkage being accompanied by increase in elongation and loss in tenacity. Low wet contraction is particularly advantageous in connection with use in tire cords wherein too large a wet contraction in processing is particularly undesirable and may seriously change the elongation and tenacity.

Table I

COAGULATING BATH 6-14-15 (H_2SO_4-Na_2SO_4-$ZnSO_4$)

	Modified Unripened	Unmodified Unripened	Ripened Control
Visose:			
Salt Index	7.7	8.4	5.0
Per Cent Xanthate Sulfur	1.35	1.40	1.10
Per Cent Na_2CS_3 Added	1.44	0	0
Per Cent Na_2CS_3 Total	2.28	0.85	1.30
Yarn:			
Tenacity, g. p. d., dry	3.93	3.20	3.71
Tenacity, g. p. d., wet	2.61	2.14	2.52
Elongation Per Cent, dry	9.1	10.4	9.1
Elongation Per Cent, wet	21.4	24.0	23.2
Per Cent Skin	100	30–50	80–90

COAGULATING BATH 9-22-1-5 (H_2SO_4-Na_2SO_4-$ZnSO_4$-$FeSO_4$)

Viscose:			
Salt Index	7.7	8.4	5.0
Per Cent Xanthate Sulfur	1.35	1.40	1.10
Per Cent Na_2CS_3 Added	1.44	0	0
Per Cent Na_2CS_3 Total	2.28	0.85	1.30
Yarn:			
Tenacity, g. p. d., dry	3.94	3.30	3.73
Tenacity, g. p. d., wet	2.51	1.86	2.29
Elongation Per Cent, dry	8.0	7.3	7.7
Elongation Per Cent, wet	18.1	14.2	18.1
Per Cent Skin	50–60	30–40	40–50

EXAMPLE II

7–6 viscose modified with alkali trithiocarbonate is prepared and spun into a 6.0–14–15 (sulfuric acid-sodium sulfate-zinc sulfate) coagulating bath under conditions otherwise as in Example I and the yarns are processed in the manner described in Example I except that the 1.44% of sodium trithiocarbonate which is added at the time of mixing is from a different source. It is prepared commercially by reacting one mol of sodium sulfide and one mol of carbon disulfide and contains only a small amount of sodium carbonate. It will be noted in Table II below, which compares the modified yarns with yarns similarly prepared from green, unmodified viscose and from ripened, unmodified, control viscose, that the commercial sodium trithiocarbonate produces the same improvements as those described in Example I.

Table II

	Modified Unripened	Unmodified Unripened	Ripened Control
Viscose:			
Salt Index	9.6	8.4	5.0
Per Cent Xanthate Sulfur	1.4	1.4	1.1
Per Cent Na_2CS_3 Added	1.44	0	0
Per Cent Na_2CS_3 Total	2.31	0.85	1.30
Yarn:			
Tenacity, g. p. d., dry	3.82	3.20	3.71
Tenacity, g. p. d., wet	2.60	2.14	2.52
Elongation Per Cent, dry	11.4	10.4	9.1
Elongation Per Cent, wet	25.0	24.0	23.2
Per Cent Skin	100	30–50	80–90

EXAMPLE III

The cotton linters viscose described in Example II, i. e. containing 1.44% of added sodium trithiocarbonate, is spun into filaments, using all conditions for producing and processing it as in Example II except that the acidity in the high zinc bath is increased from 6.0 to 9.5% sulfuric acid. The properties of the yarns, as well as those from the ripened, control viscose and the unripened, unmodified viscose are tabulated below. One advantage of the use of unripened, modified viscose is the fact that yarns with thicker skin and superior properties are obtained at the higher bath acidities under which conditions it is possible to employ high, commercially feasible spinning speeds in the high zinc bath.

Table III

	Modified Unripened	Unmodified Unripened	Ripened Control
Viscose:			
Salt Index	9.6	8.4	5.0
Per Cent Xanthate Sulfur	1.4	1.4	1.1
Per Cent Na_2CS_3 Added	1.44	0	0
Per Cent Na_2CS_3 Total	2.31	0.85	1.30
Yarn:			
Tenacity, g. p. d., dry	3.75	3.56	3.45
Tenacity, g. p. d., wet	2.31	2.10	2.20
Elongation Per Cent, dry	11.0	8.4	8.0
Elongation Per Cent, wet	22.2	16.6	21.3
Per Cent Skin	70–90	20–40	30–50

EXAMPLE IV

Xanthation is carried out in the presence of 50% carbon disulfide, based on the bone dry cellulose, and the xanthate crumbs are dissolved in a caustic solution of sodium trithiocarbonate to give a 7–6 viscose. In an unripened state, this viscose contains 1.82% xanthate sulfur and 2.90% sodium trithiocarbonate. Using all conditions for producing and processing as in Example I, this unripened, sodium trithiocrabonate modified viscose is spun respectively into the high zinc and ferrous sulfate baths. Two viscoses (ripened and unripened) made from cellulose xanthate produced by combining alkali cellulose with 50% carbon disulfide and dissolved in caustic free from added sodium trithiocarbonate are prepared and spun for comparison, the results being given in the following Table IV. It will be seen that the level of properties for the yarns from the unripened, modified viscose is higher than those for the unripened and the ripened, but unmodified control yarns. In the iron bath, the addition of sodium trithiocarbonates to the green viscose increases the skin thickness more than 100% and makes it possible to eliminate the long aging cycle which is necessary for high carbon disulfide viscoses.

Table IV

COAGULATING BATH 6-14-15 (H_2SO_4-Na_2SO_4-$ZnSO_4$)

	Modified Unripened	Unmodified Unripened	Ripened Control
Viscose:			
Salt Index	18.0	20.0	5.7
Per Cent Xanthate Sulfur	1.82	2.0	1.1
Per Cent Na_2CS_3 Added	1.44	0	0
Per Cent Na_2CS_3 Total	2.90	1.1	2.7
Yarn:			
Tenacity, g. p. d., dry	3.82	3.60	3.52
Tenacity, g. p. d., wet	2.42	2.18	2.50
Elongation Per Cent, dry	10.0	11.0	8.8
Elongation Per Cent, wet	24.6	24.0	22.0

COAGULATING BATH 9-22-1-5 (H_2SO_4-Na_2SO_4-$ZnSO_4$-$FeSO_4$)

Viscose:			
Salt Index	18.0	20.0	
Per Cent Xanthate Sulfur	1.82	2.0	
Per Cent Na_2CS_3 Added	1.44	0	
Per Cent Na_2CS_3 Total	2.9	1.1	
Yarn:			
Tenacity, g. p. d., dry	3.85	2.68	
Tenacity, g. p. d., wet	2.31	1.67	
Elongation Per Cent, dry	9.4	6.8	
Elongation Per Cent, wet	20.3	11.2	

EXAMPLE V

Cotton linters viscose containing 7% cellulose, 6% total caustic and 0.32% of added sodium trithiocarbonate (the later being included in the total caustic content) is prepared following the method described in Example I. The viscose is ripened as is normally done for unmodified viscose and spun into filaments. All conditions for spinning and processing as in Example I are used. It can be seen in the following Table V, which lists the properties of the modified yarns as well as those of similarly prepared yarns made from unmodified green and control viscoses, that measurable improvement can also be obtained in physical properties by adding sodium trithiocarbonate to viscose which has been given normal aging.

Table V

COAGULATING BATH 6-14-15 (H_2SO_4—Na_2SO_4—$ZnSO_4$)

	Modified Ripened	Unmodified Ripened
Viscose:		
Salt Index	5.0	5.0
Per Cent Xanthate Sulfur	1.1	1.1
Per Cent Na_2CS_3 Added	0.32	0.0
Per Cent Na_2CS_3 Total	1.60	1.30
Yarn:		
Tenacity, g. p. d., dry	3.97	3.71
Tenacity, g. p. d., wet	2.74	2.52
Elongation Per Cent, dry	9.3	9.1
Elongation Per Cent, wet	23.6	23.2
Per Cent Skin	90–100	80–90

COAGULATING BATH 9-22-1-5 (H_2SO_4—Na_2SO_4—$ZnSO_4$—$FeSO_4$)

Viscose:		
Salt Index	5.0	5.0
Per Cent Xanthate Sulfur	1.1	1.1
Per Cent Na_2CS_3 Added	0.32	0.0
Per Cent Na_2CS_3 Total	1.60	1.30
Yarn:		
Tenacity, g. p. d., dry	3.81	3.73
Tenacity, g. p. d., wet	2.49	2.29
Elongation Per Cent, dry	7.9	7.7
Elongation Per Cent, wet	19.6	18.1
Per Cent Skin	50–60	40–50

EXAMPLE VI

Ripened viscose is prepared as described in Example V except that 1.1% sodum trithiocarbonate is used and is spun into a bath containing 10% sulfuric acid, 14% sodium sulfate and 15%

zinc sulfate to form filaments. The spinning and processing conditions are the same as those described in Example I. The addition of sodium trithiocarbonate gives large improvement in skin thickness and physical properties in yarns which are spun at high bath acidity as is seen in the following Table VI which compares such yarn with yarn made from similarly ripened but modified viscose. One advantage of this procedure lies in the fact that the higher bath acidity permits higher spinning speeds.

Table VI

	Modified Ripened	Unmodified Ripened
Viscose:		
Salt Index	5.0	5.0
Per Cent Xanthate Sulfur	1.1	1.1
Per Cent Na_2CS_3 Added	1.1	0.0
Per Cent Na_2CS_3 Total	2.4	1.3
Yarn:		
Tenacity, g. p. d., dry	3.94	3.50
Tenacity, g. p. d., wet	2.74	2.08
Elongation Per Cent, dry	8.5	8.6
Elongation Per Cent, wet	19.7	17.3
Per Cent Skin	60–70	40–50

The term "caustic" as used throughout the specification means sodium hydroxide.

The term "unmodified" as applied to viscose throughout the examples means viscose which has not been modified by the addition of sodium trithiocarbonate whereas the modified viscose contains the added sodium trithiocarbonate.

The expression "6–14–15," for example, applied to the coagulating bath signifies 6% sulfuric acid, 14% sodium sulfate and 15% zinc sulfate in the aqueous bath and the expression "9–22–1–5," for example, applied to the coagulating bath signifies 9% sulfuric acid, 22% sodium sulfate, 1% zinc sulfate and 5% ferrous sulfate; other similar expressions have a corresponding significance; the sulfuric acid content is calculated as H_2SO_4.

In all the examples and elsewhere in the description, the sodium hydroxide (or caustic) content of the viscose, e. g. 6% as described in the examples, includes the free sodium hydroxide and the sodium (calculated as sodium hydroxide) combined in the form of sodium carbonate, sodium trithiocarbonate (including the added amount) and sodium cellulose xanthate; and the per cent by weight of sodium trithiocarbonate and of xanthate sulfur are percentages based on the weight of the viscose.

The examples specifically illustrate the addition of sodium trithiocarbonate as a modifier to the viscose. The invention contemplates a like addition, in place of sodium trithiocarbonate, of the trithiocarbonate of other alkali metals as well as other water soluble trithiocarbonates, e. g. potassium trithiocarbonate and lithium trithiocarbonate.

Either the product obtained by the reaction of carbon disulfide and sodium hydroxide, which contains one mol of sodium carbonate for every two mols of sodium trithiocarbonate, or the commercial product of Example II containing much less sodium carbonate, is effective in the practice of the invention.

The amount of alkali trithiocarbonate which should be added to the viscose to secure the best results in accordance with this invention depends to a large extent on the amount of carbon disulfide used in the preparation of the viscose, the latter amount, for most commercial viscoses, being in the range of 25% to 50% of

carbon disulfide, based on the weight of the cellulose. In explanation, the less carbon disulfide used for preparing the cellulose xanthate the lower is the resultant xanthate sulfur content, and the amount of alkali trithiocarbonate needed decreases as the xanthate content diminishes. Thus, for a 25% carbon disulfide unripened viscose, the total sodium trithiocarbonate present, including that which is added, should be not less than 1%, based on the weight of the viscose, in order to effect substantial improvements in spinning; for a 30% carbon disulfide viscose, the total sodium trithiocarbonate present should be at least 1.1%, and for a 35% carbon disulfide viscose, at least 1.3%. Generally speaking, the amount of sodium trithiocarbonate which is added to green viscose is computed so as to yield a viscose having a total content of sodium trithiocarbonate in excess of 1.3% and preferably within the range of 1.5% to 3%. While there is no critical upper limit, it is preferred that the total trithiocarbonate in the viscose shall not exceed 3% of the weight of the viscose.

As is pointed out above, unripened viscose contains a certain amount of sodium trithiocarbonate, e. g. about 0.85% for most commercial viscoses. The practical range of sodium trithiocarbonate to be added to the green viscose is, therefore, within the range of about 0.2% to about 2.25%, although a greater amount may be added if desired. Where trithiocarbonates other than sodium trithiocarbonates are used, the same weight percentages, or, alternatively, amounts containing the same weight content of combined trithiocarbonate radical may be used. Generally speaking, the amount of added alkali trithiocarbonate used is as low as possible to accomplish the purposes of the invention.

It has been observed that the optimum concentration of sodium trithiocarbonate needed to give normal filament formation and excellent properties rises as the xanthate sulfur content, i. e. the salt index, is increased. The salt index of the viscose to be spun is preferably 6.0 or above and may go as high as 20.0. Salt index is determined by the standard sodium chloride method of Reinthaler-Rowe, "Artificial Silk," 1928, page 69, which is described as follows:

The salt index is that concentration in per cent of sodium chloride at which coagulation in the form of flocks (white star-like particles) first occurs. It is determined by shaking mixtures of 10% sodium chloride and water with one drop of viscose for thirty seconds, and with each succeeding test, increasing the proportion of salt solution until one or two flocks are visible. As the xanthate substitution of the cellulose is increased, it requires higher salt concentrations to bring about coagulation.

Viscose used in the preparation of filaments by this invention may be a variety of types; for example, it may be made from wood pulp, cotton linters, mixtures of the two or even other types of cellulose. The composition of the viscose may also be varied widely. For example, it may have a cellulose content of from 4% to 10% (combined as sodium cellulose xanthate) and an alkali content of from 4% to 8%. The amount of carbon disulfide used in xanthation can be from 25% to 50%, based on the bone dry weight of the cellulose in the alkali cellulose, this basis also being that used in the examples in referring to per cent carbon disulfide. It has been found that the higher the xanthate sulfur content or

salt index of a viscose the greater are the improvements that can be obtained by adding sodium trithiocarbonate. One will normally use 30% or greater amounts of carbon disulfide, based on the dry weight of the cellulose, in xanthation, to obtain salt indices of 5.0 or over in unripened viscose. It has been shown in the examples that added sodium trithiocarbonate is effective in viscose showing salt indices from 5.0 to 20.0, but the advantage of the invention is present with spinnable viscoses of lower salt index. It is preferred that viscoses prepared in accordance with the invention be spun at a salt index of 6.0 or higher.

If desired, unripened viscose may be purified prior to the addition of sodium trithiocarbonate by washing the xanthate crumbs with methanol, then with ether, drying and dissolving in alkali. Modification of this purified viscose with sodium trithiocarbonate gives the same results of increase in yarn skin thickness and improvement in yarn properties.

Where relatively large amounts of sodium trithiocarbonate are present in the viscose, e. g. 2% or more, it is preferred that more than 4% sodium hydroxide be present in the viscose to prevent excessive gas formation due to the evolution of hydrogen sulfide. Sodium sulfite may also be used in the viscose to reduce gassing.

While the invention is most particularly applicable to continuous filaments and yarns, it may be applied to the production of staple fibers and is of benefit in the production of films, sponges and other products made from viscose.

The process may be used with advantage in a system wherein the first bath is a coagulating, substantially non-regenerating bath, e. g. a low acid, high zinc bath, and the second bath is a regenerating bath, and in this system, if desired, a third bath may be used for imparting stretch prior to, during or subsequent to regeneration.

The spinning bath may contain 4% to 11% sulfuric acid and 13% to 25% sodium sulfate. Zinc sulfate may be present in amounts of about 0.5% to 20%, preferably 1% to 15%, amounts higher than 8% being preferable when zinc sulfate is used alone as the salt of the bivalent metal. In addition to zinc sulfate, there may be present sulfates of iron, nickel, magnesium, manganese or chromium in proportions up to 10%, preferably between 0.5% and 5%. Ferrous sulfate is the preferred additional ingredient. With the addition of sodium trithiocarbonate to viscose, it is possible to obtain excellent yarns in the upper range of bath acidity under which conditions, with unmodified ripened viscose, a drop in physical properties occurs. The temperature range of good spinnability is from 40° to 65° C. On the basis of available data, it is desirable to have the bath acidity and temperatures as low as is practical for a given spinning speed in order to get optimum skin thickness and yarn properties. Each of the above concentrations should be adjusted to each other and to the composition of the viscose. It is desirable to use as high total solids content as possible in the coagulating bath to give the highest degree of gel shrinkage and improved stretchability.

In using this invention for the production of high tenacity yarn, a two-bath spinning system has been employed. One procedure comprises drawing off the freshly coagulated gel yarn with a feed wheel speed equal to or less than the jet velocity and applying all of the stretch between positively driven rollers traveling at different speeds. The thread can be given a travel of 10 to 50 inches in the secondary stretching bath which may be hot water or hot dilute sulfuric acid, e. g. water containing 2% sulfuric acid. The amount of stretch applied depends on the properties desired for the yarn, any amount of stretch used in standard practice being suitable. The invention contemplates also the use of a single bath system in which stretch is imparted to the filaments by a series of floating tension rollers having vanes on the under side, this being a single bath system involving a relatively long bath travel in order to get a substantial degree of stretch. The stretch may be applied in part in the primary or coagulated bath and the remainder in air by means of a long air travel, the yarn remaining plastic and responding to stretching by virtue of the adhering bath liquid, or the yarn may be stretched partly in the primary bath and then partly in a hot secondary stretching bath. The bath travel, where a single bath is used, may be increased to 130 to 250 inches by means of a multiple floating roller setup which gradually increases the tension on the filaments and thereby orients them by stretching them while they are plastic. The preferred method, however, is a two-bath system wherein from 60% to 100% of the stretch is imparted in a secondary bath of boiling water or water above 80° C. or a 2% sulfuric acid bath, the stretching bath preferably being a low acid bath, e. g. an aqueous bath containing up to about 3% sulfuric acid. A total stretch of 80% to 100% is preferred for producing high tenacity yarn and 20% to 30% for textile type yarns. The degree of stretch is therefore optional, depending on the use to which the yarn is to be put.

Instead of drying the stretched yarn on the collecting bobbin as is described in the above examples, it may be partially relaxed by rewinding before drying, on another bobbin at a lower tension.

While the bobbin process is illustrated in the examples for collecting the yarn, the spinning may be in accordance with the bucket process, or conveyor belt process, or a continuous process which involves purification prior to collection of the yarn. In any event, the yarn is washed free of acid and salt and is dried under tension, being preferably dried as it passes to a twister, or dried on a slasher to enable a proper control of the dry elongation of the finished product.

The skin on viscose yarn spun into sulfuric acid-sodium sulfate-zinc sulfate or sulfuric acid-sodium sulfate-zinc sulfate-ferrous sulfate baths is observed and measured in the following manner: The dried yarn is embedded in paraffin, cross-sections are cut and affixed to a glass slide by a shellac cement. After removing the paraffin in xylene, the sections are swollen in water and photomicrographs are taken. The skin is the outer shell which swells to a different extent than the core so that a fairly sharp boundary exists between the skin and the core. The proportion of skin area to core area can be estimated visually or determined accurately by means of a planimeter. The skin may be shown very graphically by a special dye technique. When cross-sections are soaked in 0.2% "Pontamine" Sky Blue dye for ten to sixty minutes, the core takes on a deep blue color while the skin remains undyed. Photomicrographs with a great contrast in shades in the skin and core are obtained using appropriate red filters. Such photomicrographs are shown in the drawings in which are illustrated the cross-

sections of two filaments spun by the technique of Example I using a 9.5–14–15

(H_2SO_4—Na_2SO_4—$ZnSO_4$)

coagulating bath, Figure 1 representing a filament spun from unripened viscose modified in accordance with this invention and illustrating a thick skinned filament and Figure 2 representing a filament spun from unripened, unmodified viscose and illustrating a thin skinned filament.

It is to be noted that this invention is concerned with the addition of sodium and other water soluble trithiocarbonates, as such, to the viscose. The practice of the invention distinguishes, for example, from the use of large amounts of carbon disulfide, e. g. in excess of 50%, based on the dry weight of the cellulose in the alkali cellulose, for the preparation of cellulose xanthate and distinguishes likewise from the addition of carbon disulfide as such to viscose.

The use of large amounts of carbon disulfide in the manner stated requires a long ripening period since normal xanthation must be carried out as usual with the ripening being longer than normal; different equipment than is normally used in the viscose process and the use of airtight containers and mixers would also be required where a high carbon disulfide percentage is used. By the addition of trithiocarbonate, on the contrary, the viscose composition may be readily and accurately controlled with a close adaptation to any desired set of spinning conditions and with the use of any carbon disulfide concentration dictated by the spinning conditions and objectives. A high carbon disulfide concentration, on the other hand, necessarily changes the xanthate sulfur concentration which seriously affects the spinning conditions.

The products of this invention in general may be used for any purposes where viscose fibers find application, for example the textile and tire cord industries. This invention makes it possible to produce yarns having a thicker skin than is normally obtained in the usual spinning process. Such yarns have the advantages of higher strength per denier and improved fatigue resistance. In addition, the yarns produced by this process have improved physical properties such as wet and dry tenacities.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

I claim:

1. A process which comprises incorporating in a freshly formed viscose a water-soluble trithiocarbonate in excess of that formed in the preparation of said freshly formed viscose and extruding resultant unripened viscose into a coagulating bath.

2. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to about 2.15%, based on the weight of said viscose, of a water-soluble trithiocarbonate in excess of the trithiocarbonate formed in the preparation of said freshly formed viscose and extruding the resultant unripened viscose into a coagulating bath.

3. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to about 2.15% of a water-soluble trithiocarbonate in excess of the trithiocarbonate formed in the preparation of said freshly formed viscose and extruding the resultant unripened viscose into a coagulating bath comprising an aqueous solution of sulfuric acid and sodium sulfate.

4. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to about 2.15% of a water-soluble trithiocarbonate in excess of the trithiocarbonate formed in the preparation of said freshly formed viscose and extruding the resultant unripened viscose into a coagulating bath comprising an aqueous solution of sulfuric acid, sodium sulfate and a sulfate of divalent metal.

5. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to about 2.15% of a water-soluble trithiocarbonate in excess of the trithiocarbonate formed in the preparation of said freshly formed viscose and extruding the resultant unripened viscose into a coagulating bath comprising an aqueous solution of sulfuric acid, sodium sulfate and zinc sulfate.

6. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to about 2.15% of a water-soluble trithiocarbonate in excess of the trithiocarbonate formed in the preparation of said freshly formed viscose and extruding the resultant unripened viscose into a coagulating bath comprising an aqueous solution comprising 4% to 11% sulfuric acid, 13% to 25% sodium sulfate and 1% to 20% zinc sulfate.

7. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to 2.15% of an alkali metal trithiocarbonate in excess of the trithiocarbonate formed by the preparation of said freshly formed viscose and extruding the resultant unripened viscose into a coagulating bath comprising an aqueous solution comprising 4% to 11% sulfuric acid, 13% to 25% sodium sulfate and 1% to 20% zinc sulfate.

8. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to 2.15% of sodium trithiocarbonate in excess of the trithiocarbonate formed in the preparation of said freshly formed viscose and extruding the resultant unripened viscose into a coagulating bath comprising an aqueous solution comprising 4% to 11% sulfuric acid, 13% to 25% sodium sulfate and 1% to 20% zinc sulfate.

9. A process which comprises modifying a freshly formed viscose by adding 0.65% to 2.15% sodium trithiocarbonate in excess of that formed in the preparation of said freshly formed viscose, extruding the resultant unripened viscose as filaments into a coagulating bath comprising an aqueous solution comprising 4% to 11% sulfuric acid, 13% to 25% sodium sulfate and 1% to 20% zinc sulfate and imparting to the coagulating filaments a substantial degree of stretch.

10. A process which comprises modifying a freshly formed viscose by incorporating 0.65% to 2.15% sodium trithiocarbonate in excess of the trithiocarbonate formed in the preparation of said freshly formed viscose; extruding the resultant unripened viscose as filaments into a coagulating bath comprising an aqueous solution comprising 4% to 11% sulfuric acid, 13% to 25% sodium sulfate and 1% to 20% zinc sulfate and imparting to the coagulating filaments a stretch of at least 20%.

11. The process of claim 10 in which the stretch is at least 20% and is applied at least in part in a secondary bath.

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