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METHOD OF PRODUCING PROLAMINE FILAMENTS

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented in any country, may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to us of any royalty thereon.

This invention relates to the production of protein filaments, and has among its objects the modification of a prolamine, such as zein, by a combined series of steps, before, during, and after spinning to produce fibers having properties heretofore unobtainable. Other objects will be apparent from the description of the invention.

Although the process of this invention is applicable to the general class of prolamines, zein is the only prolamine which has attained substantial industrial importance. The invention will therefore be described with particular regard to the production of filaments from zein.

Zein is an alcohol-soluble protein conventionally extracted from corn gluten residue, a product in the wet milling of corn for the production of corn starch. Zein is produced by extraction of this crude gluten with a lower alcohol, such as ethanol or isopropyl alcohol, precipitation and drying. Zein prepared by this or other known methods may be used in the process of the invention. It is a relatively inexpensive protein which has been found to have many valuable characteristics when spun into fibers. However, zein fibers or filaments have a tendency to "blush" and shrink when brought into contact with water. This characteristic is a serious limitation upon the use of zein fibers, especially since it has been found that the coarser fibers of the bristle type are particularly adaptable for use in brushes.

In application Serial No. 528,479, of C. D. Evans, C. W. Ofelt, and A. K. Smith, filed March 28, 1944, a process for producing fibers is described which includes spinning an aqueous alkaline dispersion of zein, the dispersion containing an aldehyde or an aldehyde-yielding agent. Fibers produced by this process, although possessing superior strength and other characteristics, have a tendency to turn white or "blush" and shrink on contact with water.

Various heat treatments have been applied heretofore in the preparation or finishing of zein

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products. In United States Patent No. 2,402,128, issued to C. D. Evans, a method is described for preventing the "blushing" of zein films by reacting zein in a solution of volatile solvent with an aldehyde at temperatures of 50° C. and over, and subsequently baking the cast film at 130° C. Films or bodies prepared in this manner have considerable resistance to "blushing." In United States Patent No. 2,156,929, issued to L. C. Swallen, a method is described for producing filaments by spinning volatile solvent solutions of zein which contain an aldehyde, into an aldehyde-containing bath and subsequently heating the filament to temperatures below 100° C. to evaporate water and promote reaction between the aldehyde and zein. As will be seen from the ensuing description, the temperatures employed in these prior patented processes are considerably lower than those required in the baking step of this invention and are insufficient to impart appreciable water resistance to the zein fibers.

Our process is essentially one for modifying the prolamine by aldehyde treatment steps and by a heat treatment or baking step. The exact mechanism of modification is not known, but we believe it is for the most part a progressive alteration of the protein through a series of successive stages of chemical reaction between the prolamine and the aldehyde. Three essential modification steps are involved which may be enumerated briefly as follows:

1. Aldehyde modification of the prolamine in an alkaline dispersion before spinning.

2. Spinning the fibers into an acid bath, the spinning being associated with a mild aldehyde cure.

3. A thorough baking treatment.

All of these steps must be followed to achieve production of the fibers possessing the improved characteristics.

The first step, which may be termed a preliminary modification of the zein while in an alkaline dispersion, is carried out within a pH range of 11.0 to 12.5. The aldehyde is preferably formaldehyde and the amount used may vary from ½ to 10 percent based on the weight of the zein. The reaction is completed in about 2 to 4 days at approximately room temperature. Instead of formaldehyde, other aldehydes, such as acetaldehyde, propionaldehyde, benzaldehyde, and fur-

fural, may be used. Furthermore, aldehyde-yielding compounds, such as trioxymethylene and hexamethylenetetramine, may be used. The amount of aldehyde introdued into the fiber may vary from 0.3 percent to 4.0 percent, based on the weight of the zein.

The second step which is similar to the "precure" of older zein modification methods may be carried out in two separate stages. When the fibers are spun, they may be run directly into an acid bath where the protein is coagulated, then drawn from this bath into another bath containing acid and the aldehyde. The second bath contains about 10 percent aldehyde, a small amount (usually about 1 percent) of a catalyst, such as ammonium sulfate, ammonium phosphate, ammonium chloride, and the like; and about 5 percent of an alkali salt, such as sodium sulfate, may be added to prevent plastering together of the filaments. Although it is not necessary, it is preferable that the negative radical of the ammonium and sodium salts correspond to the acid employed in the coagulating bath. An unnecessary mixture of acid radicals is thus avoided. For reasons of convenience the acid used should correspond in both acid baths. Any of the usual coagulant acids may be used, such as sulfuric, phosphoric, acetic, hydrochloric, and the like.

The pH of both baths ranges from about 1 to 3. The time of treatment ranges from 15 to 30 minutes at a temperature of 30° to 55° C. During this treatment about 1 percent aldehyde is introduced into the fibers.

The two acid baths may be combined to make the second step a single operation. In other words, the acid bath into which the fibers are spun, having a pH of between 1 and 3, may also contain 10 percent by weight of aldehyde, the ammonium salt catalyst, and the alkali salt. This bath is then held at a temperature between 30° to 55° C., and the fibers kept immersed for 15 to 30 minutes. The fibers drawn from the acid formaldehyde bath usually contain over 1 percent combined aldehyde.

As in the previous step, other aldehydes or aldehyde-yielding agents may be used, although formaldehyde is preferred.

After washing, stretching from 50 to 300 percent, and drying the filaments from the acid formaldehyde step, they are given a baking treatment for about from 10 to 60 minutes. The preferred conditions for baking are 160° to 170° C. for about 15 minutes. Lower temperatures require longer baking, and the lowest practical temperature is about 140° C. For example, although the reaction at 140° C. is of considerable benefit to the fibers, treatment at this temperature for 60 minutes is not equivalent in beneficial results to a 15-minute treatment at 160° C. At temperatures of 180° C. or above the filaments begin to darken and the strength begins to drop off due to thermal deterioration of the fiber. A certain amount of aldehyde is lost from the fibers during this treatment. The range of formaldehyde in the final baked filament is about 0.5 to 2.5 percent.

The exact chemical mechanism of the steps of this invention is not known. It is believed that the aldehyde may have been introduced during the two preceding steps as chemically combined aldehyde, either by direct chemical union or by the formation of addition complexes. It is entirely possible that prior to the baking step the aldehyde is present in both forms.

The process is a much quicker and simpler procedure for producing prolamine fibers than any known previously. The fibers produced are higher quality and capable of more extensive uses than previous prolamine fibers. They have greatly improved water resistance and the shrinkage is reduced lower than ever before. In spite of the fairly drastic conditions for baking, it is remarkable that the strength is not materially decreased nor the color of the dry fiber materially changed.

Omission of the formaldehyde treatment in the initial step results in fibers which blush easily and do not have the greatly improved shrinkage characteristics. This is illustrated by the data of Table III, which is set forth below. The second step of spinning the fibers into an acid bath, the spinning being associated with the mild aldehyde cure, is, of course, necessary to obtain a satisfactory fiber. Fibers without the acid coagulation or the mild cure would have no appreciable strength and little elasticity. The baking step is, of course, essential before appreciable water resistance or decreased shrinkage is attainable.

The following examples illustrate the invention:

EXAMPLE I

A sample of commercial alcohol-extracted and unmodified zein was used in preparation of filaments. The procedure was as follows:

First Step

Nine hundred g. of zein was mixed with 4800 ml. of cold water until a smooth slurry was obtained. To this slurry was added 135 g. of urea followed by the slow addition of 1000 ml. of .4N sodium hydroxide from a separatory funnel. The function of the urea is a denaturing agent to accelerate aging of the protein. Thirty ml. of formalin (40 percent formaldehyde, equal to 1.34 percent formaldehyde based on the weight of the zein) was mixed with 200 ml. of .4N sodium hydroxide and added through the separatory funnel. The reaction mixture was stirred and mixed with a high-speed stirrer, stirring being continued for one hour after addition of all ingredients.

A low viscosity dispersion resulted which was filtered through a fine filter. It was then stored under controlled conditions (22° C. for 3 days). During this period, deaeration, ageing, reaction with the formaldehyde and the development of spinning viscosity are all accomplished.

Second Step

Filaments were spun from the above-described solution into an acid bath containing 800 ml. of acetic acid and 12 l. of water. A 40-hole, 0.040" diameter jet was used. The filaments were withdrawn from this coagulation bath, washed, and stretched before being dropped loose into the mild formaldehyde curing bath. Curing may be accomplished by two methods, namely, a batch or slow cure and a continuous or fast cure. Both types of cures were carried out on separate samples of filaments in this example.

In the batch cure the tow of filaments was given a slight stretch before being dropped loose into a large curing tank. The curing bath was made up in the following proportions: 12 l. of water, 600 ml. of 40 percent formalin and 40 g. of ammonium chloride. The bath had a pH of about 2.0. The filaments, when dropped into the bath, formed a sort of cake in the tank. For the

cure, the bath containing the filaments was allowed to stand for 27 days at room temperature. At the end of the seventeenth day the formaldehyde content of the filaments was found to be 2.30 percent. At the end of the twenty-seventh day the formaldehyde content was 2.82 percent.

The continuous or fast method of curing is as follows: The washed tow of filaments was stretched slightly and dropped loose into a curing bath consisting of 10 percent formaldehyde, 1 percent ammonium sulfate, and 5 percent sodium sulfate. The pH of the bath was about 2.5. Two different runs were made, the first being a 30-minute cure at 33° C.; the second being a 30-minute cure at 50° C. Formaldehyde content of the filaments in the 33° C. cure was found to be 1.87 percent. In the 50° C. cure it was found to be 1.73. After curing by either the slow or fast method the filaments were withdrawn, washed, stretched, and dried continuously in a hot air countercurrent system.

THIRD STEP

The following Table I illustrates the change in strength of the zein fibers as the baking temperatures are increased. The term "raw fiber" refers to the unbaked fiber. The terms "dry strength" and "knot strength" refer to the load in grams for individual filaments of substantially equal diameter at 70° F. and 65 percent relative humidity. The knot strength was determined after tying an overhand knot in the filament. It will be noted that the strength of the raw zein fibers is slightly less than the baked fiber at temperatures below about 160° C. As the baking temperature is increased, the strength begins to drop slowly until at 180° C. the fiber begins to be adversely affected. Between these two temperatures, both the dry strength and the knot strength, although slightly decreased, are not appreciably below the strength of the raw fiber. As would be expected, temperatures above 180° C. begin to cause deterioration of the fiber.

Table I also shows the effect of baking temperatures upon the shrinkage of zein fibers. In every case the fibers had been baked for 15 minutes and the shrinkage determined by an 18-hour treatment of the fibers in water at room temperature. As may be noted, the shrinkage, over 25 percent in the unbaked fiber, is gradually reduced as the temperature of baking is increased until a minimum is reached at about 160° C., at which temperature the shrinkage remains below 7 percent as the baking temperature is increased.

Table I

Baking Temperature °C.	Strength, grams		Shrinkage, (Per Cent)
	Dry	Knot	
100	280	180	26
122	280	195	17
140	265	200	12
160	265	190	6
180	255	165	5
200	215	150	5
Raw (unbaked)	270	185	29

The effect of baking on strength and shrinkage,

using the batch and continuous cure is shown in Table II, following:

Table II

	Strength, grams		Shrinkage, (Per Cent)
	Dry	Knot	
Batch cure:			
Raw	270	185	26
Baked	265	185	5
Continuous cure:			
Raw	282		38
Baked	306		6

We have discovered that beneficial effects of our invention are more pronounced in processes for making coarse or bristle type fibers. Nevertheless, the finer textile fibers show considerable improvement. The following table illustrates the effect of formaldehyde in the dispersion, i. e., in the initial or preliminary modification of fibers prepared by procedure similar to that of Example I. In the initial step the formaldehyde treatment was omitted for control fibers for the purpose of comparing the resulting shrinkage. In every case the heating step was carried out by baking at 167° C. for 15 minutes. The shrinkage in every case was determined by an 18-hour treatment of the fibers in water at room temperature.

Table III

Example	HCHO in dispersion	Shrinkage 18-hr. Room Temperature, Per Cent
Coarse Fibers:		
2 Raw	No	43
2 Baked	No	18
3 Raw	No	43
3 Baked	No	20
4 Raw	Yes	29
4 Baked	Yes	5
5 Raw	Yes	38
5 Baked	Yes	6
Textile Fibers:		
6 Raw	No	59
6 Baked	No	55
7 Raw	No	50
7 Baked	No	45
8 Raw	Yes	49
8 Baked	Yes	25
9 Raw	Yes	58
9 Baked	Yes	38

Having thus described our invention, what we claim is:

1. A process for the production of a prolamine filament comprising reacting an aqueous alkaline dispersion of a prolamine with an amount of aldehyde equal to from ½ to 10 percent based on the weight of the prolamine, spinning the dispersion into an acid bath to coagulate the prolamine, curing the spun filament in an acid-aldehyde bath of pH from 1 to 3 at a temperature of from 30° C. to 55° C., removing the filament, washing, stretching, and drying it, and then heating the dried filament at a temperature between 140° C. and 180° C.

2. The process of claim 1 wherein the prolamine is zein.

3. The process of claim 1 wherein the aldehyde is formaldehyde.

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No references cited.