

July 29, 1958

H. S. JENKINS ET AL
MANUFACTURE OF PROTEIN FIBERS

2,845,362

Filed Dec. 3, 1956

Fig. 1

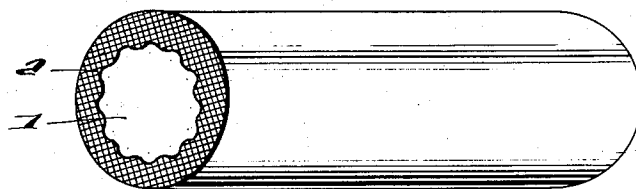


Fig. 2

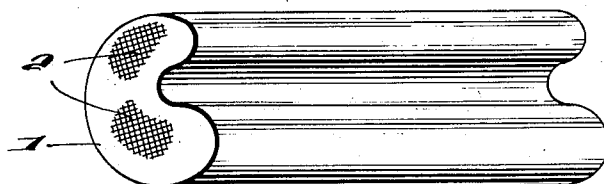
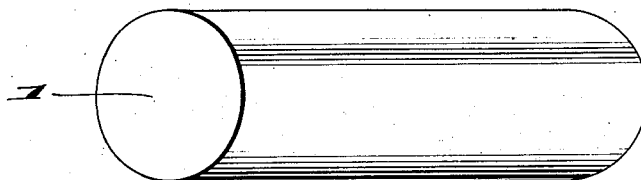


Fig. 3



INVENTORS
Herschel Sidney Jenkins
John R. Magee Jr.
Herbert Seth Morgan Jr.
BY Bernard M. Saffian
Pierce, Scheffler & Parker ATTORNEYS

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MANUFACTURE OF PROTEIN FIBERS

Herschel Sidney Jenkins, Chesterfield, Va., John R. Magee, Jr., Norwich, Conn., Herbert Seth Morgan, Jr., Chesterfield, Va., and Bernard M. Saffian, Norwich, Conn., assignors to Virginia-Carolina Chemical Corporation, Richmond, Va., a corporation of Virginia

Application December 3, 1956, Serial No. 626,007

18 Claims. (Cl. 106—153)

Many types of processes for making fibers from both animal and vegetable protein materials have been described in the prior art. The protein materials have different properties depending on their origin, i. e., animal or vegetable. In addition, both animal and vegetable proteins have many sub-types that have varying properties and fiber-forming tendencies. It might be said that for almost every type of protein there is a process that converts it to a fiber.

This invention relates to a process for the production of fibers from the prolamines. The prolamines are vegetable proteins. The invention relates further to an improved process for making prolamine fibers in the two to two hundred denier range. More particularly, the invention is concerned with an improved process for making improved zein fibers in the two to two hundred denier range. Zein is a prolamine.

By improved fibers we mean fibers having improved properties. The fibers produced by the processes of the prior art had good dyeability but inferior tenacity and chemical resistance, or else they had good tenacity and chemical resistance but inferior dyeability. In addition, these fibers have been off-round and/or opaque. The fibers produced by the process of our invention not only have good dyeability, tenacity, and chemical resistance, but they are also round and have no opaqueness, either on the surface or in the interior of the fiber.

The terms used above have the following meanings so far as our invention is concerned:

Tenacity—tensile strength expressed in grams per denier.

Chemical resistance—ability to withstand bleaching without appreciable loss in physical strength or appearance.

Dyeability—ability to withstand acid dyeing at the boiling point without large loss in physical strength or appearance.

In the past, protein fibers have been made by at least two processes. The first of these processes is known as the "dry spinning" method. In this type process the protein raw material is made into a dough by mixing with an organic solvent. This dough is subjected to high shear stresses and then forced through a spinnerette into a gas atmosphere. As the filaments pass from the spinnerette, the solvent evaporates and a dry fiber is produced. Small as well as large denier fibers have been made. However, because of the many problems associated with this type process, because the fibers produced are brittle and because of the high cost of the specialized equipment needed, the method has never achieved commercial significance.

The second type process for making protein fibers is known as the "wet spinning" method. In this process, the protein raw material is dissolved in an aqueous alkaline solution. This solution is extruded into an acidic coagulation bath through a spinnerette, and the coagulated

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fiber filaments are formed. Thereafter, a tow of fibers is treated in various processing steps, such as stretching, curing, washing, etc., and may be bleached and baked. This process has achieved commercial success because of its ease of operability and because of its relatively low processing costs. However, there have been many problems associated with this type process and there have been certain limitations necessarily imposed on the fibers produced therefrom.

Perhaps two of the biggest problems associated with the successful commercial manufacture of protein fibers by the wet method have been:

(1) Lack of a process which yields good fibers at all deniers.

(2) Lack of a process which gives fibers of superior quality in all of the three major physical properties, i. e. tenacity, dyeability and chemical resistance.

It is an object of this invention to provide a wet method process by which prolamine fibers are made in the two to two hundred denier range. It is also an object of this invention to provide a wet method process which gives prolamine fibers of superior chemical resistance, dyeability and tenacity at all deniers in the above range. Thus, by accomplishing these objects of our invention, we have done away with two of the most objectionable problems that have in the past plagued the protein fiber manufacturers.

It is a further object of our invention to provide a wet method process which produces low, medium and high denier prolamine fibers that are round and clear and have good luster. Prolamine fibers produced in the past have often been deficient in one or more of these properties and it appears that their importance and relationship with the properties of chemical resistance, tenacity and good dyeability have been overlooked. This is to say that we have found that the clearer and more nearly round the fiber, the more superior are the above properties.

Three different types of fibers are illustrated in the accompanying drawings in which:

Fig. 1 is a diagrammatic representation of a greatly magnified perspective and cross-sectional view of a type A fiber,

Fig. 2 is a similar representation of a type B fiber, and Fig. 3 is a similar representation of a type C fiber.

Referring to Fig. 1 it will be seen that the type A fiber is circular in cross-section and has a clear transparent central portion 1 and an opaque, striated surface portion 2. The type B fiber of Fig. 2 is not circular in cross section and has a clear, transparent outer portion 1 with opaque, striated portions 2 in its interior. This type of fiber may be referred to as being peanut shaped in cross-section. The type C fiber of Fig. 3 is circular in cross section and is clear and transparent throughout. Type C fibers are produced by the practice of our invention. Type A and type B fibers show poor behavior in at least one of the properties of dyeability, chemical resistance and tenacity. Type C fibers exhibit superiority in all three of these properties. In addition, type C fibers generally have higher luster than either type A or type B fibers.

It is well known that most wet-method fiber processes consist of four major steps:

- (1) Solubilization—also called spin solution preparation
- (2) Regeneration—also called coagulation
- (3) Orientation—also called stretching
- (4) Insolubilization—also called hardening

While each of these steps is important, we have found

that solubilization is critical in the production of the type C fibers. It is in this step that the most important changes in the protein molecule take place. It is in this step that the globules of prolamine material are broken down and then prepared for regeneration in a different form. And it is in this step that the coagulability of the prolamine in fibrous form is determined. By coagulability we mean the inclination of the prolamine in solution to form type C structured fibers. That is, a prolamine solution of poor coagulability tends to form type A or type B fibers in a given coagulation bath. But a prolamine solution of good coagulability tends to form type C fibers in the same coagulation bath. Thus, it is another object of our invention to provide prolamine solutions of good coagulability.

We have found, surprisingly, that all the above objects are accomplished by the addition of a water-soluble, ionizable salt to the prolamine solution before it is spun into the coagulation bath. Examples of such salts are Na_2S , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_3 , NaCl , CaCl_2 , $\text{Al}_2(\text{SO}_4)_3$, $\text{Na}_2\text{S}_2\text{O}_4$, NH_4Cl and sodium thioglycolate. This is entirely new and unpredictable, for nowhere in the prior art have we found any indication that such a step would make possible:

- (1) Spinning of protein fibers of two to two hundred denier from the same spin solution
- (2) Spinning of round, clear fibers
- (3) Spinning of fibers of improved chemical and physical properties in all denier ranges

The invention will be more fully described and illustrated hereinafter with reference to the production of zein fibers.

Broadly speaking, our process is defined by the general write-up below:

Zein raw material having an alkali gel time of 25 to 40 minutes is preferred. By alkali gel time is meant the time in minutes required, by heating at 45°C ., for an aqueous zein dispersion containing 2.5% by weight of NaOH and 16% by weight of zein raw material to reach a viscosity of 80 poises at 45.0°C . as measured by the Brookfield viscometer at 1 R. P. M. A dispersion of zein of from about 16% to about 22% by weight is prepared by slurring the zein in water at a temperature of about 15°C . to 30°C ., preferably about 25°C . To this slurry are added from 1.2% to 2.0% NaOH and from about .01% to about 2.5% of the required salt, the percentages of NaOH and salt being based on the zein content by weight. All of the alkali is added to the slurry over a period of about five minutes. When the addition is complete, the smooth zein dispersion is heated from about 1 minute to about 60 minutes at a temperature of from 25°C . to 45°C . At this time the viscosity at 38°C . and measured at 1 R. P. M. on the Brookfield viscometer is from 5 to 2000 poises.

To the dispersion at this point from about 1.0% to about 6% by weight of formaldehyde, based upon the weight of zein, is added in the form of a 37% formalin solution or as polyoxymethylene in equivalent amount. Also added at this time is from about 0.01% to about 0.1% by weight of NaOH based on the weight of zein. This last addition of NaOH is for neutralization of the formic acid present in the formaldehyde.

The resulting mixture is stirred for a period of about 10 minutes to insure a smooth, homogeneous dispersion, and is deaerated under reduced pressure. The dispersion is spun using the conventional Vicose extrusion pump, candle filter and spinnerettes. The spinning viscosity is normally from about 60 to about 25,000 poises at 25°C . measured at 1 R. P. M. on the Brookfield viscometer.

It will be obvious to one skilled in the art that certain of the above steps could be changed chronologically without departing from the invention. For example, the

required salt could be added to the spin solution just prior to deaeration. The particular time at which the salt is added to the spin solution is not critical. As a matter of fact, the salt may be added to the raw zein material or to the water before the raw zein material is added. The invention comprises the inclusion of the salt in the solution at any stage prior to the extrusion of the solution into the coagulation bath.

The lower limit of salt addition is given as 0.01% based on the weight of the zein content of the solution, this being the smallest amount that will give an appreciable effect. The preferred salt addition is generally within the range from .25% to .75%. The upper limit of salt addition for all salts and all zein solutions has not been determined. The optimum amount varies with the particular system i. e. the character of the zein raw material, the concentration of the zein solution, the concentration of NaOH in the zein solution, the concentration of formaldehyde in the zein solution and the particular salt used. By interpolation 2.5% has been calculated to be the approximate upper limit of useful salt addition.

The coagulation bath is one that is normally used in the art. It consists essentially of water, sulfuric acid, sodium sulfate, formaldehyde which leaches into the bath from the spin solution and hydrated silica.

To give optimum coagulation, the sulfuric acid and sodium sulfate contents may be varied inversely with length of time that the spun fiber is maintained in the bath. We have found, however, that the following coagulation bath is preferred.

The sulfuric acid content of the coagulating bath is maintained within the range from 10.5 to 11.5% by weight and preferably at 11.0%. The sodium sulfate concentration of the coagulating bath may vary within the range from 0 to 2% by weight but in practice preferably is maintained at about 1.2%. No formaldehyde is added to the coagulating bath as such but tends to leach out of the spin solution and to build-up in the coagulating bath. Since a higher concentration of formaldehyde in the coagulating bath gives rise to difficulties we have set an upper limit of 0.5% by weight. The hydrated silica content of the coagulating bath is maintained within the range from 2.25% to 2.75% by weight and preferably at 2.5%. It serves to prevent sticking of the filaments due to heat and pressure when the filaments are in a plastic state after coagulation during the precuring and stretching but it has no effect upon the dyeing or color of the fiber. Its presence in the coagulating bath avoids the use of goulac which heretofore has been used as a protective colloid to prevent sticking of the fibers but which we have found to be not only a dye resist which adds color to the fiber but also to be ineffective to prevent sticking of the fibers in our process.

The temperature of the coagulating bath is maintained within the range 75° to 77°F . and preferably at 76°F . This close temperature control may require the provision of means for heating or cooling depending upon the atmospheric conditions. This however is a feature of apparatus which may be provided by one skilled in that art and need not be described in the disclosure of our invention.

The coagulation time, i. e., the length of time that the spun fiber is maintained in the coagulating bath, cannot be stated in seconds but we have found that a spinning speed of 31 feet per minute with the spinnerette submerged to a depth of 5 inches in the coagulation bath gives satisfactory results. It has been found in practice that the coagulation time may vary considerably, e. g. 50% from the time corresponding to the figures given above.

As is stated at the outset, the essential characteristics of the fiber are determined by the conditions in the spin solution and in the coagulating step. The remaining steps of the process may be carried out in accordance with the

prior art. However we have worked out suitable or preferred conditions for the subsequent steps of precuring, stretching, saturation and postcuring which will now be described.

Precuring is carried out by maintaining the fiber tow leaving the coagulating bath and wet with coagulating bath solution in an atmosphere of air at a humidity of 95% to 100% to prevent evaporation and at a temperature of from 75 to 77° F., preferably 76° F. for a period of from 28 to 32 minutes, preferably 30 minutes. The liquid content of the tow during precure will vary from 60-70% at the start to 45-55% at the end. At the end of the precuring operation the tow is washed with water by passing the tow between squeeze rolls and by delivering water to said squeeze rolls at a temperature of 70° to 80° F., preferably 76° F. This washing operation removes the bulk of the hydrated silica and the bulk of the acid from the fiber.

The fiber tow then passes from the washing step of the precuring operation to the stretching operation. The tow is stretched in a liquid bath which consists essentially of water but may contain from 0 to 0.5% by weight of sulfuric acid, from 0 to 1% by weight of sodium sulfate, from 0 to 0.5% by weight of formaldehyde and from 0 to 0.5% by weight of silica carried into the stretching bath with the tow. The amount of carryover will depend upon the efficiency of the washing step of the precuring operation. Increase of the sulfuric acid, sodium sulfate and formaldehyde contents of the stretching bath above the limits noted is prevented, if necessary, by renewal of the bath with water. The stretch bath temperature is maintained at 140 to 145° F., preferably 143° F. and the degree of stretch is maintained within the range from 295% to 320%, preferably at substantially 295%. The time of stretching is maintained within the range from 1.6 to 2.5 minutes.

and 0 to 2% by weight of sodium sulfate and is from 95% to 100% saturated with sodium chloride. The liquid content of the tow leaving the saturator is within the range from 48% to 52% by weight.

The tow leaving the saturator is passed to the postcure treatment where it is subjected to a temperature of from 110° to 125° F., preferably 112° F. for a period of 115 to 125 minutes, preferably 120 minutes in an atmosphere of air at a relative humidity of 95% to 100%.

Other treatments may follow the postcuring treatment such as washing, drying, baking, bleaching, finishing, etc., but since such treatments are not embraced by our present invention they will not be described.

While we have described the specific conditions which we have found by extensive experience to give the best results from the dissolving of the zein in the preparation of the spin solution through the postcuring treatment it is to be understood that we consider our invention to reside primarily in the first operation described, i. e., the addition of any of the above named salts in the preparation of the spin solution, because this step is critical for the production of fibers of the highest quality with respect to tenacity, chemical resistance and dyeability. The other operations, including coagulation may contribute to the final result but if the first operation is not properly performed, no subsequent procedure, so far as we are aware, will give the desired final product. On the other hand a fiber which has been formed from a properly prepared spin solution may be coagulated and finished in a variety of ways as disclosed in the prior art with more or less satisfactory results with respect to the three principal properties of tenacity, chemical resistance and dyeability.

To illustrate the results obtained by the practice of our invention, we have obtained the following data from a great number of experiments.

TABLE I
Test results on zein fibers from spin solutions containing salts

Approx. Denier	Unbleached				Bleached				Bleached and Acid Dyed			
	W. T.	D. T.	W. E.	D. E.	W. T.	D. T.	W. E.	D. E.	W. T.	D. T.	W. E.	D. E.
3.....	.70	1.36	28	28	.67	1.19	36	35	-----	1.03	-----	42
15.....	.76	1.57	27	24	.62	1.15	31	30	-----	1.00	-----	34
22.5.....	-----	1.04	-----	30	-----	.75	-----	27	-----	.68	-----	28
106.....	-----	1.15	-----	29	-----	.73	-----	18	-----	.63	-----	15
109.....	-----	.80	-----	28	-----	.64	-----	11	-----	.62	-----	12
180.....	.75	.80	19	18	-----	-----	-----	-----	-----	-----	-----	-----

W. T.=wet tenacity.
D. T.=dry tenacity.
W. E.=wet elongation.
D. E.=dry elongation.

From the stretching operation the fiber tow is delivered to the saturator. The tow remains in the saturator from 2 to 3 minutes depending upon the speed of operation; the time being always sufficient to effect complete saturation of the tow with the postcuring solution and complete replacement of the water and loosely held chemicals in the tow as it comes from the stretching operation. The saturation also serves to "set" the stretch except for a small relaxation shrinkage which occurs during postcuring.

The temperature of the postcuring solution is maintained within the range from 128° F. to 132° F. and preferably at 130° F.

The postcuring solution is a water solution containing 0.5 to 1% by weight, preferably 0.75% of formaldehyde, 4.5 to 5.5% by weight, preferably 5.0% of sulfuric acid

These results show that the use of salts in the spin solution makes possible the production of zein fibers in all sizes from about 2 to about 200 denier. In addition, the fibers produced by our process are highly resistant to acid dyeing and bleaching. They suffer only slightly in tenacity after such treatments.

To further illustrate the improvements resulting from the use of salts in the spin solution, the following experiments were made.

Preparation of 3 denier zein fibers

EXAMPLE I

In the following description all parts are by weight. 860 parts of zein A (Corn Products Refining Co.) was slurried into 2983.7 parts of water at 18° C. 12.8 parts

of NaOH and 6.2 parts of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were dissolved in 115.2 parts of water. This solution was added slowly with stirring over a period of five minutes to the zein slurry. After this addition, the smooth zein dispersion was heated at 38° C. until the viscosity at 38° C. and measured at 1 R. P. M. on the Brookfield viscometer was approximately 800 poises.

To the dispersion at this point was added 108.1 parts of 37% formalin solution and 0.4 parts of NaOH dissolved in 3.6 parts of water. The NaOH solution and the formalin solution were mixed just prior to addition to the zein dispersion. The total spin dispersion at this point was 4000 parts.

The dispersion was stirred for a period of ten minutes to insure smoothness and homogeneity. The entrapped air was then removed deaeration under reduced pressure. The viscosity at this point was approximately 2800 poises at 25° C., at 1 R. P. M. on the Brookfield viscometer. The dispersion was extruded through a 1500 hole .003 inch spinnerette and coagulated in the bath described above. The coagulated fibers were then treated according to the further steps as described i. e. precuring, washing, stretching, saturating, postcuring, washing, baking, etc.

TABLE II

Test results on three denier zein fibers

Fibers From—	Unbleached ¹			
	D. T.	W. T.	D. E.	W. E.
Example I.....	1.36	.76	29	33
Example II.....	1.25	.76	40	41
Example III.....	1.10	.68	28	34

¹ These values are for raw fiber tested by the twist bundle technique

The data presented in Table III below shows further experimental work that illustrates the feasibility of making fibers in all denier ranges by the use of salts in the spin solution. It should be reemphasized that no known prior art process has shown the production of fibers in all denier ranges. From Table III it will be seen that we were unable to make even a poor fiber at 15 denier or above without the salts present. But when salts were added, good fibers of as high as 191 denier were made. The experiments were made within the limits of the process variables set out above, and the more important variables are included in the table.

TABLE III

Example No.	Denier Spun	Salt Added	Percent Salt	Vis. at 38° C.	Percent NaOH	Natural Properties ¹				Type Structure	Fiber Shape
						W. T.	D. T.	W. E.	D. E.		
IV.....	3	Na_2S	.25	768	1.35	.70	1.36	28	28	A.....	Round.
V.....	3	Na_2S	.50	704	1.80	.49	.93	34	36	C.....	Do.
VI.....	3	Na_2S	.75	800	1.80	.50	1.03	37	33	C.....	Do.
VII.....	3	Na_2S	1.00	800	1.80	.58	.72	50	27	C.....	Do.
VIII.....	15	Na_2S	.25	768	1.35	.76	1.57	27	24	A and C mixed.	Do.
IX.....	15	None	-----	320	1.60	Not Possible to Spin A Fiber				A and C mixed.	Do.
X.....	26	Na_2S	.25	768	1.35	.78	1.63	24	24	A and C mixed.	Do.
XI.....	28	Na_2S	.25	240	1.65	.57	1.21	29	28	C.....	Do.
XII.....	66	Na_2S	.25	280	1.65	.64	.81	18	25	C.....	Do.
XIII.....	66	None	-----	320	1.60	Not Possible to Spin A Fiber				C.....	Do.
XIV.....	137	Na_2S	.25	280	1.65	.71	.87	15	20	C.....	Mixed Round and Off-Round.
XV.....	158	Na_2S	.25	600	1.80	.70	.96	22	11	C.....	Do.
XVI.....	191	Na_2S	.25	880	1.80	.57	.83	14	7	C.....	Round.
XVII.....	2.2	$(\text{NH}_4)_2\text{SO}_4$	.25	184	1.65	-----	.92	-----	39	C.....	Do.
XVIII.....	22.5	$(\text{NH}_4)_2\text{SO}_4$	.25	184	1.65	-----	1.04	-----	30	C.....	Do.
XIX.....	47.1	$(\text{NH}_4)_2\text{SO}_4$	.25	184	1.65	-----	1.15	-----	27	C.....	Do.
XX.....	106.1	$(\text{NH}_4)_2\text{SO}_4$	.25	184	1.65	-----	1.15	-----	29	A and C mixed.	Do.
XXI.....	2.5	NaCl	.25	152	1.65	-----	.92	-----	37	C.....	Do.
XXII.....	3.4	NaCl	.77	575	2.00	.48	.94	39	33	A.....	Do.
XXIII.....	24.2	NaCl	.25	152	1.65	-----	.92	-----	29	C.....	Do.
XXIV.....	41.8	NaCl	.25	152	1.65	-----	.90	-----	27	C.....	Mixed Round and Off-Round.
XXV.....	109.4	NaCl	.25	152	1.65	-----	.80	-----	28	C.....	Off-Round.
XXVI.....	2.3	NH_4Cl	.25	960	1.65	-----	.98	-----	28	C.....	Round.
XXVII.....	21.1	NH_4Cl	.25	960	1.65	-----	1.08	-----	23	C.....	Do.
XXVIII.....	39.0	NH_4Cl	.25	960	1.65	-----	.99	-----	19	C.....	Do.
XXIX.....	156.9	NH_4Cl	.25	960	1.65	-----	.89	-----	18	C.....	Do.

¹ These values are for raw fiber tested by the no-twist bundle technique.

EXAMPLE II

The same experiment was made as in Example I except that 0.25% of sodium chloride based on the zein replaced the sodium sulfide.

EXAMPLE III

The same experiment was made as in Example I except that 0.25% of sodium thioglycolate based on the zein was added in place of the sodium sulfide.

The table below shows the test results on the fibers obtained from Examples I, II, and III.

The results in Table III clearly indicate that the inclusion of salts in the spin solution makes possible the production of zein fibers having good properties in all denier ranges from about 2 to about 200. From the data in Table III for each salt there appears to be an optimum amount needed which depends on the various other variables present in a given spin solution, e. g., percent alkali, viscosity, etc.

Other salts have been tested. For example, .25 percent of each of the salts named in Table IV was included in the spinning of a 20% zein dispersion containing 2.0 per-

cent NaOH and 5% formaldehyde. The dispersions were prepared as set out above, spun, and the resulting fibers had the following properties.

7. Process as defined in claim 1 in which the salt is sodium chloride.

TABLE IV

Example No.	Salt Added	Denier Spun	Natural Properties							
			No Twist				With Twist			
			W. T.	D. T.	W. E.	D. E.	W. T.	D. T.	W. E.	D. E.
XXX	Na ₂ SO ₄	3.4	.55	.98	35	31	.77	1.29	42	38
XXXI	Na ₂ SO ₄	31.2	.44	.94	24	25				
XXXII	Na ₂ S ₂ O ₄	3.5	.49	.84	47	37	.72	1.08	57	48
XXXIII	Na ₂ S ₂ O ₄	36.8	.38	.85	24	26				
XXXIV	CaCl ₂	3.7	.54	1.05	35	29	.80	1.13	41	37
XXXV	CaCl ₂	41.3	.34	.81	6	5				
XXXVI	(Al) ₂ (SO ₄) ₃	3.5	.42	.86	46	30	.61	1.10	59	37
XXXVII	(Al) ₂ (SO ₄) ₃	39.4	.50	.85	13	9				
XXXVIII	Na ₂ SO ₃	3.0					.70	1.12	38	40

In summary, the data presented shows that the inclusion of salts in the spin solution makes possible the production of zein fibers in the denier range of from about two to about two hundred. At the same time, such use of salts definitely makes possible the production of improved fibers having better chemical resistance to acid dyeing and bleaching, better tenacities and improved internal structure, i. e., roundness and clarity.

We claim:

1. In a process for the production of prolamine fibers comprising the steps of dissolving the prolamine in an aqueous alkaline solution and spinning the resulting solution into an acidic coagulating bath the improvement which consists in incorporating from about 0.01% to about 2.5% of a water-soluble ionizable salt of the group consisting of sodium sulfide, sodium sulfate, ammonium sulfate, sodium sulfite, sodium chloride, calcium chloride, aluminium sulfate, sodium hydrosulfite, ammonium chloride and sodium thioglycolate based upon the weight of the prolamine in said solution.

2. Process as defined in claim 1 in which the prolamine is zein.

3. Process as defined in claim 2 in which the zein has an alkali gel time within the range from 25 minutes to 40 minutes and the zein solution contains from about 16% to about 22% by weight of zein and from about 1.2% to about 2% by weight of NaOH and from about 1% to about 6% by weight of formaldehyde based on the weight of the zein content of the solution.

4. Process as defined in claim 3 in which the salt addition is within the range from 0.25% to 0.75% of the weight of the zein content of the solution.

5. Process as defined in claim 1 in which the prolamine is zein and the aqueous alkaline solution is a water solution of NaOH.

6. Process as defined in claim 1 in which the salt is sodium sulfide.

8. Process as defined in claim 1 in which the salt is ammonium chloride.

9. Process as defined in claim 1 in which the salt is calcium chloride.

10. Process as defined in claim 1 in which the salt is sodium sulfate.

11. As a new product an aqueous alkaline solution of a prolamine, said solution containing from about 16% to about 22% of prolamine and from about 0.01% to about 2.5% by weight, based upon the weight of the prolamine, of a water-soluble ionizable salt of the group consisting of sodium sulfide, sodium sulfate, ammonium sulfate, sodium sulfite, sodium chloride, calcium chloride, aluminium sulfate, sodium hydrosulfite, ammonium chloride and sodium thioglycolate.

12. A new product as defined in claim 11 in which the prolamine is zein.

13. A new product as defined in claim 12 in which the solution contains from about 16% to about 22% by weight of zein and from about 1.2% to about 2% of NaOH, based on the weight of the zein.

14. A new product as defined in claim 11 in which the salt is sodium sulfide.

15. A new product as defined in claim 11 in which the salt is sodium chloride.

16. A new product as defined in claim 11 in which the salt is ammonium chloride.

17. A new product as defined in claim 11 in which the salt is calcium chloride.

18. A new product as defined in claim 11 in which the salt is sodium sulfate.

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