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ARTIFICIAL PRODUCT AND METHOD FOR PRODUCING SAME

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This invention relates to a process for the production of articles from proteins which comprises stretching a coagulated, globular protein to 200% to 2000% of its original size. The invention relates particularly to the production of artificial fibers and pellicular products from proteins by the uniform stretching thereof until the cross-section of the fibers or pellicles has been reduced to one-half to one-twentieth of their original value. In the case of pellicles, the stretching will take place in both the longitudinal and transverse directions whereas in the case of fibers they need only be stretched longitudinally. The invention relates particularly to those proteins included in the classes of globulins, prolamines and phosphoproteins.

It is an object of this invention to provide a process for the preparation of improved fibers and pellicles from globular proteins.

It is a further object of this invention to provide a process for the stretching of fibers and films composed of globular proteins to many times their original dimension in an aqueous bath whereby to obtain improved products.

It is another object of this invention to provide a process for the stretching of globular proteins taken from the class consisting of globulins, prolamines and phosphoproteins in the form of fibers and films to many times their original dimensions in an aqueous bath having an elevated temperature whereby to obtain improved products.

It is still another object of this invention to produce the novel products obtainable by the above mentioned processes.

Other objects of the invention will appear hereinafter.

The objects of the invention may be accomplished, in general, by the stretching of a fiber or pellicle composed of a coagulated, globular protein in an aqueous bath, having an elevated temperature. It is preferred that the protein fibers and pellicles are composed of globulins, prolamines and phosphoproteins in their globular state, and that the stretching operation be carried out in an aqueous salt bath having a temperature of 50° C. to 140° C.

It is essential that the proteins before being stretched are in their coagulated but globular state. That is, they should not be degenerated or denatured before the stretching operation. Since some coagulating agents will also degenerate or denature the proteins, it is necessary to choose a coagulating agent which will coagulate the protein used without denaturing the same.

The following illustrative examples will serve to show certain specific details of the invention, however, it is to be understood that the specific details as set forth in the examples are not to be considered as limitative of the invention.

Example I

Casein fibers are spun from a solution having the following composition:

	Grams
Casein	100
Water	558
Concentrated ammonium hydroxide	8

The casein used is preferably a high grade lactic acid precipitated casein. The casein solution is spun through an ordinary forty-hole viscose rayon spinneret into a coagulating bath having the following composition:

	Grams
Water	1370
Concentrated sulfuric acid	204
Anhydrous sodium sulfate	284
Aluminum sulfate (hydrate)	160

The diameter of the spinneret holes are preferably of the order of 0.004 inch. The casein fibers will coagulate very rapidly but will retain their globular state, that is, they will not become denatured. They are then passed into a bath where they are stretched by means of rolls which can be operated at any speed differential necessary to obtain the desired amount of stretch. The composition of the bath in which the stretching is carried out is approximately 20% sodium chloride, and the temperature of the bath is preferably maintained between 60° C. and 85° C., depending upon the amount of stretch desired. When it is desired to impart a stretch of from 300% to 600% to the casein fibers, it is desired that the temperature of the bath be maintained at about 60° C. to 65° C. When the stretch to be imparted to the fibers is from 600% to 1200% of their original length, it is preferred that the temperature of the stretching bath be maintained at between 65° C. and 75° C., and when the stretch to be imparted is from 1200% to 1700% of their original length, it is preferred that the temperature of the bath be maintained at between 75° C. and 85° C. Stretching devices, such as for example, stretching rolls operating at differential speeds for imparting a predetermined amount of stretch to the fibers are well known in the art.

After the stretching operation, the fibers are washed with cold water and dried with or without tension. It has been found that a wool-like

crimp will develop in the stretched fibers during the drying if they are removed from the collecting bobbins before the drying operation, and are dried without tension. The crimping effect is apparently due to the result of a partial regain during the tension-free drying of the stretch which has been given the fibers.

The casein fibers prepared in accordance with the above described method and stretched from between 300 to 1700% of their original length have their molecules oriented parallel to the fiber length. This is clearly shown by an examination of the fibers under polarized light. The stretched fibers show parallel extinction and, when viewed under polarized light through a gypsum one wave length plate, show beautiful interference colors. The degree of orientation appears to increase with the increase in the amount to which the fibers have been stretched. The stretched casein fibers have considerably higher tensile strength than similar unstretched fibers and they are also more flexible and durable. The fibers appear to have these above described characteristics whether they have been allowed to dry with or without tension.

The most desirable amount of stretch to be imparted to the casein fibers in accordance with the details of the present example is estimated to be from 900% to 1400% based on the observed properties of the stretched fibers.

If desired, the casein fibers prepared in the manner above prescribed may be treated with a hardening agent such as formaldehyde to improve their water-resistance. These fibers may also be treated with other agents such as sizes and the like according to known practices of the industry.

The following two examples illustrate the preparation of protein fibers treated with a hardening agent such as formaldehyde.

Example II

A casein solution having the same composition as above described with reference to Example I is extruded through a spinneret into a coagulating bath consisting of 5% sulfuric acid, and is then led into a stretching bath containing 10% sodium chloride which is maintained at a temperature of 65° C. to 70° C. The fibers, which are still in their globular state, are stretched in the hot salt bath to approximately 900% of their original length. After the stretching operation, the fibers are passed through cold water and then into a bath consisting of 1% sulfuric acid and 2% formaldehyde. The fibers are permitted to remain in the formaldehyde bath for from 5 to 30 seconds after which they are washed again with water and dried. The casein fibers prepared in this manner show a high degree of orientation and properties similar to those of the fibers prepared according to Example I except that they are somewhat more brittle and considerably more water resistant.

Example III

A sulfuric acid precipitated casein solution having substantially the composition of the casein solution given in Example I, is extruded through a spinneret into a coagulating bath comprising a 10% solution of sulfuric acid and is then passed immediately into a stretching bath maintained at a temperature of from 65° C. to 70° C. and comprising 10% sodium chloride, 1% sulfuric acid and 2% formaldehyde. The viscosity of the above mentioned casein solution is somewhat higher than that of the solution described in Example I and the spinning is preferably carried out at a temperature of from 40° C. to 50° C. The fibers prepared in accordance with this example are still in their globular state and are stretched 900% of their original length after which they are washed with cold water and dried. These fibers have properties similar to those described in Example II and show a high degree of orientation when examined under polarized light.

If desired, wetting or sizing agents may be added to the above mentioned stretching bath. When casein fibers are prepared in the above manner with the use of a stretching bath containing 10% sodium chloride, 1% sulfuric acid, 2% formaldehyde and 0.5% sodium lauryl (n-dodecyl) sulfate or sulfonated castor oil, they show properties similar to those described under the above mentioned examples but have a considerably softer feel and are somewhat more flexible.

The following example illustrates a method for the production of protein fibers including the treating of the fibers with a bath having a pH approximately equivalent to the isoelectric point of the protein.

Example IV

Casein fibers are prepared from the casein solution described in Example I, by coagulation in 10% sulfuric acid. After coagulation, the fibers are washed with water and then passed into a salt bath at a temperature of 65–70° C. and having a pH of approximately 4.3. The composition of the bath is as follows:

	Grams
Disodium phosphate crystals	32.6
C. P. citric acid crystals	34.9
Water	932.5

In this bath, the protein fibers are stretched approximately 900% of their original length. The stretched filaments are then washed with water and dried as described under Example I. The fibers have properties similar to those of Example I.

In another similar experiment 2% formaldehyde is added to the bath which is at a pH of 4.3 and stretched fibers are prepared as before. In properties, these fibers are very like those of Example II.

In some cases it may be desirable to use protein solutions which contain modifying agents such as waxy materials, pigments, softening agents, and the like in the preparation of protein fibers by the stretch spinning process which is an object of this invention. The following example illustrates the preparation of cassein fibers from a casein solution containing a small amount of palmitic acid.

Example V

The spinning solution used has the following composition:

	Grams
Sulfuric acid precipitated casein	100
Palmitic acid	2
Water	558
Concentrated ammonium hydroxide	10

This solution is spun in the manner described in Example I using the coagulating bath of Example I. The fibers are stretched approximately 900% of their original length at a temperature of about 70° C. in a 20% sodium chloride bath. Afterwards the fibers are washed with cold water and dried. The resultant filaments are similar

in appearance when examined under polarized light to those described previously and also show improved tensile strength over unstretched fibers prepared from a similar composition. These stretched casein fibers have a somewhat softer feel than those prepared from a casein solution which does not contain palmitic acid.

Example VI

Fibers are prepared from a solution of the following composition:

	Grams
Lactic acid precipitated casein	100
Palmitic acid	2
Paraffin wax (M. P. 62–4° C.)	4
Water	558
Concentrated ammonium hydroxide	10

Dispersion of the wax in this composition is accomplished by passing the composition through a colloid mill at a temperature of 70–85° C. The composition is spun into the precipitating bath described under Example I. The fibers are stretched, in 20% sodium chloride solution at a temperature of about 70° C., approximately 900% of their original length, following which they are washed with cold water, treated with a solution comprising 2% formaldehyde and 1% sulfuric acid, again washed with cold water, and dried. These fibers show parallel extinction when examined under polarized light and are quite similar in properties to those described under Example II above. However, they appear to be somewhat more water resistant than the fibers prepared by the method of Example II.

The stretching process may also be applied to strips of protein. The strips may be prepared in any suitable manner known to the art; for example, by extrusion of the protein solution through a slot into a coagulating bath or by evaporation of solvent from a flowout of the protein solution cast on a drum or belt. The following example describes the application of the stretching process to strips of casein prepared by evaporation of water from a flowout of a casein solution on a chromium plated plate to which has first been applied a thin coating of nitrocellulose. The strips are prepared in a width of approximately one inch and with a thickness of about 0.003".

Example VII

The casein solution described in Example I is used for the preparation of the strips. After evaporation of the water at about 45–60° C. the strips are removed from the casting plate, treated with a 5% solution of sulfuric acid, and stretched approximately 500% of their original length in a 20% sodium chloride solution maintained at a temperature of 70–80° C. Afterwards the strips are washed with cold water, treated with a 5% solution of glycerol in water containing approximately 2% formaldehyde, and dried under tension. The resulting strips show a high degree of orientation when examined under polarized light and greatly improved tensile strength in the direction of stretch. They also show an appreciable increase in flexibility along a crease made perpendicular to the direction of stretch and appreciably increased tear resistance when the tear is made perpendicular to the direction of stretch. The tensile strength perpendicular to the direction of stretch is considerably decreased as is also the tear resistance parallel to the direction of stretch. The strip is extremely brittle when folded so that the crease is parallel to the direction of the stretch.

In order to obtain a uniform improvement in properties of the sheet in all directions, it is necessary to stretch the sheet uniformly in both the longitudinal and transverse directions.

Example VIII

Sheets of casein approximately 6" x 6" square and 0.004" thick which have been prepared by solvent evaporation from flowouts of the casein solution described in Example I, are stretched uniformly in both the longitudinal and transverse directions in a 20% sodium chloride bath at a temperature of approximately 75–80° C. The sheets are stretched approximately 100% of the original length in each direction. Thus the thickness of the sheet is decreased to approximately 0.001". After the sheets have been stretched, they are treated further in the same way as the strips described in the preceding example. Under polarized light, these sheets do not show parallel extinction when viewed through the plane of the sheet. This indicates that the protein molecules are arranged at random in the plane of the sheet. However, when viewed edge-on, these sheets show a high degree of orientation. The physical properties of the sheets are uniform in all directions and are considerably improved over those of a similar casein sheet which has not been stretched.

The following two examples illustrate the practice of this invention as applies to another protein, namely zein prepared from corn.

Example IX

Fibers are prepared from zein by extrusion of a 20% solution of zein in 80% alcohol into a coagulating bath comprising 5% sodium chloride. The spinneret used is the usual forty-hole viscose spinneret having holes approximately 0.004" in diameter. After coagulating without denaturing the filaments, they are washed with cold water and passed into a stretching bath maintained at a temperature of 90–95° C. The stretching bath is water. The fibers are stretched approximately 600% of their original length. They are then passed into cold water and dried. The stretched fibers show a high degree of orientation when examined under polarized light and show greatly improved tensile strength as compared with similar fibers which have not been stretched. In addition, they appear to be appreciably more flexible and more durable than unstretched zein fibers.

Stretches as high as 1000–1400% can be achieved under the conditions given above. The best results are obtained when the amount of stretch is approximately 500–1000% of the length of the original length of the zein fibers. Salt solutions are not generally satisfactory for use as stretching baths in the case of zein unless the salt concentration is extremely low. It appears that sodium chloride solutions containing as little as 5% sodium chloride do not soften zein filaments satisfactorily even at 95° C. for applying the high elongation which are required in the practice of this invention.

Example X

A sheet of zein approximately 6" x 6" square and 0.004" thick is stretched on a tenter frame in water at 95° C. The sheet is stretched uniformly in the longitudinal and transverse directions, approximately 100% in each direction.

After the stretching operation, the sheet is washed with cold water and dried. The properties of the stretched sheet are very similar to those of the stretched casein sheet described above under Example VIII.

The proteins which may be used in the practice of this invention include those falling in the classes of globulins, prolamines, and phosphoproteins. Broadly, the class of globulins includes simple proteins which are heat coagulable, insoluble in water, but soluble in dilute solutions of salts of strong bases and acids. Specific examples of globulins are edestin from cotton-seed; peanut seed proteins; and glycinin, the soya bean protein. The protein class called prolamines comprises the simple proteins which are insoluble in water, soluble in 80% alcohol, and usually not heat coagulable. Specific examples are gliadin from wheat, hordein from barley, and zein from corn. Phosphoproteins are conjugated proteins in which the prosthetic group contains phosphoric acid. Specific examples are casein and vitellin.

In the practice of this invention the amount of stretch which is applied to fibers or strips of protein may vary from 200–2000% of their original length and preferably they are stretched at least 300% of their length. In the case of sheets of proteins which are stretched uniformly in both the transverse and longitudinal directions, the amount of stretch may be such that the thickness of the sheet is decreased to one-half to one-twentieth its original value and preferably at least one-third of its original value. Although very good results can be obtained by imparting stretches of 200% or 300% and up, it has been found that products having an exceptionally desirable orientation of molecules can be produced when imparting thereto stretches of 900% and up.

The stretching may be accomplished in any suitable manner by a method already known to the art. In the case of fibers it may be accomplished by rollers driven at various peripheral speeds and in the case of sheets it may be accomplished by the use of tentering frames or machines. Alternately tubes of the protein may be produced and expanded by means of air or liquid pressure against a form. The stretching operation is carried out at elevated temperatures in a medium which has a softening action on the protein. The medium contains some water which is the most effective softening agent known for proteins. The stretching bath may consist of pure water or of salt solutions and in many cases the salt solution chosen is preferably one which has a pH equivalent to the isoelectric point of the protein. In addition the stretching bath in some cases may comprise various mixtures of organic solvents and water; for example, alcohol-water mixtures, and mixtures of water with the monoalkyl ethers of glycols, or the like. In some cases it may be desirable to carry out the stretching operation in steam or mixtures of steam with air or other inert gases. If desired the stretching baths may contain hardening agents for the protein among which may be mentioned formaldehyde, formamide, the various tanning agents, dimethylol urea, phenol-formaldehyde reaction products, or any other hardening agent known to the art.

The protein may also be treated with a hardening agent after the stretching operation by any suitable method; for example, by heat coagulation, by treatment with inorganic salts or with tanning agents, etc. The treatment with the hardening agent may be of such nature that the stretched undenatured protein is denatured whereby to render the same permanently insoluble in acid and alkaline solutions.

The temperature at which the stretching operation is carried out may vary from 50–140° C. and preferably from 60–100° C.

The protein compositions from which the fibers, pellicles and sheets are prepared may contain any of the modifying agents known to the art; for example, wetting agents such as Turkey red oil, long chain acid sulfates which may be in the form of their salts, long chain acids, long chain amines, amides of long chain acids, waxes, wax-like materials, oils, fats, synthetic and naturally occurring resins including the phenol-formaldehyde condensation products, the urea-formaldehyde condensation products, both of which may be hardened if desired, either during or after the stretching operation, pigments, delusterants, dyes, and the like. In addition, after the stretching operation the stretched fibers, pellicles and sheets of proteins may receive any desired subsequent treatment according to practices which are well known in the art. They may be sized, water-proofed; for example, by treatment with a wax emulsion; moisture-proofed, with the various compositions known to the art, for example a pyroxylin-resin-wax lacquer, etc.

Among the advantages of this invention may be mentioned the improved properties of the articles so treated. These include greatly improved tensile strength, improved flexibility, durability, and elongation. In addition in the case of fibers, the application of the large amount of stretch results in the preparation of filaments of extremely fine denier. Thus, the invention provides a method for preparing protein articles which are useful in the textile fields, in the wrapping fields, and for many other purposes. It also provides protein fibers, pellicles and sheets which because of their improved properties are much more suitable for use in these fields than similar articles produced from proteins which have been described in the prior art. Naturally these articles possess all the inherent desirable properties of protein materials. Thus the fibers show a remarkable affinity for wool dyes, and in many other ways closely resemble the naturally occurring fibers, wool and silk, for example, in their behavior with various chemicals, in their appearance, feel, and thermal properties.

Sheeting which may be prepared according to the practice of this invention has the advantage that in many cases it is edible because the material is protein in nature. This is of particular importance when the sheeting is to be used for wrapping foodstuffs. Furthermore, when stretched tubing is prepared from protein materials according to the practice of this invention, it may be used with advantage for wrapping sausages and is particularly attractive for this purpose because of its edibility.

By the term "globular" or "undenatured" as applied to proteins is meant a protein which is in its reversible state and which is therefore soluble in the usual protein solvents such as dilute salt solutions, dilute alkali or acid, and aqueous alcohol. When a protein is denatured, on the other hand, it is rendered permanently irreversible and insoluble in any of the usual protein solvents.

The stretched undenatured or globular protein products of the present invention have certain

utility in their undenatured state even though they may be soluble in slightly alkaline solutions. In the form of threads, for example, they can be used in the production of certain types of fabrics from which they can be later dissolved to form novel woven goods.

Obviously many changes and modifications can be made in the above detailed described methods without departing from the nature and spirit of the invention. It is therefore to be understood that the invention is not to be limited except as set forth in the appended claims.

I claim:

1. As a new article of manufacture, a protein structure taken from the group consisting of globulins, prolamines and phosphoproteins which has been stretched from 300% to 2000% of its original size while in the globular state.

2. As a new article of manufacture, a casein structure which has been stretched from 300% to 2000% of its original size while in the globular state.

3. As a new article of manufacture, a zein structure which has been stretched from 300% to 2000% of its original size while in the globular state.

4. As a new article of manufacture, a glycinin structure which has been stretched from 300% to 2000% of its original size while in the globular state.

5. The method which comprises preparing a solution of a globular protein taken from the class consisting of globulins, prolamines and phosphoproteins, forming a structure from said protein solution, coagulating said structure while retaining its globular state, stretching said coagulated, globular protein structure to 300% to 2000% of its original size in an aqueous bath having a temperature of 50° C. to 140° C., and drying the same.

6. The method which comprises preparing a solution of a globular protein taken from the class consisting of globulins, prolamines and phosphoproteins, forming a structure from said protein solution, coagulating said structure while retaining its globular state, stretching said coagulated, globular protein structure to at least 900% of its original size in an aqueous bath having a temperature of 50° C. to 140° C., and drying the same.

7. The method which comprises preparing a solution of casein in the globular state, forming a structure from said casein solution, coagulating said structure while retaining its globular state, stretching said coagulated, globular structure to 300% to 2000% of its original size in an aqueous bath having a temperature of 50° C. to 140° C., and drying the same.

8. The method which comprises preparing a solution of zein in the globular state, forming a structure from said zein solution, coagulating said structure while retaining its globular state, stretching said coagulated, globular structure to 300% to 2000% of its original size in an aqueous bath having a temperature of 50° C. to 140° C., and drying the same.

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