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ZEIN FILAMENTS

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My invention relates to the production of protein filaments suitable for use in the manufacture of fabrics and the like. More specifically, my invention relates to the production of artificial protein fibres having improved strength and water-resistance.

It is well known that artificial fibres can be produced from regenerated cellulose or from cellulose esters, and such fibres have now come into extensive commercial use. However, the processes for the production of such fibres are relatively expensive and have certain disadvantages, particularly in difficulty of producing uniform products. In all of the methods now in use it has been found necessary to "ripen" the cellulose solutions prior to extrusion and even then it is necessary to blend a number of different batches in order to secure approximate uniformity. The processes previously employed have various other disadvantages, particularly with regard to dyeing and obtaining suitable lustre. In view of the proteinaceous nature of real silk, it has been attempted to produce artificial silk fibres from proteins, but up to the present time such attempts have been entirely unsuccessful. It has been impossible to secure solutions of the proteins previously employed without undesirably changing their chemical nature and the products obtained have lacked strength and water-resistance.

I have now discovered that very satisfactory filaments may be secured by extruding zein solutions into a coagulating fluid while simultaneously contacting the zein with a reactive aldehyde, and subsequently subjecting the resulting filament to elevated temperatures. It will be apparent that my invention is capable of various modifications depending upon the nature of the zein solutions employed and upon the nature of the coagulating fluid. For example, the latter may comprise either a liquid or a gas and the reactive aldehyde may be incorporated in the zein solution, in the coagulating fluid, or in both. A number of these modifications will be discussed in more detail below.

One embodiment of my invention comprises the use of solutions of zein in organic solvents containing free formaldehyde or other reactive aldehyde. Such solutions are described in copending application Ser. No. 41,776, filed Sept. 23, 1935. According to the process of this application, the zein solutions may be prepared simply by adding the desired amount of formaldehyde or other aldehyde to a solution of zein in aqueous ethyl alcohol or a similar solvent such as methyl alcohol, "carbitol" (di-ethylene glycol), "cellosolve" (mono-ethyl ether of ethylene glycol), diacetone alcohol or the like. The zein concentration of the solution may be adjusted to any suitable value for extrusion, depending upon the size and nature of the orifice, the pressure to be employed, etc. An amount of aldehyde equivalent to 2% of free formaldehyde, based on the weight of the zein, is usually required to give satisfactory strength and water-resistance to the product. Larger amounts, for example up to 50% by weight, can usually be satisfactorily employed, but I prefer, generally, to use from 2–5% by weight.

Although the solutions described above are satisfactory from the standpoint of extrusion to form suitable filaments, I generally prefer to incorporate a plasticizer in order to obtain the desired degree of flexibility and resilience in the product. Any suitable plasticizer for zein, such as dibutyl tartrate, monobutyl phthalate, or p-toluene methyl sulfonamide, may be used. Suitable zein solutions containing plasticizers are disclosed in copending application Ser. No. 38,976, filed Sept. 3, 1935. Such solutions may be prepared by any satisfactory procedure such as simply incorporating the desired amount of plasticizer into the solutions previously described. Amounts of plasticizer up to 20% or more, based on the weight of the zein, will generally be suitable, and for most purposes from 10–20% will be satisfactory.

The zein solutions described above may be extruded in any type of apparatus suitable for use with cellulose acetate or other cellulose solutions. The standard spinnerettes may be used and the degree of pressure may be adjusted to correspond to the size of the orifice and the viscosity of the solution in accordance with known practice in this regard. The solution may be extruded into air, in which case the coagulation will take place due to the evaporation of solvents, or it may be extruded into water or other liquid coagulating medium. After solidification of the filament and before winding, it is necessary to apply heat in order to obtain satisfactory initial strength. If a gaseous coagulating fluid is employed, heated gas will serve both to evaporate the solvents and to effect the reaction between the zein and reactive aldehyde. If a liquid coagulating medium is used, the filament should pass through a heated chamber prior to winding. Any suitable means may be employed for this purpose and the heat treatment may be effected simultaneously with other treatments such as imparting the desired amount of tension or twist to the filament. For

example, in either of the cases mentioned above, the heating could be effected in a vertical tower through which heated air is passed counter-current to the travel of the filament. The heating should be effected at temperatures not substantially above 100° C. in view of the water content of the material and the possible deleterious effect of higher temperatures upon proteins. Temperatures of 60–90° C. will be found to be quite satisfactory and at such temperatures a treatment of approximately 5 minutes will usually impart sufficient strength to the material.

It will be found that the reaction between zein and the aldehyde will continue to completion upon storage at atmospheric temperatures. However, at such temperatures the reaction is relatively slow and I therefore prefer to subject the filament to further heating to impart initial water-resistance. For this purpose, the material may be baked at temperatures of 60–90° C. for a period of 8–10 hours. This operation may be carried out at any suitable stage of the processing, for example, when the filament is first spooled, but is preferably effected when the material is in a loose form, as in skeins.

A second modification of my invention comprises the use of solutions of zein in aqueous formaldehyde without organic solvents. It is disclosed in copending application Ser. No. 38,971, filed Sept. 3, 1935 that aqueous formaldehyde exerts a solvent and plastifying effect upon zein. According to the process of this application, zein is kneaded with aqueous formaldehyde to obtain a mass suitable for the production of plastics. Such solutions will usually be too viscous for satisfactory extrusion, so that for the present purpose a more dilute solution should be prepared. By the use of suitable apparatus, additional plasticizers may be incorporated into the solution and these will generally be found to be beneficial from the standpoint of reducing viscosity and aiding extrusion. Solutions of this type may be employed in the same manner as the solutions in aqueous organic solvents discussed above. The coagulating fluid may comprise either a liquid or a gaseous medium and the procedures discussed above will apply to these alternative procedures.

A further modification of my invention comprises the use of zein solutions without aldehydes, in which case the solution is extruded into a medium containing the desired concentration of formaldehyde or the like. For this purpose solutions of zein in aqueous organic solvents, such as the alcoholic solutions obtained by the process of my copending application Ser. No. 20,402 filed May 8, 1935, may be employed and, as in the preceding examples, plasticizing agents may be incorporated if desired. Such solutions may be extruded into aqueous formaldehyde or a solution of other reactive aldehyde, or they may be extruded into a gaseous medium containing formaldehyde vapor or the like. The same general procedure as to extrusion and heat treatment previously described applies equally to the present modification.

The products obtained by any of the above procedures will be found to have satisfactory strength and to have excellent water-resistance after final cure. It will be seen that no "ripening" processes are necessary and that a uniform product may be secured in accordance with any of the procedures specified. Filaments of desirably low denier may readily be obtained and any of the standard types of yarns may be produced. The materials will be found to have excellent appearance and satisfactory elasticity and resilience. The filaments will generally be found to have wet strength, elastic recovery and abrasion resistance superior to the artificial cellulose fibres previously employed. These properties and other advantages previously pointed out make the products of this invention especially suited for use in the textile industry for any of the purposes for which artificial cellulose fibres have previously been employed.

It will be apparent to those skilled in the art that further modifications of my invention are possible and that various equivalent materials may be employed. Various modifying agents may be incorporated into the solutions and any of the known procedures may be applied to the extrusion and subsequent treatment of the filaments. Spirit-soluble dyes may be incorporated into the organic solvent solutions or the final products may be dyed according to known procedures for protein plastics. In general it may be said that any equivalents or any modifications of procedure which would naturally occur to those skilled in the art may be employed without departing from the scope of my invention.

My invention now having been described, what I claim is:

1. Process for the production of zein filaments which comprises: extruding a solution of zein through a filament forming orifice into an aqueous coagulating medium containing formaldehyde; withdrawing the filament and heating the same to evaporate water and promote reaction between the formaldehyde and zein.

2. Process for the production of zein filaments which comprises: extruding an alcohol solution of zein containing formaldehyde through a filament forming orifice into an aqueous coagulating medium; withdrawing the filament from said medium, and subjecting it for a short time to a current of air heated to a temperature not in excess of 100° C., skeining the filament and baking the same at a temperature of 60°–90° C. for about 8–10 hours.

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