

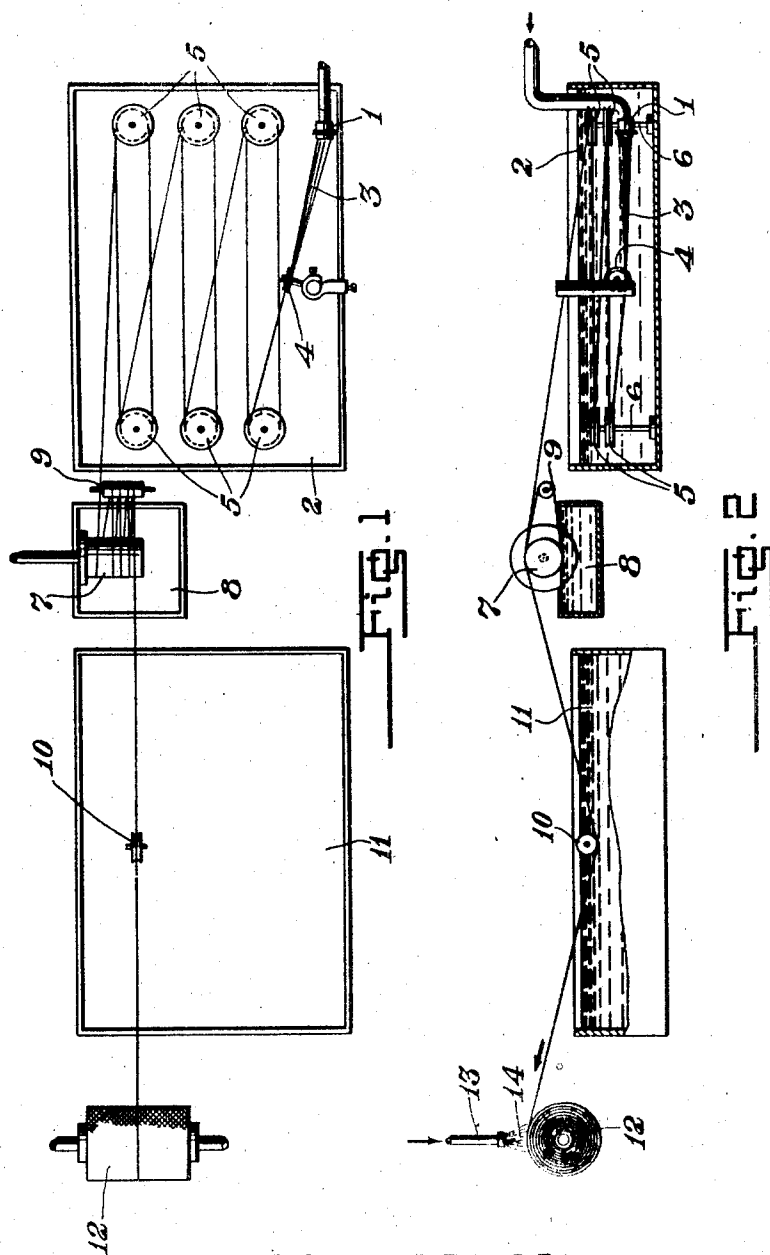
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SHAPED PROTEIN STRUCTURES AND THEIR PREPARATION

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SHAPED PROTEIN STRUCTURES AND THEIR PREPARATION

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This invention relates to the production of shaped structures from proteins and more particularly to the production of novel synthetic protein fibers and the like.

By the term "fibers and the like," as used herein and in the appended claims, is meant filaments, fibers, yarns and threads of any denier or cross-sectional shape and bands or tows consisting of any number of such filamentary articles.

It has been the usual practice to prepare synthetic protein fibers from globulins, phosphoproteins, or prolamines by dissolving them in aqueous caustic alkali or other solvents such as alkaline salts, amines, quaternary ammonium hydroxides, organic acids, and alcohol. The solutions have been extruded through an appropriate orifice into a coagulating bath generally containing a mineral acid and inorganic salts. Then the fibers have been withdrawn from the bath and hardened with formaldehyde. Many variations of this basic process have been proposed. They include incorporation of plasticizers and other agents in the protein spinning solution, incorporation of such materials as formaldehyde, other tanning agents, and organic acids in the coagulating bath, stretching of the fibers either during coagulation or at a later stage in the process, and hardening the shaped product with formaldehyde and/or other tanning materials under a multiplicity of conditions involving various concentrations of the hardening agents, various temperatures and times of treatment, and various concentrations of added salts and acids. A process is also known in which casein fibers coagulated in one bath are removed from the bath, subjected to a preliminary hardening treatment, stretched, and then subjected to a second hardening treatment without allowing them to contract.

However, in spite of the many improvements which have been made since the basic process was proposed, protein fibers produced by any of the prior art processes are unattractive commercially in many respects. They possess low tenacity, less than 1.0 g./d. (i. e., less than 1.0 gram per denier), and particularly low wet strength, less than 0.5 g./d. They also possess substantially no orientation when examined by X-rays. In addition, their elastic recovery from stretch and modulus of elasticity are far below those of wool.

It is an object of this invention to convert proteins into shaped structures, particularly filaments, fibers, yarns and threads. It is a further object of this invention to accomplish this

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conversion under conditions which result in synthetic fibers and the like having dry and wet tenacities of at least 1.2 and 0.6 g./d., respectively, when tested on the Scott incline plane tester at 60% relative humidity and 21° C. Another object is to provide fibers whose elastic recovery from stretch and modulus of elasticity are much closer to those of wool than those of synthetic protein fibers hitherto produced. Still another object is to provide a process for the manufacture of shaped protein structures having a relatively high degree of orientation as shown by X-rays. Orientation as shown by X-rays is not to be confused with that shown by birefringence measurements and other measurements involving the use of polarized light. A low degree of orientation may be detected by means of birefringence measurements but the orientation must be of a relatively high order before it can be detected by means of X-rays. Still another object is to provide shaped protein fibers which have a skin on their outer surface, as shown in the cross-section of the wet fibers. Additional objects will become apparent from an examination of the following description and claims.

These and other objects and advantages are accomplished by the herein described invention which broadly comprises extruding an aqueous alkaline solution of a water-insoluble globular protein containing 10-30% protein into a coagulating bath containing 0.5-10% of a strong mineral acid, at least 10% of one or more water-soluble inorganic salts, and formaldehyde, stretching the formed filaments 25-300% in the coagulating bath, further stretching them at least 50% of the maximum draw ratio in a hot concentrated aqueous solution of a salt material selected from the group consisting of water-soluble neutral and acid-reacting salts of mineral acids and admixtures of said salts, at a temperature above 60° C., and further treating the resultant stretched filaments with an aqueous formaldehyde solution containing one or more water-soluble inorganic salts.

By the term "strong mineral acid" as employed herein and in the appended claims is meant a water-soluble inorganic acid having a dissociation constant greater than 1×10^{-2} .

By the expression "water-soluble" as used herein and in the appended claims is meant a compound which is soluble in water to the extent of at least 5 grams per 100 cubic centimeters of water at 20° C.

By the term "inorganic salt" as used herein

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and in the appended claims is meant a salt of a metal and an inorganic acid.

The maximum draw ratio for a fiber or the like which is being stretched between rotating rollers is the ratio between the peripheral speed of the faster roller and the peripheral speed of the slower roller when the rollers are operating at such speeds that the fiber is being stretched to a point just below that at which the fiber will break.

By the term "neutral salt" as employed herein and in the appended claims is meant a salt which, when admixed with water, provides a solution having a pH of about 7; while by the term "acid-reacting salt" is meant a salt which, when admixed with water, produces a solution having a pH of less than 7.

In the process of this invention the preparation of the spinning solution is accomplished by agitating a portion of casein with water for several minutes. Then the alkali in the form of a concentrated aqueous solution is added with thorough agitation. The solution becomes homogeneous in about 30 minutes at room temperature. Homogeneity is accomplished in a shorter space of time if the solution is continually agitated. Before spinning it is customary to filter the solution and deaerate it under vacuum to avoid stoppages in the spinneret and discontinuity in the spinning.

In the process of my invention I have found the usual gear pump, candle filter, and viscose type spinneret satisfactory for use. The number of orifices in the spinneret has little effect except on the rate of fiber production, so that spinnerets containing either one or a multiplicity of orifices may be employed. From the spinneret the solution is extruded directly into a coagulating bath containing chemicals which facilitate the transformation of the solution from a liquid fiber to a solid fiber. A suitable bath may be described as one having a density greater than 1.1 and containing inorganic salts such as sodium sulfate or sodium chloride, a strong mineral acid, and formaldehyde. The coagulating bath is fitted with yarn driven rollers, mounted so that they can freely rotate on suitable shafts, in such a manner that the filaments issuing from the spinneret may be led around the rollers before removal from the coagulating bath and may be subjected to stretching during travel between the various rollers.

The coagulated and partially stretched filaments are removed from the bath by means of a positively driven godet wheel. The lower portion of the godet wheel is run in a buffered salt solution such that the filaments are washed and the excess acid from the coagulating bath is partially removed. From the godet wheel the filaments are passed through a hot concentrated sodium chloride solution by means of appropriate guides and rollers and are then wound on a positively driven bobbin. The peripheral speed of the bobbin is higher than that of the godet wheel such that the filaments are stretched during passage through the hot sodium chloride solution. During collection on the bobbin, the filaments are kept moist with a spray of concentrated sodium chloride solution.

The filaments are then hardened with formaldehyde on the bobbin in a solution such as one containing 7.6% sodium chloride, 3.9% aluminum sulfate, and 3.3% formaldehyde. The filaments are then washed and, if desired, are treated with nitrous acid, ketene, or acetic anhydride to

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render them more resistant to wet processing. They are then allowed to dry on the bobbin. The filaments may be twisted, used in continuous filament form, or cut into staple.

The following examples are given for illustrative purposes and are not intended to place any restrictions or limitations on the herein described invention. In said examples, unless otherwise stated, all percentage quantities of the protein are based on its dry weight. Measurements and proportions of all chemicals are given in terms of anhydrous rather than hydrated weight.

Tenacities and elongations of multifilament yarns are given in terms of measurements made with a constant specimen-rate-of-load type testing machine (Scott incline plane tester model IP2) using a loading rate of 4 grams per denier per minute (A. S. T. M. designation: D258-42) and a distance between clamps of four inches. One end of the conditioned yarn specimen is fastened in the carriage clamp, located four inches from the left hand clamp. The other end of the yarn is then passed through the left hand clamp and over the roller on the tension device. Sufficient tension is applied to the yarn end to balance the tension device and the left hand clamp is fastened. The machine is started and allowed to trace a stress-strain curve for the yarn on the chart provided. When the yarn breaks, a mark is made on the chart showing the position of the pen at the time of break. From the location of the point the tenacity and elongation of the specimen may be read on the chart. Tenacities are based on original yarn dimensions. When tested similarly on this machine, a sample of recent, 200 denier, 35 filament, 3 twist, textile grade, oiled, viscose rayon is found to have tenacities of 1.9, 0.9 and 1.6 g./d. and elongations of 24, 26 and 16% dry, wet and loop respectively at 60% relative humidity (R. H.) and 21° C.

Tenacities and elongations of staple fibers are given in terms of measurements made on single filaments with a modified Richard's dynamometer which for a sample of five denier, fine, domestic wool gives values of 1.3 and 1.1 g./d. for tenacities and 32 and 37% for elongations, dry and wet respectively. The Richard's dynamometer employed was obtained from the Jules Richard Company, 25 Rue Melingue, Paris, France.

Orientation by means of X-rays is determined by exposing the fiber specimen to filtered copper radiation during one hour with a distance of 5 cm. between the specimen and the plate. The X-ray negative is developed and analyzed photometrically. From the density of silver deposit at any given point in the negative it is possible to calculate the intensity of the X-rays impinging on that point during the exposure. The extent of orientation of the specimen is expressed in terms of the average ratios of the calculated X-ray intensities at the equator of the picture to that at 90 degrees from the equator for the inner and outer rings. These ratios are called orientation numbers. Thus an orientation number of one denotes that the specimen shows no orientation whereas ratios progressively greater than one denote progressively higher degrees of orientation.

Example I

A spinning solution containing 22% of high grade commercial granulated hydrochloric acid casein and 1.4% sodium hydroxide is made by agitating the casein with the necessary amount of water for several minutes and adding the so-

dium hydroxide in the form of a 10% aqueous solution with thorough agitation. In about thirty minutes at room temperature with occasional agitation the solution becomes homogeneous. It is then filtered at 20-60 pounds gauge pressure through an assembly of filter cloth and wire screen. The filtrate is centrifuged to aid in removing the air bubbles. The amount of centrifuging necessary varies with the amount of air introduced during filtration and the viscosity of the solution. For this composition, one-half hour at 1500 R. P. M. has been found sufficient. Deaeration of the solution is completed by subjecting it to reduced pressure at about 0.5 lb./sq. in. absolute for one hour.

This composition is spun in ordinary viscose spinning apparatus as illustrated in Figure II, which is a vertical section of the apparatus and Figure I which is a plan view of the same. The solution is fed under 20 lbs./sq. in. gauge pressure to a gear pump, not shown, which forces the material through a candle filter and spinneret 1 into the coagulating bath 2. The spinneret has 40 orifices, each of which has a diameter of about 0.004". The coagulating bath 2 contains 20% sodium sulfate, 4% aluminum sulfate, 4% glucose, 2% sulfuric acid and 3% formaldehyde, and is maintained at a temperature of 45° C. In the coagulating bath 2 the filaments 3 issuing from the spinneret 1 are passed under the convergence roller 4 and then around twelve rollers or pulleys 5, each of which has a circumference of 8.1 cm. in the groove, six of which are mounted at each end of the coagulating bath 2 in such a manner that they are free to rotate about the vertical shafts 6. The length of filament travel in the coagulating bath 2 is of the order of 400 inches. From the last roller 5 the filaments 3 are led directly to a 6" diameter glass godet wheel 7 operated at 34 R. P. M. Under these conditions the first roller 5 in the coagulating bath operates at a speed of about 136 R. P. M. and the filaments 3 are stretched about 50% between the first roller 5 and the godet wheel 7.

The lower portion of the godet wheel 7 is run in a solution 8 at room temperature comprising 16% sodium sulfate, 5% monosodium phosphate and 0.9% disodium phosphate at pH 5.0.

This buffer bath 8 serves to rinse off excess coagulating bath carried on filaments 3 and to partially neutralize the sulfuric acid thereon. The godet wheel 7 is fitted with an idler roll 9, such that several wraps may be taken around the wheel 7 to prevent filament slippage. From the godet wheel 7 the filaments 3 are led under a roller 10 immersed in a 20% sodium chloride solution 11 at 89° C. and then directly to the wind-up bobbin 12. The wind-up bobbin 12 is operated at a speed of 1670 in./min. such that the filaments 3 are stretched about 160% during passage through the hot sodium chloride solution 11. The length of the filament travel in the sodium chloride stretching bath 11 is about 18 inches.

While the filaments 3 are being collected on the wind-up bobbin 12, they are sprayed by means of nozzle 13 with 20% sodium chloride solution 14 to keep them moist. When sufficient yarn is wound on the bobbin, the bobbin is removed from the wind-up machine and immersed in a solution containing 7.6% sodium chloride, 3.9% aluminum sulfate and 3.3% formaldehyde for about 16 hours at room temperature. At the end of this time the hardened filaments are thoroughly washed on the bobbin with water neutralized with

very dilute ammonium hydroxide solution and allowed to dry on the bobbin. When dry, the filaments are twisted four 8 turns per inch on a conventional ring twister.

The forty-filament yarn thus prepared has a denier of about 240. When it is examined by X-rays it is found to have an orientation number of 1.24. In addition, it has tenacities of 1.66, 0.85, and 1.38 grams per denier (g./d.) dry, wet, and loop, respectively, elongations of 19, 25, and 15% dry, wet, and loop, respectively, elastic recovery from 4% stretch of 89%, elastic recovery from 8% stretch of 78%, and modulus of elasticity of 32 g./d., all tests being carried out at 60% relative humidity (R. H.) and 21° C. These properties are much higher than those of prior art commercial casein fibers or those of casein fibers produced by any previously known process. In fact, the best prior art commercial casein fibers, available in the form of staple fibers only, have tenacities of less than 1.0 and less than 0.4 g./d. dry and wet, respectively, at 60% R. H. and 21° C.

The yarn thus prepared is sized and woven into a continuous filament fabric without difficulty. Alternatively it may be converted into staple yarn, sized and woven into a spun fabric likewise without trouble. This is in marked contrast to the behavior of present prior art commercial synthetic protein fibers which are so weak except for very coarse yarns that they must be mixed with other fibers such as wool, cotton and rayon in order to withstand yarn and fabric preparation satisfactorily.

Example II

A casein spinning solution having a viscosity of about 65 poises is prepared as in Example I. The coagulating bath is the same as that used in Example I, except for substitution of 4% zinc sulfate for 4% aluminum sulfate. In addition, the last six rollers used in the coagulating bath in Example I are replaced with six rollers having a circumference of 10 cm. in the groove and having vanes on the lower side in order to increase their resistance to turning in the bath. Due to the greater force required to turn these rollers, the filaments are stretched to a greater extent than in Example I, even though the godet roll is operated at the same speed. In the hot sodium chloride solution the filaments are stretched about 135% and wound up on the bobbin at the rate of about 1500 in./min. During this second stretching step the filaments are under a tension of about 70% of the maximum obtainable tension which may be measured by increasing the wind-up speed to a point just short of that at which filament breakage occurs.

After winding up on the bobbin, the filaments are hardened first in a bath containing 24% sodium chloride, 1.9% formaldehyde, and 1.1% sodium acetate at pH 7 for one hour. They are then transferred to the final formaldehyde hardening bath employed in Example I and hardened 15 hours longer. The filaments are then thoroughly washed on the bobbin in running water and subjected to treatment in a solution containing 10% sodium sulfate and 7% sodium nitrate for two hours at room temperature. This after-treatment renders the filaments more resistant to hot aqueous baths such as are encountered in dyeing and in hot laundering. The filaments are then washed further and allowed to dry. Part of the yarn is tested in this form.

Another part is twisted four turns per inch before testing.

The forty-filament untwisted yarn thus prepared has a denier of 191, tenacities of 1.80, 0.85 and 1.51 g./d. dry, wet and loop, respectively. The twisted yarn has a denier of 194, tenacities of 1.87, 0.85, and 1.60 g./d. dry, wet, and loop, respectively, elastic recovery of 89% from 4% stretch and 79% from 8% stretch, and modulus of elasticity of 32 g./d., all tests being made at 60% R. H. and 21° C. In addition, when the yarn is examined by X-rays it is found to have an orientation number of 1.25. These properties are outstanding compared with those of other known casein fibers. The relatively high degree of orientation as shown by X-rays is especially noteworthy.

Samples of prior art commercial soya protein and casein fibers examined with X-rays similarly have shown orientation numbers of 1 to 1.05, denoting substantially no orientation.

Example III

A casein spinning solution having a viscosity of about 40 poises and a pH of 11.1 is spun under conditions similar to those outlined in Example II. The coagulating bath contains an additional component, 0.1% cetyl pyridinium bromide, added to inhibit fouling of the spinnerets. The yarn is stretched about 63% between the first coagulating bath roller and the godet wheel and about 153% between the godet wheel and the windup bobbin, which is operated at a speed of 1630 in./min. After the filaments are collected on the bobbin, they are given a final formaldehyde hardening treatment in a bath containing 16% sodium chloride, 4% aluminum sulfate, and 3% formaldehyde for 15 hours at room temperature. They are then washed, dried on the bobbin, and twisted two S turns per inch.

The forty-filament yarn thus prepared has a denier of 185, tenacities of 1.8, 0.80, and 1.6 g./d. dry, wet, and loop, respectively, elongations of 20, 24, and 15% dry, wet, and loop, respectively, elastic recovery of 91% from 4% stretch and 76% from 8% stretch, and modulus of elasticity of 29 g./d., all measurements being made at 60% R. H. and 21° C. In addition, the fibers, when swollen with water and examined in cross-section under the microscope, are seen to possess a skin on their outer surface. This skin is similar to that observed in viscose rayon fibers. It has been observed in no other synthetic protein fibers produced by previously known processes.

The skin probably results mainly from the special conditions of coagulation. Although not known definitely it is believed to depend on the length of bath travel, the acidity of the bath and the presence of formaldehyde in the bath. In a coagulating bath of low acidity it is possible that the formaldehyde gels and partially hardens the outside of the freshly extruded filaments before neutralization of the fiber interior can occur. Then, perhaps, further neutralization of the core of the filament takes place slowly through this surface gel or skin which acts as an osmotic membrane. A long coagulating bath travel permits complete neutralization of the whole fiber and more complete reaction with the formaldehyde. These effects are perhaps aided by the travel through the secondary stretching bath. Thus a stronger fiber having a skin and a more dense core may be produced than is possible otherwise. A dense strong fiber at this stage of the process is highly important since it permits

more work to be done on the fiber during stretching. The resultant fiber has a higher orientation and higher physical properties than one on which less work can be done.

Example IV

A soya protein spinning solution is prepared containing 18% dry soya protein and 1.8% sodium hydroxide. Following filtration and deaeration, it is found to have a viscosity of about 92 poises and a pH of about 12.5. It is delivered to the spinneret and coagulated with a bath containing 20% sodium sulfate, 4% zinc sulfate, 4% glucose, 2% sulfuric acid, 3% formaldehyde, and 0.1% stearyl trimethyl ammonium bromide which is maintained at a temperature of 45° C. The coagulating bath is fitted with six rollers each having a circumference of 8.1 cm. in the groove. The godet wheel is operated at a speed of 20 R. P. M. In the second stretching step in the hot sodium chloride solution the filaments are stretched about 280% and wound up at a speed of about 1430 in./min. Thereafter, the filaments are hardened first in a bath containing 20% sodium chloride, 1.1% sodium acetate, and 1.9% formaldehyde and then in a bath containing 7.6% sodium chloride, 3.9% aluminum sulfate, and 3.3% formaldehyde at room temperature. Following the final formaldehyde hardening, the filaments are thoroughly washed, dried on the bobbin, and twisted two S turns per inch on a ring twister.

The forty-filament soybean protein yarn thus prepared has a denier of 154, tenacities of 1.2, 0.60, and 1.12 g./d. dry, wet, and loop, respectively, elongations of 23, 27, and 21% dry, wet, and loop, respectively, elastic recovery of 75% from 4% stretch and 60% from 8% stretch, and modulus of elasticity of 29 g./d., all measurements being made at 60% R. H. and 21° C. In addition, when the yarn is examined by X-rays it is found to have an orientation number of 1.15. Although these properties are somewhat inferior to those of the casein yarns described above, they are very much better than the properties of prior art commercial soya protein fibers and the properties of soya fibers prepared by any other known prior art process. The best prior art commercial soya protein fibers have tenacities of less than 0.8 and 0.4 g./d. dry and wet, respectively, and orientation numbers, as measured by X-rays of about 1.0.

Example V

A spinning solution containing 20% dry peanut protein and 1.27% sodium hydroxide has a viscosity of about 103 poises and a pH of 12.5. It is spun in a manner similar to that described in Example IV except that the coagulating bath contains 1% acid and 1% formaldehyde and no cation-active, surface-active agent, the coagulating bath temperature is 30° C., the coagulating bath is fitted with twelve rollers such that the filament travel is of the order of 400 inches, and the filaments after passage through the hot sodium chloride stretching bath are wound up at a rate of about 1450 in./min. such that the total stretch between the godet wheel and the windup bobbin is 290%. The final hardening with formaldehyde is carried out in the same way as the hardening of the soya protein fibers described in Example IV. After the 40-filament yarn is washed and dried on the bobbin, the resultant untwisted yarn is found to have tenacities of 1.35 and 0.60 g./d. dry and wet, respectively, and elongations of 14% and 13% dry and wet, respectively

at 60% R. H. and 21° C. Its orientation number, modulus of elasticity and elastic recovery from stretch are of the same order as those of the soya protein yarn described in Example IV. These fibers are stronger than any known prior art peanut protein fibers. Measurements of peanut protein fibers prepared by previously known processes have given tenacities of less than 0.9 and 0.3 g./d. dry and wet, respectively, at 60% R. H. and 21° C., and orientation numbers, as measured by X-rays, of about 1.0.

It is to be understood that the hereinbefore disclosed specific embodiments of this invention may be subject to variation and modification without departing from the scope thereof. However it is critical to the obtainment of the novel products of this invention, and more particularly to the production of protein fibers and the like possessing a dry tenacity of at least 1.2 g./d. and an orientation number of at least 1.15, that the steps of (1) coagulation in an acidic bath containing formaldehyde and salts, (2) stretching in said coagulating bath, (3) further stretching in hot salt solution and (4) further treatment with formaldehyde, be carried out in the order named and that none of the steps be omitted. If this procedure is adhered to, the fibers obtained not only will have high strength but also, surprisingly enough, will be found to possess a different structure from that of prior art protein fibers. They will be found to possess a skin on their outer surface whereas prior art protein fibers do not. Perhaps even more important, they will be found to be oriented as shown by X-rays whereas fibers prepared from globular proteins by any other process are practically devoid of X-ray orientation.

These differences in structure which are characteristic of the fibers of this invention have been found to be correlated with tenacities and other fiber physical properties such as elastic modulus. For instance fibers showing substantially no orientation by X-ray examination have low tenacities whereas those which show relatively high orientation have high tenacities. In general fibers having an orientation number of 1.15 or greater have dry tenacities of 1.2 g./d. or higher.

The proteins useful in this invention are the water-insoluble globular proteins belonging to the group consisting of phosphoproteins, prolamines and vegetable globulins. Example of vegetable globulins are the globulins of wheat, soybeans, cotton-seed and peanuts; while examples of prolamines are the gliadin of wheat, zein of corn, and hordein of barley; and examples of phosphoproteins are casein from milk and vitelline from egg-yolk.

Any good commercial grade of the aforementioned proteins is satisfactory. Many proteins unavailable commercially may be satisfactorily prepared by a process similar to that used by R. F. Nickerson (U. S. 2,194,835) for the preparation of cotton-seed protein. Methods of preparation which involve subjecting the protein materials to high temperatures or concentrated alkali at any stage in their preparation should be avoided since these cause undesirable changes in the proteins. Casein is the preferred phosphoprotein because of its availability, standardized preparations, and susceptibility to the process of my invention. The vegetable globulins most suitable for the process of my invention are those derived from soybeans, cotton-seed, or peanuts. Zein is the best known and most suitable pro-

lamine. When the process of my invention is applied to zein, it is found that exceptionally high degrees of stretch may be applied to the fibers in the secondary stretch bath involving stretching in a hot salt solution. Degrees of stretch above 2000% are possible.

The basic agents used in the preparation of the alkaline solutions of this invention are water-soluble alkaline reacting compounds such as inorganic bases, including caustic alkalies and basic salts of alkali metals and ammonia, or organic bases such as amines, quaternary ammonium hydroxides, and tertiary sulfonium hydroxides. The strong bases such as sodium hydroxide, potassium hydroxide, tetramethyl ammonium hydroxide and trimethyl sulfonium hydroxide are especially suitable. Of these, on account of its ready availability and the superior fibers had therewith, I prefer sodium hydroxide.

The concentration of protein in the spinning solution and the ratio of protein to alkali preferably are regulated in order to give a solution having suitable viscosity for spinning and yielding fibers having optimum properties. Thin solutions are not suitable for spinning since they leak during pumping, readily deform after issuance from the spinneret, and generally give inferior fiber properties. Very viscous solutions are difficult to filter, deaerate, and force through the lines of the spinning equipment. Generally the optimum viscosity range for spinning lies between 20 and 150 poises.

Solutions having suitable viscosity may be prepared either by using relatively low protein and alkali concentrations or by using relatively high concentrations of both protein and alkali. Generally better fibers result from the use of high protein concentrations. However, since this necessitates the use of high alkali concentration, great care must be taken to avoid alkali degradation of the protein. Thus it is highly important to obtain the proper balance between the protein and alkali concentrations during preparation of solutions having proper viscosities.

Using a good grade of protein, spinning solutions may be prepared containing from 10 to 30% by weight protein and alkaline reacting compound in the range of from 4 to 12% based on the weight of the protein. The preferred limits vary with the protein being used since the various proteins display different solubility characteristics. Thus for casein the optimum range for the dry protein content of the spinning solution is from 15% to 25% and for the sodium hydroxide content based on the protein is from 5% to 7%. For soybean protein the corresponding optimum ranges are 10% to 20% for the protein and 7% to 11% for the alkali. The amount of alkali used varies to some extent depending on the thoroughness with which the precipitated protein is washed during its isolation. It is essential, however, that the protein spinning solution should contain alkaline reacting material in amount sufficient to provide a pH of at least 9. The novel fibers and the like of this invention are only had when the protein spinning solution, employed in the process of this invention, has a pH within the range of from 9 to 13; while protein fibers and the like of optimum properties are produced when the pH of the spinning solution is within the range of from 10 to 12.5.

In order to avoid unnecessary and extensive alkali degradation of the proteins, it is preferred to spin them as soon as possible after they have

become homogeneous and have been filtered and deaerated.

Spinning of the aforementioned aqueous alkaline protein solutions is effected by extruding the protein solution into an aqueous coagulating bath. Said coagulating bath determines the properties of the final products to a large extent and must be adjusted to the particular composition being shaped to obtain optimum properties. Coagulating baths such as are used in viscose spinning are not suitable. For the preparation of filaments according to the present invention it is essential that the coagulating bath contain formaldehyde, from 0.5 to 10% by weight of a strong mineral acid or admixture of strong mineral acids, and a high percentage of a water-soluble inorganic salt or an admixture of water-soluble inorganic salts.

While appreciable effects are had when the coagulating bath contains as little as 0.1% formaldehyde by weight, optimum results are only obtained when the formaldehyde content of said bath is at least 0.5%, and preferably is within the range of from 0.5% to 10% by weight.

While appreciable effects are obtained when the coagulating bath contains as much as 10% of a strong mineral acid, it is preferred, on account of the superior products thereby obtained, that the strong mineral acid content of said bath should be within the range of from 0.5% to 5% by weight. While any strong mineral acid, for example, hydrochloric, nitric, sulfamic, and sulfuric acids, may be employed in my coagulating bath, I prefer to use sulfuric acid in view of its ready availability and the superior products had therewith.

The coagulating bath should contain a high percentage of a water-soluble inorganic salt or admixture of water-soluble inorganic salts. The minimum salt content necessary is of the order of about 10% by weight; while the upper limit is determined by the solubility of the inorganic salts in the coagulating bath composition. While any water-soluble inorganic salt is adapted for use in the coagulating bath, water-soluble metal sulfates provide superior coagulating baths and hence are preferred. Examples of said metal sulfates include aluminum, aluminum potassium, aluminum sodium, magnesium, potassium, sodium and zinc sulfates. The salts which are most readily available and which provide most satisfactory coagulating baths are the sulfates of sodium, zinc and aluminum.

Coagulating bath temperatures of 20–80° C. may be used. However, it is preferred to use temperatures within the range of from 40° C. to 70° C. since optimum filament properties result when temperatures within this range are employed. If too low temperatures are used, fiber properties are below normal and the salts in the bath tend to crystallize. At higher coagulating bath temperatures the rate of reaction between the formaldehyde in the bath and the protein is higher and the amount of stretch which may be applied to the fibers is decreased. However, it is believed that in spite of the lower degree of stretch more work can be done on the fibers. This results in fibers having a higher degree of orientation and enhanced physical properties. At the same time high coagulating bath temperatures increase the tendency of spinnerets to become fouled and plugged. Although it has been found that this tendency may be minimized by incorporating less than 1% of a cation-active surface-active agent in the coagulating bath, it is

still an important factor in determining the upper temperature limit.

It is to be understood that the filaments must be stretched in the coagulating bath in an amount from 25% to 300% of their length as formed. Said stretching may be effected by fitting the coagulating bath with rollers or pulleys such that the filaments may be subjected to a long travel therein and may be stretched during passage around the rollers. This results in fibers and the like having much higher physical properties than those in which all the stretch is applied in the secondary stretch bath comprising a hot salt solution.

After the filaments have been coagulated, partially hardened, and stretched in the coagulating bath, and have been led to the godet wheel, it is preferred to rinse off excess coagulating bath solution and partially neutralize the excess acid which is carried from the coagulating bath in order to avoid too rapid contamination of the secondary stretching bath. This is accomplished by immersing the lower portion of the godet wheel in an appropriate buffer bath. A suitable bath contains both neutral salts present in rather high concentration to inhibit swelling of the fibers, and buffering agents to adjust the pH between 3 and 8. A pH of 5 is preferred. Formaldehyde may also be present in this bath to harden the filaments further before the secondary stretching step.

The speed at which the godet wheel is operated determines the amount of stretch applied to the filaments in the coagulating bath. It has been found that for the production of the best fibers and the like this speed is more or less critical. Thus, if the speed is too low, the filaments are insufficiently stretched in the coagulating bath. If it is too high, the final fibers and the like have sub-normal physical properties. In the coagulating bath after the filaments have contacted the first roller, degrees of stretch between 25% and 300% may be applied. For typical casein and soybean protein solutions and a low rate of delivery to the spinneret it is preferred to stretch the filaments from 50% to 150% in the coagulating bath following the first roller, since fibers and the like having optimum tenacity are thus produced.

The coagulated and partially stretched filaments issuing from the coagulating bath are subjected to further stretching in a hot concentrated aqueous solution of a water-soluble neutral or acid-reacting salt of a mineral acid or admixture of said salts. While any water-soluble salt of a mineral acid which in water provides a solution having a pH of not more than about 7, e. g., aluminum sulfate, zinc sulfate, ammonium sulfate, is adapted for use in my secondary stretching bath, I prefer, on account of the superior fibers and the like formed therewith; to employ secondary stretching baths comprising a sodium salt of a strong mineral acid or admixture of said salts. Sodium chloride and sodium sulfate provide fibers and the like having most desirable properties and are therefore preferred salts. The use of alkaline-reacting salts, especially the strongly alkaline salts, is to be avoided; but my secondary stretching bath may contain water-soluble salts of organic acids, e. g., sodium acetate and potassium formate, if desired. Generally the salt concentration should be above 5% and the temperature above 60° C. Preferred salt concentrations lie within the range of from 10% to 30% and temperatures within the range of from 70° C. to

110° C. Temperatures in excess of 60° C. are necessary in order to obtain appreciable stretching. In the secondary stretching step, other things being equal, higher degrees of stretch generally result in higher dry and wet tenacities in the final product. However, excessively high degrees of stretch cause frequent yarn and filament breakage. The preferred amount of stretch for a typical solution is within the range of from 50% to 90% of the maximum draw ratio, the draw ratio being the ratio between the peripheral speed of the windup and the peripheral speed of the godet wheel. The maximum draw ratio for a given fiber or the like is the highest amount of secondary stretching, i. e., the maximum ratio between the peripheral speed of the windup and the peripheral speed of the godet wheel, to which the filaments may be subjected without breaking. Said maximum draw ratio varies to a certain extent from fiber to fiber, depending upon the specific kind of water-insoluble globular protein employed and the conditions obtaining during the coagulating and first stretching step, but it may readily be determined by experimentation.

If desired, a multiple roller set up may be used in the second stretching step such that the filaments are subjected to a longer travel in the bath and a lower rate of stretch than when one roller is used alone. The actual amount of stretch or per cent stretch in the secondary stretching bath is less important than the draw ratio. Depending upon the protein being spun, the spinning solution formulation, and the coagulation conditions, the actual amount of stretch may be as low as 25% or greater than 2000%. In general casein filaments are stretched from 50% to 300%, soya and peanut protein filaments from 100% to 800% and zein filaments 1000% and up.

The final formaldehyde insolubilization of the filaments may be effected in any known manner with solutions of formaldehyde and various salts. A preferred procedure involves first hardening the fibers in a bath containing formaldehyde, sufficient sodium chloride to practically saturate the solution, and a small amount of sodium acetate. This is followed by treatment in a second bath containing formaldehyde, sodium chloride, and a water-soluble inorganic salt of aluminum or a heavy metal, such as chromium or zinc. Filaments hardened in this manner have been found to stick less during unwinding following the final hardening and washing than when the hardening is carried out in other types of baths. It is preferred for the production of highly attractive fibers and the like that the final formaldehyde hardening of the filaments should take place while said filaments are held under fixed longitudinal dimensions.

In order to give the filaments high resistance to hot dilute acid baths such as are encountered in dyeing and to other hot aqueous systems, further treatment of the filaments with formaldehyde at elevated temperatures, with ketene, sodium nitrite solution, or with acetic anhydride is desirable. Additional treatment may be applied to the yarn as desired, including treatments to neutralize excess acid or alkali, treatments to prevent shrinkage and loss or orientation, treatment with softening agents, and treatments with oils or sizes to assist in weaving.

As hereinbefore stated, the novel fibers and the like which are produced by the process of this invention comprise water-insoluble globular protein filaments selected from the group consisting of regenerated phosphoprotein, prolamine

and vegetable globulin filaments, and have dry and wet tenacities based on original dimensions of at least 1.2 and 0.6 g./d. respectively as measured on the Scott incline plane tester at 60% R. H. and 21° C. Said threads and the like also have an orientation number, as measured by X-rays, of at least 1.15. Furthermore, as determined on the Richard's dynamometer at 60% R. H. and 21° C., said threads and the like have an elastic recovery from 4% stretch of at least 70% after a recovery time of one minute, an elastic recovery from 8% stretch of at least 50% after a recovery time of one minute, and a modulus of elasticity of at least 20 g./d.

The casein fibers and the like of this invention have dry and wet tenacities based on original dimensions of at least 1.5 and 0.75 g./d. respectively, an orientation number of at least 1.2, an elastic recovery from 4% stretch of at least 80%, an elastic recovery from 8% stretch of at least 60%, and a modulus of elasticity of at least 25 g./d.

The process of this invention possesses advantages not previously combined in a single process. Furthermore, the shaped protein products of this invention possess advantages not previously combined in protein materials. For instance, as compared with prior art protein fibers and the like, the fibers and the like of this invention have markedly superior dry and wet tenacities, orientation numbers, elastic recovery from stretch and modulus of elasticity. As a consequence, said fibers and the like are particularly useful as textile fibers. They may be used to prepare high grade fabrics, such as those used for dresses and suits, containing 100% synthetic protein yarns. In contradistinction thereto, prior art synthetic protein fibers and the like are so weak that they must be mixed with other fibers such as wool, cotton and/or rayon in order to withstand yarn and fabric preparation satisfactorily. My novel fibers may not only be used alone, but may also be blended with other fibers, such as rayon, cellulose acetate, wool, nylon, or cotton to produce more attractive products from the standpoint of either cost or physical attractiveness.

Synthetic protein fibers, as exemplified by casein, with low filament deniers (3 and below) have been prepared according to the process of this invention. These low filament denier fibers can be readily converted into staple yarns having deniers of less than 600, and, in fact, they have been converted into staple yarns having deniers as low as 75. The preparation of yarns of this degree of fineness is an outstanding technical achievement in view of the fact that the bulk of wool fibers is made into yarns having deniers of 200 or higher. These desirable properties are not only had in yarns consisting entirely of the novel protein fibers of this invention but are also retained by yarns consisting of not less than 75% by weight of said fibers admixed with up to 25% by weight of prior art textile fibers such as wool, cotton, rayon and the like. Fine yarns are greatly desired since they allow a wider range of choice of fabric construction and since they permit the preparation of fine fabrics which have a more pleasing handle, feel and appearance than coarse fabrics. Fine yarns have been impossible to obtain with previous synthetic protein fibers.

Continuous filament yarns from water-insoluble globular proteins, for example, casein, having a denier of 120 and 60 filaments in the cross

section have been prepared using the herein described process. Fabrics having a finished count of well above 40 (warp) by 40 (filling) can be prepared and, in fact, continuous filament casein yarns as above described have been woven without difficulty into fabrics having a finished count of 130 (warp) by 80 (filling). The fabrics are characterized by exceptionally high resilience, excellent draping qualities, and a handle intermediate between that of a silk and that of a fine worsted fabric.

In addition, 60 filament, 120 denier continuous filament casein yarns produced by this process have been woven as the pile of a velvet using a commercial velvet loom and a construction in the range of those now used for high quality, transparent velvets. The satisfactory performance in the weaving of the casein yarns prepared in accordance with this application is of great significance since velvet weaving is the most severe weaving test to which a yarn can be put.

For comparison with worsted men's wear fabrics, water-insoluble globular protein fibers having a filament denier of 2 and prepared by the process of this application have been converted into staple yarn having a denier of 320. This yarn has been woven without difficulty into a 2 by 2 twill weave fabric having a finished count of 50 by 50. These fabrics are characterized by high resilience and a striking similarity to very fine worsted fabrics in feel.

Thus, this invention makes possible for the first time the preparation of fine, continuous, synthetic protein filaments having a denier below 3 and having sufficient strength for handling in the form of fine yarns. This invention also makes possible the preparation of fine synthetic protein staple yarns having deniers as high as desired and as low as 75. In accordance with the practice of this invention, there can also be prepared 100% synthetic protein fabrics having finished counts as low as desired and at least as high as 130 (warp) by 80 (filling). These objects cannot be accomplished with synthetic protein fibers produced by prior art processes, principally due to the fact that such fibers are too low in strength.

By the terms "denier," "count," "warp," "filling," "pile" and "twill" as employed herein and in the appended claims are meant said terms as defined in the glossary beginning at page 781 of the "Rayon and Staple Fiber Handbook," 3rd edition (1939), by Mauersberger and Schwartz, published in the Rayon Handbook Company.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

Having described the present invention, the following is claimed as new and useful:

1. In a process for obtaining synthetic protein fibers and the like, the steps of extruding an aqueous alkaline solution of a water-insoluble globular protein selected from the group consisting of phosphoproteins, prolamines and vegetable globulins, said solution containing from 10% to 30% by weight of protein and having a pH of at least 9, into an aqueous coagulating bath containing at least 0.5% by weight of formaldehyde, from 0.5% to 10% by weight of acid selected from the group consisting of strong mineral acids and admixtures of said acids, and at least 10% by weight of salt material selected from the group

consisting of water-soluble inorganic salts and admixtures of said salts, stretching the resultant formed filaments from 25% to 300% in the coagulating bath, further stretching said filaments at least 50% of their maximum draw ratio in a hot concentrated aqueous solution of salt material selected from the group consisting of water-soluble neutral and acid-reacting salts of mineral acids and admixtures of said salts, and then immersing the resultant stretched filaments in an aqueous formaldehyde hardening solution.

2. In a process for obtaining synthetic protein fibers and the like, the steps of extruding an aqueous sodium hydroxide solution of a water-insoluble globular protein selected from the group consisting of phosphoproteins, prolamines and vegetable globulins, said solution containing from 10% to 30% by weight of protein, and sodium hydroxide within the range of from 4% to 12% based on the weight of the protein, into an aqueous coagulating bath having a temperature within the range of from 20° C. to 80° C. and containing at least 0.5% by weight of formaldehyde, from 0.5% to 10% by weight of sulfuric acid, and at least 10% by weight of salt material selected from the group consisting of water-soluble metal sulfates and admixtures of said sulfates, stretching the resultant formed filaments from 25% to 300% in the coagulating bath, further stretching said filaments at least 50% of their maximum draw ratio in an aqueous salt solution having a temperature of above 60° C. and containing at least 5% by weight of salt material selected from the group consisting of water-soluble neutral and acid-reacting salts of mineral acids and admixtures of said salts, and then immersing the resultant stretched filaments in an aqueous hardening bath containing formaldehyde and a water-soluble inorganic salt.

3. In a process for obtaining synthetic casein fibers and the like, the steps of extruding an aqueous casein solution containing from 15% to 25% casein by weight and from 5% to 7% sodium hydroxide based on the weight of the casein, into an aqueous coagulating bath having a temperature within the range of from 40° C. to 70° C. and containing from 0.5% to 10% by weight of formaldehyde, from 0.5% to 5% by weight of sulfuric acid, and at least 10% by weight of sodium sulfate, stretching the resultant formed casein filaments from 50% to 150% in the coagulating bath, further stretching said filaments an amount within the range of from 50% to 90% of their maximum draw ratio in an aqueous salt solution having a temperature within the range of from 70° C. to 110° C. and containing from 10% to 30% by weight of salt material selected from the group consisting of water-soluble sodium salts of strong mineral acids and admixtures of said salts, immersing the resultant stretched filaments in an aqueous formaldehyde hardening bath containing sodium chloride and sodium acetate, and subsequently immersing said filaments in a second aqueous formaldehyde hardening bath containing sodium chloride and a salt selected from the group consisting of water-soluble inorganic salts of aluminum and heavy metals, said filaments being held under fixed longitudinal dimensions while in said aqueous formaldehyde hardening baths.

4. In a process for obtaining synthetic soybean protein fibers and the like, the steps of extruding an aqueous soybean protein solution containing from 10% to 20% of said protein by weight and from 7% to 11% sodium hydroxide based on

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the weight of the protein, into an aqueous coagulating bath having a temperature within the range of from 40° C. to 70° C. and containing from 0.5% to 10% by weight of formaldehyde, from 0.5% to 5% by weight of sulfuric acid, and at least 10% by weight of sodium sulfate, stretching the resultant formed soybean protein filaments from 50% to 150% in the coagulating bath, further stretching said filaments an amount within the range of from 50% to 90% of their maximum draw ratio in an aqueous salt solution having a temperature within the range of from 70° C. to 110° C. and containing from 10% to 30% by weight of salt material selected from the group

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consisting of water-soluble sodium salts of strong mineral acids and admixtures of said salts, immersing the resultant stretched filaments in an aqueous formaldehyde hardening bath containing sodium chloride and sodium acetate, and subsequently immersing said filaments in an aqueous formaldehyde hardening bath containing sodium chloride and a salt selected from the group consisting of water-soluble inorganic salts of aluminum and heavy metals, said filaments being held under fixed longitudinal dimensions while in said aqueous formaldehyde hardening baths.

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