

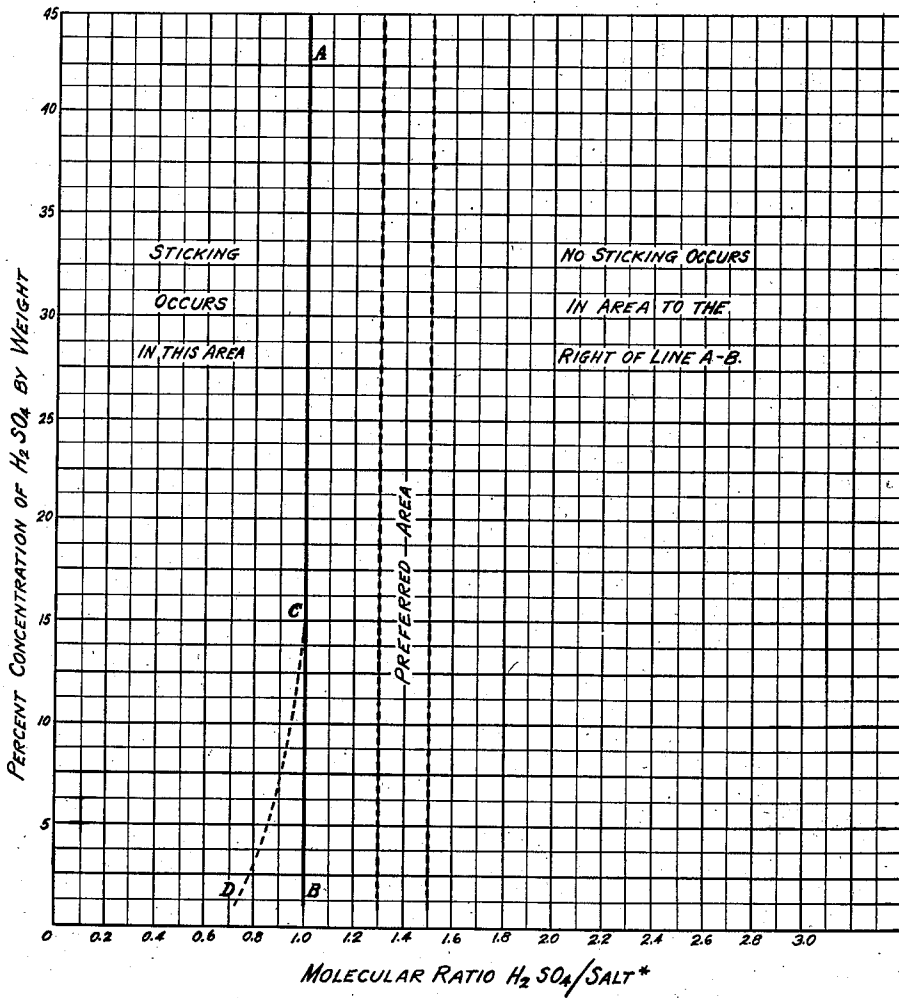
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MANUFACTURE OF ARTIFICIAL MATERIALS

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\* SALT INCLUDES:  $Na_2SO_4$ ,  $K_2SO_4$ ,  $(NH_4)_2SO_4$

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## UNITED STATES PATENT OFFICE

2,339,408

## MANUFACTURE OF ARTIFICIAL MATERIALS

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This invention is directed to improvements in or relating to the production of casein and other proteins and shapes prepared therefrom. More particularly, this invention relates to the preparation of strong artificial threads from casein and other proteins.

At present synthetic fibers are generally prepared from cellulose and its derivatives by a process including the formation of viscous solutions of said cellulose derivatives, extruding the solutions into precipitating baths to form a plurality of filaments which are then twisted into threads. These artificial fibers have an elementary composition of cellulose substantially the same as that of cotton fibers and consequently, though differing somewhat in appearance, these artificial fibers, like cotton, are cold to the touch, that is, they are not good insulators for heat, are inflammable and are not adapted to be dyed with the wool or silk dyestuffs.

It is also well known that artificial threads can be manufactured by a process involving the dissolution of proteins, such as casein, in alkaline solutions and the subsequent extrusion of the solution through spinnerets into acid precipitating or spinning baths. Although great advances have been made in recent years, these present processes have not proved completely satisfactory, since there is a definite tendency for the precipitating casein to stick on the face of the spinneret or spinning orifice and in the formation of multi-filament threads there has been a great tendency of the individual filaments to stick together which resulted in a product of low strength. Furthermore, unless special treatments have been used in preparing the casein in the production of the fiber, the strength of the protein thread produced is very low. Attempts to increase the strength of the protein fiber by the methods used in the preparation of viscose rayon, namely, by applying stretch to the freshly formed thread, have not been very effective and the usual result is merely breaking of the protein thread before sufficient tension can be applied to increase the mechanical strength of the fiber. In addition, it has been impossible to use the commercial grades of casein because of their non-uniformity, improper solubility and various other undesirable properties.

Ferretti, an authority in the commercial development of artificial casein fibers, stated in a recently issued British Patent No. 483,731, that the various types of casein which are at present produced throughout the world are unsuitable for the regular production of artificial fibers. Fer-

retti further indicated that they are entirely too viscous to spin and filaments formed therefrom stick together and produce compact, hard and brittle elements. The British patent further points out that it is necessary to devise special methods for precipitating casein under special conditions to obtain a material suitable for the regular manufacture of artificial textile fibers.

To further emphasize the difficulty encountered in obtaining casein of suitable characteristics for forming artificial threads, attention is directed to the British Patent, No. 487,115 to N. V. O. Research, which sets forth that the casein is generally too variable in properties and that the viscosity of its solutions decreases considerably with time. A method of specially preparing casein for use in the production of fibers is disclosed in British Patent No. 487,115 which method comprises heating the moist casein directly following the precipitation without an intermediate drying to a temperature of between 50° and 100° C. This, of course, produces a casein substantially different from the commercial casein on the market today and one which, because of its specific properties, could not be substituted for those in general commercial use.

Furthermore, while the use of specially prepared casein has somewhat reduced the sticking of fibers, the problem had not been completely solved. At the time of the present invention difficulty was still being experienced in the manufacture of textile fibers formed principally of casein and the like as considerable sticking developed between the fibers and also at the face of the spinneret, and suitable acid spinning baths had not yet been conceived for overcoming this difficulty.

It is an object of the present invention to overcome the difficulties discussed above and the invention contemplates a process involving the employment of a commercial grade of casein, produced in a normal manner, for use in the preparation of shaped masses, particularly in the preparation of fibers therefrom.

It has been found that strong, flexible, non-tacky filaments and threads of good color and other desirable physical and chemical properties can be simply and economically prepared from casein and other proteins. The present invention advantageously employs a commercial grade casein which is usually supplied in the trade in a dried condition. One particularly important procedure for using such casein as contemplated by this invention comprises the treatment of the casein in a dry form by heating it for a suitable

period at an elevated temperature. Alternatively, but slightly less satisfactory, the dry commercial casein may be moistened or wetted with control of the hydrogen ion concentration and then heated for a period at an elevated temperature.

It has also been discovered that in the process of spinning casein solutions to form filaments and the like, an acid spinning or precipitating bath can be utilized which will overcome the sticking at the spinneret face and between the filaments in a multi-filament yarn or thread.

The ordinary commercial casein is made suitable for the manufacture of artificial threads and the like, by heating a dry, acid-precipitated casein of low mineral content in an oven at a temperature of 55 to 120° C. for a period of 8 to 72 hours. Under special operating conditions, the same results may be secured by heating at a higher temperature for shorter periods. For example, dry casein may be heated to a temperature of about 150° C. between heated plates, heated rolls or the like for very short periods of a few seconds or minutes. The temperature and the heating time are usually mutually dependent. Thus, if the temperature is low, a longer period of heating is required and vice versa. Likewise, both time and temperature depend upon the particular type of casein which is used. The actual time and temperature of the heat treatment are determined by trial for each type of casein. These factors are chosen such that the casein is not appreciably discolored and can be dissolved in dilute alkali solutions. Examples of specific treatments of casein are given later in the description of this invention.

The casein may be heated in any suitable type of oven. For example, the oven may be an ordinary drying oven in which there is no means of controlling the humidity or it may be an oven which can be operated at a definite humidity.

Casein treated in the above manner is partially denatured to the extent that its solubility in water and in dilute alkali is lower than the untreated casein. Further, casein denatured in this way when reasonably promptly dissolved in dilute alkali yields solutions which are uniform and stable and have superior spinning qualities than the spinning solutions formed from casein prepared by any other methods. Solutions prepared from casein treated according to this method have a higher viscosity than those prepared from untreated casein. This is especially advantageous in that solutions of lower concentration can be spun which results in a better control of the spinning process and consequently a more uniform product.

The novel heat treatment of the protein apparently results in a change in the configuration of the protein molecule as confirmed by X-ray and other data. Before such treatment, the protein molecules are not of a linear nature and cannot be aligned with one another. However, after the heat treatment the protein is denatured and the molecules thereof are made more linear. When the thread is stretched, the linear molecules are oriented and made more nearly parallel with each other.

It was found that when applying this denaturing process to the protein, the resulting characteristics imparted thereto are not quite permanent, that is, upon storing, for example, about one week at room temperature the desirable characteristics resulting from the denaturation of the protein tend to disappear. Denatured casein which has been stored for any appreciable length

of time, will yield a solution in dilute alkali which has a lower viscosity and less satisfactory spinning properties than a similar solution prepared from freshly denatured casein. Thus it is obvious that better results can be obtained by the use of freshly denatured protein in the preparation of the casein solution.

Casein prepared according to this method may be dissolved in dilute alkali and the usual type of baths may be utilized in the spinning procedure. The resulting yarn or thread has good mechanical strength and can be stretched considerably to orient the casein molecules and materially increase the strength of the finished fibers.

In the alternative method, the dry, acid-precipitated casein of low ash content is suspended in water and the hydrogen ion concentration of the mixture is preferably adjusted to a pH of about 4.1. The suspension of wet or the moist casein is then heated from 1 to 8 hours at a temperature preferably between 45 and 95° C. Here again the time and temperature are mutually dependent and both also vary with the type of casein employed. The best results are obtained when the temperature to which the wetted casein is heated lies between 65 and 95° C.

The heating of the casein may be carried out in a closed container by means of steam or the casein may be heated while suspended in water. If the heating takes place while the casein is suspended in water, the water may be either neutral, weakly acid or weakly alkaline. It has been found, however, that the best results are obtained when the hydrogen ion concentration is brought to and maintained at a pH of about 4.1.

After the casein has been subjected to the above heat-denaturing process, it may be filtered off, washed and centrifuged or pressed to remove excess water.

The casein in the condition thus obtained has more uniform physical properties and when dissolved in alkali gives solutions which are more stable and have better spinning qualities due to the partial denaturation of the protein which takes place during the above treatment.

It was also found that the moist denaturing process is partly reversible upon storage of the material and accordingly freshly denatured casein should be used for preparation of the spinning solution.

Artificial threads and like products produced from such casein solutions possess more uniform physical properties than those heretofore produced. In fact, such threads have a dry tenacity above 0.8 gram per denier which is considerably stronger than casein yarns manufactured by previous methods. The spinning may be carried out in precipitating baths of known composition and particularly in the novel acid spinning baths in which salts are added to maintain a definite acid/salt ratio as hereinafter more fully described. Because of the greater strength of the freshly precipitated fiber of the present invention, more stretch may be applied thereto in order to further increase its mechanical strength and to orientate the protein molecules. Without the heat-denaturing step the molecules of casein are in such form or arrangement that orientation cannot be accomplished by application of tensile stress.

It should be noted that fibers, spun from casein which has been treated according to the dry method of heating referred to above, have better

physical properties than those prepared from casein treated by the second or wet method of heating.

Another feature of this invention in the substantial improvement of protein threads of all types, is the elimination of the sticking of the filaments to the face of the spinneret and the sticking of the filaments to one another by the use of a precipitating bath that contains sulphuric acid and alkali metal or ammonium salts in which the ratio of the molecular concentration of acid divided by the molecular concentration of salt is at least 1 (or only slightly below 1 with the addition of other constituents and lower acid concentrations).

In order to more fully illustrate the importance of the ratio and concentration of the ingredients of the bath employed, reference is made to the accompanying drawing wherein the molecular ratio of sulphuric acid to alkali metal and/or ammonium sulphate is plotted against the concentration of sulphuric acid in weight per cent. The line AB at a molecular ratio of 1.0 represents the minimum concentration for baths which contain only sulphuric acid and alkali metal or ammonium salts. The area to the left of this line represents ratios of acid/salt which, if employed for precipitating the protein would result in a sticking action between filaments and the fouling of the spinneret. However, the area to the right of the line AB represents molecular ratios of acid/salt with which no sticking or fouling is encountered. The molecular ratio of acid/salt may be anything above 1 but it is preferably in the range of from 1.3 to 1.5, usually at 1.4. The dotted line CD represents a safe minimum below 1 if sufficient quantities of such hardening compounds as magnesium sulphate and/or zinc sulphate and the like are present in baths of dilute acid concentration.

It has been found that great improvements in protein threads of any type can be obtained by use of such substances as zinc sulphate, magnesium sulphate, glucose and similar materials in the spinning bath. The presence of these substances gives additional strength to the filaments being spun so that a more substantial stretch can be employed, which accordingly results in a stronger orientation of the casein molecules in the filaments, thereby giving to them a corresponding greater mechanical strength. Aside from the compounds mentioned above, the spinning bath may at the same time contain other soluble compounds such as nickel sulphate, aluminum sulphate, potassium alum, tin salts, glycerine, organic and inorganic acids. The bath may contain cation active materials, including dodecyl pyridinium chloride and other alkyl halide derivatives of pyridinium and ammonium compounds; or any other ingredients may be added to the spinning bath which permit control of the interfacial tensions between protein solution, spinning bath and spinneret. Such control facilitates spinning. Generally speaking, the interfacial tensions are reduced by this addition. The spinning bath can also contain other hardening or tanning agents such as aldehydes, aromatic sulphonic acids and methylene condensation products of aromatic compounds but these compounds are not essential.

It should be emphasized at this point that in calculating the salt concentration for the acid/salt ratio, only the content of sodium, potassium and ammonium sulphates need be considered.

The following detailed description will serve to give a better understanding of the complete, preferred process. While the details given hereinafter are important for best operation, they are not intended to be limiting as the invention and its broad aspect relates to the general features disclosed.

The material employed is a carefully prepared casein or a higher grade commercial casein having a minimum ash content which has been prepared by acid precipitating under controlled pH and temperature conditions so as to produce the more soluble form of casein, containing only a small amount of impurities such as inorganic salts and so forth. The casein may be one that has been precipitated at a pH in the range of 4.1 to 4.6 and at a temperature below 50° C. Any of the common purifying methods such as digestion, resolution and re-precipitation, and so forth, may be employed, the object being to prepare a material of the highest degree of purity and uniformity possible. The casein is preferably heat-denatured by treating it in a suitable oven in a dry state at a temperature between 55 and 150° C. for a period from a few minutes to 72 hours. The heat-denatured casein is allowed to cool and then suspended in about four times its weight of water in which it is soaked for about one hour. Dilute alkali, such as a sodium, potassium and/or ammonium hydroxide solution, is then added to the casein-water mixture while continuously stirring until a good dispersion is obtained. During this step the casein goes into solution causing an increase in the solution viscosity. This viscosity increase materially assists in mechanically breaking up the larger particles during the stirring and hence a better dispersion of the casein results. Additional water is then introduced to adjust the concentration of the casein solution to the desired degree. The water, alkali, and any other ingredients, including the casein, should be relatively pure and have uniform properties in order to obtain strong, uniform yarns.

Other substances can be incorporated into the spinning solution but they are not essential. Examples of substances which may be added to the spinning solution are coloring, pigments, delustering, and softening substances such as dyes, oils, titanium dioxide, chlorinated diphenyl, pine oil, turpentine, and other volatile oils that will be removed to effect a pitted surface, dodecyl triethyl ammonium iodide or hydroxide and other cation active quaternary ammonium or pyridinium compounds.

The casein solutions are purified by passing through filters in the manner normally used in the rayon industry. After filtration, the purified solutions are deaerated under vacuum to remove all air bubbles and dissolved or occluded gases and if necessary they may then be permitted to mature before spinning.

Materials resistant to chemical attack and which will not contaminate the spinning solution, spinning bath, or the resulting fibers, are used in the construction of the spinning equipment, tanks, feed lines, filters, spinnerets, spinning bath troughs, pumps, yarn take-up mechanism, and other apparatus used in the manufacture of the fiber. Apparatus employed in the casein fiber production may be substantially the same as that used in the rayon industry.

In order to form the fibers, the casein solution is extruded through spinnerets into a sulphuric

acid precipitating bath in which there is dissolved sodium sulphate, cation active materials, and zinc or magnesium sulphate, the molecular ratio of sulphuric acid to sodium sulphate being approximately 1.4 to 1.0. The spinning bath, which has been rendered and maintained pure by filtration, is held at a relatively uniform concentration by the addition of the necessary ingredients, either continuously or intermittently. The bath temperature may vary between room temperature and 75° C. but is preferably held at a constant temperature within the preferred range of 45° to 55° C. With a spinning bath such as that described above there is no fouling of the spinnerets due to stickiness of the precipitated casein nor is there sticking between the individual filaments of the thread being spun. The selection of cation active materials, examples of which were given above, permits regulation of the interfacial tensions which play a part in the spinning process, prevents fouling of the spinneret orifices, and gives more desirable properties such as softer and better feel to the casein yarn.

Tension is preferably applied to the precipitating yarn or thread during spinning in order to obtain a much stronger and uniform yarn or thread of casein. The tension may be applied by friction guides, rollers driven by the thread or by passing over one or more rollers driven at different speeds from the take-up speed of the spools, pots, or reels. A plurality of stretching steps can be given with or without intermediate washing and/or drying. In addition, a compensation of the inside-outside dyeing of the cake or spool may be made by a variation of the stretch during spinning. However, it is not essential that tension be applied but the filaments may also be spun freely into the bath.

If desired, the threads after formation in the acid precipitating bath can be given a subsequent hardening or insolubilizing treatment with metal salts, aldehydic materials such as formaldehyde and/or agents which react in a manner similar to aldehydes. The finished threads are washed, given a slight twist and, if desired, are treated with a textile oil such as a sulphonated soap and/or hydrocarbon oil. In addition to the preliminary or partial denaturing imparted to the casein as set forth above, the invention further contemplates a supplementary denaturing of the finished thread. A completely denatured casein is insoluble even in alkali so that only partial denaturation can be effected prior to final treatment. If, however, a further heat treatment is applied to the finished thread it is rendered more insoluble thereby increasing its tenacity and making it more suitable for commercial purposes. In utilizing this said heat treatment it has been determined that the thread may be first subjected to the normal drying temperatures and then heated to about 125° C. for approximately one hour.

Although the description has been directed mainly to the spinning of the casein in the form of multi-filament threads for textile materials or strong yarns for cords and tire cord, the process may be modified in order to form the casein into films, staple fibers, ribbons, and various other shapes. The finished forms can be coated with other substances such as chlorinated rubber compounds, rubber hydrochloride, rubber, nitrocellulose compositions, synthetic resins, and so forth.

The following examples will serve to illustrate modifications of the present invention:

*Example I.*—A technical grade of commercial

acid precipitated casein of low mineral content is heated for 48 hours in an ordinary drying oven at a temperature of 70° C. The casein is allowed to cool to room temperature and is then dissolved in dilute aqueous sodium hydroxide to form a solution containing 14% casein and 0.2% free sodium hydroxide.

This solution is then spun at 50° C. into an aqueous precipitating bath consisting by weight of 15% zinc sulphate, 5% sodium sulphate, and 5% sulphuric acid. The casein solution is spun to a total titre of 300 denier through a spinneret having 90 orifices of 75 microns diameter. The filaments thus extruded are passed for a distance of about 50 cm. through the bath after which the yarn is subjected to a tension of 30 to 35 grams.

A thread produced by a process involving the steps set forth above has uniform properties and superior mechanical strength. The thread may be insolubilized by treating in 15% formic aldehyde solution, rinsing it in water and drying it at 50° C. The final thread is flexible, has uniform physical properties and good mechanical strength and shows no evidence of sticking between the individual filaments.

*Example II.*—A technical grade of commercial acid precipitated casein of low mineral content is suspended in four times its weight of water. Hydrochloric acid is added to adjust the hydrogen ion concentration of this mixture to a pH of 4.1. After holding the mixture at a temperature of 70° C. for three hours, it is cooled to room temperature and the casein is filtered off. The casein is washed with water, pressed for the removal of excess liquid therefrom and is immediately dissolved in dilute aqueous sodium hydroxide to form a casein solution containing 14% casein and 0.2% free sodium hydroxide.

This casein solution is then spun into an aqueous spinning bath consisting by weight of 20% sodium sulphate and 20% sulphuric acid. The casein solution is spun to a total titre of 300 denier through a spinneret having 90 orifices of 75 microns diameter. Before the yarn is wound onto a rotating bobbin it travels through the spinning bath for a distance of 50 cm. The yarn is spun at a rate of 100 meters per minute.

The following spinning bath compositions may be substituted for those described in the above two examples:

|                     | Composition (by weight)                              | Acid/salt<br>Mol. ratio |
|---------------------|------------------------------------------------------|-------------------------|
| <i>Example III.</i> | Sulphuric acid (100%), 5.0%; sodium sulphate, 7.3%   | 1.0                     |
| <i>Example IV.</i>  | Sulphuric acid (100%), 12.0%; sodium sulphate, 17.5% | 1.0                     |
| <i>Example V.</i>   | Sulphuric acid (100%), 19%; ammonium sulphate, 26%   | 1.0                     |

Bath compositions which also contain the preferred hardening agents are given in the following examples:

|                      | Composition (by weight)                                                                      | Acid/salt<br>Mol. ratio |
|----------------------|----------------------------------------------------------------------------------------------|-------------------------|
| <i>Example VI.</i>   | Sulphuric acid (100%), 9%; sodium sulphate, 10%; zinc sulphate, 10%                          | 1.2                     |
| <i>Example VII.</i>  | Sulphuric acid (100%), 8%; potassium sulphate, 11%; glucose, 10%                             | 1.3                     |
| <i>Example VIII.</i> | Sulphuric acid (100%), 5%; sodium sulphate, 5%; glucose, 20%                                 | 1.4                     |
| <i>Example IX.</i>   | Sulphuric acid (100%), 8%; sodium sulphate, 8%; magnesium sulphate, 15%                      | 1.4                     |
| <i>Example X.</i>    | Sulphuric acid (100%), 16%; sodium sulphate, 16%; magnesium sulphate, 15%; zinc sulphate, 1% | 1.4                     |

A bath of high acid/salt ratio is disclosed in Example XI.

|                | Composition (by weight)                                              | Acid/salt<br>Mol. ratio |
|----------------|----------------------------------------------------------------------|-------------------------|
| Example XI.... | Sulphuric acid (100%), 15%; sodium sulphate, 5%; zinc sulphate, 15%. | 4.4                     |

Spinning baths having an acid/salt ratio less than 1.0 but of low acid content and containing the preferred hardening agents are given in the following examples:

|                 | Composition (by weight)                                                           | Acid/salt<br>Mol. ratio |
|-----------------|-----------------------------------------------------------------------------------|-------------------------|
| Example XII...  | Sulphuric acid (100%), 3%; sodium sulphate, 5%; zinc sulphate, 15%; glucose, 10%. | 0.8                     |
| Example XIII... | Sulphuric acid (100%), 7.0%; sodium sulphate, 11.3%; zinc sulphate, 15.0%.        | 0.9                     |

If calcium ions are present in the spinning solution in order to produce a strong fiber, the following spinning bath containing an acid and a soluble calcium salt thereof will be particularly satisfactory and economical:

|                  | Composition (by weight)                 |
|------------------|-----------------------------------------|
| Example XIV..... | Acetic acid, 10%; calcium acetate, 20%. |

The presence of a large amount of calcium salt in the bath permits the reaction of the calcium with the casein to form an acid insoluble product. Without this material present in the bath the straight acid would very likely leach the calcium from the fiber. In baths of this nature it is, of course, essential that the acid employed form a suitable calcium salt. Other agents which do not precipitate calcium and are compatible may be used in these spinning baths, for example, sodium acetate, magnesium acetate, zinc acetate, glucose, etc.

Yarn formed from casein, mixtures of proteins or mixtures of casein and viscose produce a strong yarn more suitable for cord construction for tires, belts and the like inasmuch as these proteins give unusually improved adhesion to the rubber. The cords for these purposes may be constructed from casein fibers, mixtures of casein fibers and other fibers (rayon, cotton, etc.), yarn spun from casein-viscose mixtures, and any combination of these materials. It has been known to prepare casein-viscose mixtures for spinning into a thread suitable for textile purposes only but prior to the present invention it has not been possible to prepare a mixed fiber having suitable properties such as strength, small elongation, flexibility and resiliency for the preparation of cord tires, belts and the like.

The preparation of casein-viscose solutions for the purpose of spinning mixed fibers may be carried out in any manner which results in a spinning solution containing casein and viscose. A preferred method for the production of such solutions is to prepare a solution of casein, preferably denatured, by dissolving the casein in alkali as described in the examples hereinbefore given. A separate viscose solution is prepared by soaking sheets of cellulose in alkali, pressing said sheets to remove the excess caustic and the more alkali soluble forms of cellulose, shredding the alkali cellulose sheets, aging the shredded material to reduce the viscosity of the final product, reacting

the shredded alkali cellulose with carbon disulphide to form cellulose Xanthate and dissolving same in dilute caustic soda to yield a viscose solution containing a little over 7% cellulose and about the same percentage of alkali. The viscose solution as thus prepared is aged for a suitable period to improve the spinning characteristics and then added to and mixed with the denatured casein solution. It has been found that especially high quality filaments and high tenacity yarns are obtained with a solution which contains a major proportion of casein and a minor proportion of cellulose. The casein-viscose mixture is aged for 24 hours, filtered and deaerated by a strong vacuum under controlled temperature conditions. The solution may be then extruded into any of the conventional baths used for casein fiber production. Preferably, the novel casein spinning baths discussed above should be employed to obtain fibers of the best physical properties. If, however, the casein content is decreased, the bath constitution approaches that of the conventional viscose spinning baths. With higher cellulose content spinning solutions, it is preferable that the spinning bath contain a high magnesium content, for example 8% by weight.

The filaments formed in the bath are drawn off and given a suitable stretch, for example 40% during spinning. In order to increase the water resistance of the casein fiber, the yarn is given a preliminary washing with a dilute solution of formaldehyde or of other insolubilizing agents and then washed with water. The wet washed yarn is then given an additional stretch before drying by any suitable method. Highly satisfactory results have been obtained by drawing the yarn between two godets driven at different speeds after which they are wound onto spools under tension for drying. This method of restretching the washed yarn is highly advantageous in that it not only gives a superior yarn but also permits spinning of a spool of yarn under less tension thereby making the washing step very much easier, and making it possible to spin heavier, more economical, yarn packages. In this connection it should be noted that a second stretching step may be performed before washing but this involves washing of a tightly wound spool of yarn containing residual acid from the precipitating bath while if the package of yarn is wound under light tension it may be readily washed, subsequently restretched and only the drying step is performed on the tightly wound package. By either of these methods it is possible to achieve an almost unlimited control of the elongation properties of the yarn. Although the process has been described in connection with spinning onto spools or bobbins, it will be understood that these steps are also adapted to pot spinning methods. The term "washing" as used herein contemplates simple washing acid-free; washing and desulphurizing; or washing, desulphurizing and bleaching. It will, of course, be recognized that the yarn is partially dried during the stretching step and that the drying is completed on the final package in a suitable manner.

This step is capable of extremely wide adaptation to different processes and it will be understood that the second stretching can be performed in connection with the twisting operation by applying a tension to the yarn as it comes off the first spools to be twisted and rewound. As an important stage in the preparation of a tire yarn to prevent loss of strength in cabling and to thereby produce a cable of highly desirable

properties, there is a finishing applied to the yarn in at least one stage of the spinning operation. The finish employed is primarily a softening agent which has no deteriorating effect on the yarn, on the rubber stock of the tire, or on the bonding action between these elements. This is a highly important aspect of the process of this invention since it has been found to improve the strength of the cable from 10 to 50% but has no appreciable effect on the single yarn. Among the materials which can be advantageously used for this purpose are monopole oils and lecithin, the former comprising primarily sulphonated soaps such as the sodium soap of sulphonated olive oil.

The finishing agent may be applied to the yarn as such or as a solution or emulsion with any suitable vehicle. Good effects are obtained from the addition of a finish during washing, subsequent to the washing and drying stages or during the first twisting. It has been found that at least 3% of monopole oil based on the weight of the dry yarn appears to be the preferred concentration for most purposes. Results obtained indicate very clearly that softening agents are much better than lubricating finishes in connection with yarns to be plied or plied and cabled. For example, a dilute mineral oil emulsion finish has little or no effect on improving the strength of the finished cable over that of the single yarn while a softening agent yields improvements in strength running as high as 50%. It would seem that such finishing of the single yarn is essential for the production of a smooth, well-formed, compact cable which will have the maximum strength obtainable from a given yarn.

It is, of course, desirable that the yarn be lubricated to some extent to prevent breakage or other damage during handling and if the softening agent does not impart sufficient lubrication a suitable lubricant may be blended therewith.

It has been found that the manner in which the yarn, ply and cable twists are related in a cord prepared particularly for use in a tire or the like, is of substantial importance, although many variations may be had without seriously impairing the properties of the finished cord. If a yarn having a twist not less than seven turns per inch is used, the ply twist may be equal to less than twice the yarn twist. For example, when a yarn twist approximating seven turns per inch is employed, five yarns may be plied with a twist of thirteen turns per inch. However, if a yarn having a low twist, such as three turns per inch, is employed the preferred ply twist is equal to at least twice the yarn twist.

Relatively small quantities of viscose do not adversely affect the stability and superior adhesion to the rubber of the casein yarn but they do materially improve its physical strength. As pointed out above, the proportions of casein and cellulose can be varied greatly, ranging from 100% protein to a major proportion of cellulose but in the preparation of fiber of the present type, the casein, preferably, is in excess of the cellulose. It is to be noted that in this discussion all treatments of a mixed casein-cellulose fiber can be applied to a fiber containing no cellulose.

It is an important feature of this invention that all apparatus, used in the preparation of any of these fibers, that comes in contact with the substances entering into the formation thereof, be composed of a material which resists corrosion and which will not contaminate said substances. It has been found that nickel is a suitable con-

struction material and can be used for the filter presses, conduits, and so forth either in whole or as a lining or coating thereof.

It is to be understood that while the discussion is generally directed to the preparation of fibers, it is intended to cover filaments, threads, yarns, cords, ribbons, foils, sheets or other products usually produced by extrusion or spinning. The invention has been described in detail in order that those skilled in the art may practice the same, but it is obvious that it is not to be restricted to the specific details described, the invention being limited only by the scope of the appended claims.

What we claim is:

1. In a process of forming threads, ribbons, sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing precipitated and dried casein by heating the same in a dry state at a temperature between 55° and 120° C. for a period of 8 to 72 hours, dissolving the said casein in an alkaline solution and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

2. In a process of forming threads, ribbons, sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing precipitated and dried casein by heating the same in a dry state at a temperature between 55° and 120° C. for a period of 8 to 72 hours, dissolving the said casein in an alkaline solution and mixing the same with a minor proportion of viscose and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

3. In a process of forming threads, ribbons, sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing precipitated and dried casein by wetting the same with water and heating at a temperature of at least 45° C., dissolving the said casein in an alkaline solution and mixing the same with a minor proportion of viscose and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

4. In a process of forming threads, ribbons, sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing the said casein by suspending the same in water having a pH of about 4.1 and heating the said suspension from 1 to 8 hours at a temperature between 45° and 95° C., dissolving the said casein in an alkaline solution and mixing the same with a minor proportion of viscose and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

5. In a process of forming threads, ribbons,

5 sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing precipitated and dried casein by heating the same at a temperature between 45° and 120° C. for a period of 1 to 72 hours, dissolving the said casein in an alkaline solution immediately after denaturing and before the casein reverts to its prior condition, and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

10 6. In a process of forming threads, ribbons, sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing precipitated and dried casein by wetting the same with water and heating at a temperature of at least 45° C., dissolving the said casein in an alkaline solution before the casein reverts to its prior condition, and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

15 7. In a process of forming threads, ribbons, sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing the said casein by suspending the same in water having a pH of about 4.1 and heating

the said suspension at a temperature of at least 45° C., dissolving the said casein in an alkaline solution before the casein reverts to its prior condition, and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

20 8. In a process of forming threads, ribbons, sheets and the like by extrusion of an aqueous solution containing casein into an acid precipitating bath, the steps that comprise denaturing the said casein by suspending the same in water having a pH of about 4.1 and heating the said suspension from 1 to 8 hours at a temperature between 45° and 95° C., dissolving the said casein in an alkaline solution before the casein reverts to its prior condition, and extruding the said solution into a precipitating bath comprising sulphuric acid and a salt selected from the class consisting of ammonium and alkali metal sulphates in which the molecular ratio of the said acid to the said salt is in a range of 1.3 to 1.5.

25 9. The step of preparing casein suitable for use in spinning filaments, ribbons and sheets that comprises heating the same in a dry state at a temperature between 55° C. and 120° C. for a period of 8 to 72 hours and dissolving the casein in an alkaline solution.

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