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FIBERS FROM ZEIN

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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, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to us of any royalty thereon.

This invention relates to zein, and has among its objects the obtaining of a dispersion of the zein in a simple and economical manner, which dispersion can be spun to produce fibers of superior tensile strength and other characteristics, and such other objects as will be apparent on consideration of the following specification.

Zein is an alcohol-soluble protein conventionally extracted from the crude gluten residue which is obtained as a byproduct in the wet milling of corn for the production of corn starch. This crude gluten, which contains the zein, also contains cellulose, hemicellulose, and some starch and oil. Conventionally, it is dried and then extracted with either ethyl or isopropyl alcohol. After purification of the removed alcoholic solution, the zein is precipitated by the addition of cold water to the solution and is removed. Upon careful drying, a friable product is obtained which is readily soluble in aqueous alcohols.

In the usual processes of forming protein fibers from zein, spinning is accomplished from alcoholic zein solutions. These solutions are usually spun into air by the well-known technique employed in spinning cellulose acetate fibers, known as the dry process.

According to this invention, aqueous alkaline dispersions of zein can be prepared within a certain pH range having such concentrations and viscosities that zein fibers can be produced by spinning the dispersion into a suitable coagulating acid medium. In this manner, the use of expensive organic solvents is eliminated and the elaborate solvent-recovery system which is used in dry spinning of the fibers is not required. Also, fibers produced from the alcohol and other organic solvent solutions of zein have shown poor strength, are brittle, and usually require incorporation of plasticizers to give satisfactory properties. In contrast, with the process of this invention fibers have been prepared from alkaline dispersions of zein without plasticizers which are very flexible, are of low denier and have strength greater than that of wool.

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The alkaline zein dispersions of this invention are preferably formed in a medium having a pH of about 11 to 12.8 and with proportions of ingredients that give a viscosity of about from 10 poises to 1,000 poises. As dispersing agents, hydroxides of the alkali metals, particularly either sodium hydroxide or potassium hydroxide, may be used. The dispersions are conveniently prepared by adding the desired amount of the aqueous alkali metal hydroxide to a deaerated cold water suspension of the zein, avoiding temperatures over 40° C. Concentration of the alkali metal hydroxide can be varied to give a pH over the above-described limits, and the viscosity of the dispersion will depend upon both the concentration of alkali metal hydroxide and the proportion of zein, which proportion may be about from 15 to 25 parts of zein per 100 parts of water used in the water suspension of the zein. The exact concentration of zein and the viscosity desired depend upon the conditions of extrusion, speed and pressure of pumps, size of spinnerette orifice, temperature of solutions, temperature of the coagulating medium, and so forth, all relative to the spinning process.

If desired, other ingredients may be added to the alkaline zein spinning dispersion as, for example, aldehydes or aldehyde-yielding agents and other curing agents, plasticizers, softeners and other such modifiers, and wetting and other conditioner agents. Also, other substances may be added which will become activated during latter stages of the spinning process as, for example, compounds activated in the coagulating medium or activated by heat during passage of the fibers through washing and drying chambers after spinning.

The aqueous zein dispersions can be satisfactorily extruded through any of the standard spinnerettes commonly used in the rayon industry. The 500-hole spinnerettes with hole diameters of .003 inch or .004 inch have been found satisfactory.

The composition of the coagulating medium may vary widely, but it is essential that the medium be quite strongly acid. The most satisfactory media contain both a strong mineral acid and an organic acid. Satisfactory results have been obtained with mixtures of either sulfuric or hydrochloric acid with acetic acid. Other organic acids, such as formic, propionic and lac-

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tic, can be substituted for the acetic acid. Various salts as, for example, aluminum sulfate, zinc sulfate, magnesium sulfate, calcium chloride and sodium chloride, may be incorporated with the coagulating medium as dehydrating and denaturing agents. Various aldehyde and other tanning or curing agents, such as formaldehyde, glyoxal, formamide, hexamethylenetetramine, acetaldehyde, and so forth, may also be incorporated into the coagulating medium.

However, because of the slow reaction of zein with formaldehyde, it is preferable to add formaldehyde directly to the spinning dispersion, and, depending upon the type of product desired, the alkaline aldehyde-zein dispersion may be allowed to age and mature before spinning. That formaldehyde may be added to such a high protein concentration as contained in the dispersion in the manner of this invention is unexpected, since to add aldehydes directly to other proteins, such as soybean, casein, gelatin, albumin, and so forth, and yet retain a material which can be spun, is impossible, since with these proteins gelation occurs immediately.

By adding formaldehyde directly to the spinning dispersion, the objectionable use of formaldehyde in the coagulating medium is overcome, and if greater curing is necessary, it may be performed on the spun fiber at a later stage in the process. Adding the formaldehyde directly to the spinning dispersion also aids in obtaining a more rapid rate of coagulation, thus permitting the fiber tow to be withdrawn from the coagulating medium at a very rapid rate and under considerable tension. For example, tows of 500 fibers have been withdrawn from the coagulating medium at a rate of 4.5 feet per second and higher.

Instead of formaldehyde, aldehyde-forming substances, such as trioxymethylene, trioxane, and so forth, may be used. The dispersion can be made up containing 10 percent or more of formaldehyde.

A substantial equivalent of the alkaline aldehyde-zein dispersion is also obtained by first treating the zein with the aldehyde, as described, for example, in patent application Serial No. 429,576, now Patent No. 2,392,084, filed February 4, 1942, by Evans et al. According to this process, the zein is dissolved in aqueous alcohol or in acetone, and is given a heat treatment in the presence of an active aldehyde.

According to the present invention, aldehyde-treated zein of the application referred to above is recovered from the solution by precipitation, is washed, and is carefully dried. The aldehyde-treated zein may then be dispersed in the aqueous alkali metal hydroxide to form the alkaline-aldehyde-zein dispersion.

The use of salts in the coagulating medium as above mentioned aids in obtaining a better surface denaturation of the protein with considerably less tendency of the fibers to adhere and plaster together in this medium. This aids in obtaining a thorough subsequent washing with a more complete removal of the salts, acids and other soluble materials from the fibers. After coagulation, the fibers should be washed in water until substantially salt and acid free. Washing baths should be constantly circulated and maintained at constant temperatures. Temperatures of 30° to 35° C. are desirable, although temperatures have been varied from 25° to 95° C. with workable results. However, at the higher temperatures the tow becomes softened and must be

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handled very carefully to avoid breaking and plastering together of the individual fibers.

Preferably, the fiber tow should be maintained under tension at all times during the process, and not allowed to collect in bunches or skeins during the spinning. Fibers after being thoroughly washed may be dried while traveling through heated chambers, temperatures being graduated so that the final drying is at a higher temperature than the initial drying. Final drying temperatures as high as 135° C. may be used.

Liquid coagulating media suitable for use in the process of this invention are given in the following formulae:

Formula 1

	Parts
Water	120
Concentrated sulfuric acid	4 to 7
Glacial acetic acid	3 to 6

Formula 2

	Parts
Water	120
Concentrated sulfuric acid	4 to 7
Glacial acetic acid	3 to 6
Sodium chloride	2.5 to 9

Formula 3

	Parts
Water	120
Concentrated hydrochloric acid	4
Glacial acetic acid	4
Calcium chloride	2 to 10

Formula 4

	Parts
Water	120
Concentrated sulfuric acid	4 to 7
Lactic acid (85 percent)	3 to 6

Examples of details in carrying out the process of this invention follow.

EXAMPLE I

400 parts of powdered zein was thoroughly wetted with sufficient cold water to cover it. After wetting, the formed paste was placed in a vacuum desiccator and vacuum applied and released a few times to insure complete deaeration and a thorough wetting of all the zein particles. More water was then added and the mixture worked into a smooth, thin paste to remove all coarse particles. 8.4 parts of sodium hydroxide in solution was then slowly added with stirring to give a uniform, clear dispersion. Since so little alkali is needed, it is expedient to add it as a 0.4 normal solution, thus avoiding any localized high concentration of the alkali. In this example, the total water content was about 2,000 parts. If air is beaten into the dispersion at this point of the process, it is necessary to remove it by centrifuging or other means.

This particular dispersion as made up had a pH of 11.95 and a viscosity of 93 poises. It was allowed to age for a day and the viscosity had increased to 98.5 poises. The dispersion was spun through a 500-hole spinnerette with holes of .003 inch diameter into a standard coagulating medium of the composition given in Formula 1 above. Fibers from this dispersion were suitably cured and dried and gave a tensile strength of 1.17 g. per denier.

Other similarly conducted examples, with some change in the proportion of ingredients and other details of procedure, are grouped in the following table:

Table 1

Example	Zein, parts	Sodium Hydroxide, parts	Total Water, parts	pH	Aging, hours	Viscosity, poises	Tensile Strength, g./denier
I (above)-----	400	8.4	2,000	11.95	24	98.5	1.17
II-----	400	8.0	2,000	11.86	0	34.6	-----
III-----	400	7.2	2,000	11.63	0	23.5	-----
IV-----	400	9.2	2,000	12.10	5	62.7	1.16
V-----	350	11.2	2,000	12.30	0	41.5	-----
VI-----	500	7.3	2,000	11.30	0	1,020.0	-----

Other examples in which formaldehyde was used in the alkaline zein dispersion are given in Table 2 below, procedures similar to that of Example 1 being followed, except that the Formalin was added by mixing 40 percent formaldehyde with the 0.4 normal sodium hydroxide before addition to the zein-water mixture.

Table 2

Example	Zein, parts	Sodium Hydroxide, parts	Formalin, parts	Total Water, parts	pH	Aging, hours	Viscosity, poises	Tensile Strength, g./denier
VII-----	400	6.4	12.5	1,987	11.30	{ 0 24	{ 53.5 263.00	{ .86 1.23
VIII-----	400	8.0	13.0	1,987	11.85	{ 0 0	{ 35.2 62.73	{ ----- -----
IX-----	400	8.4	26	1,974	11.97	{ 0 22	{ 62.73 263.00	{ ----- -----

EXAMPLE X

According to this example, 123 g. of autoclaved aldehyde-treated zein obtained as described above was wetted with 508 ml. of water, and a dispersion made by addition of 177 ml. of 0.4 normal sodium hydroxide, following in general the procedure of Example I, giving a dispersion having a pH of 11.95 and a viscosity of 16.3 poises. When spun without aging into a coagulating medium of the type given in Formula 1, fibers were obtained which when suitably cured and dried gave a tensile strength of .74 g. per denier.

The pH range required in the alkaline zein dispersion is quite well defined. Unless substantially complete dispersion of the zein is obtained, the product cannot be spun to give satisfactory fibers. The pH range depends somewhat upon the concentration of the zein. Regardless of concentration, however, in water, the percent of total nitrogen dispersed (which is a measure of zein dispersion) is 0. With a concentration of 2.5 g. of zein per 100 ml. of potassium hydroxide solution, it has been found that the percent of total nitrogen dispersed remains about 0 up to a pH of about 11.0, rises slightly up to a pH of about 11.3, rises sharply to 100 percent up to a pH of about 11.6, remains at 100 percent up to a pH of about 12.8, thereafter dropping sharply. With higher concentrations of zein, the range is generally similar, except that a somewhat greater percentage of total nitrogen is dispersed with the lower pH values. With a concentration of 5.0 g. zein per 100 ml. of potassium hydroxide solution at a pH of about 11, the percent of nitrogen dissolved is about 10, rising sharply to 100 at a pH of about 11.5, whereas with a concentration of

10.0 g. of zein per 100 ml. of potassium hydroxide solution at a pH of 10.7, the percent of nitrogen dispersed is about 40, rising sharply to 100 at a pH of about 11.3.

Having thus described the invention, what is claimed is:

1. The process of forming fibers comprising cold mixing zein with an aqueous alkali metal hydroxide to produce a dispersion having a pH range of about from 11 to 12.8, the proportion of zein used being such as to give a viscosity of about

from 10 poises to 1,000 poises, and spinning the dispersion in a liquid coagulating acid medium containing a strong mineral acid and an organic acid.

2. The process of forming fibers comprising cold mixing zein with an aqueous alkali metal hydroxide to produce a dispersion having a pH range of about from 11 to 12.8 said dispersion containing an active aldehyde-yielding agent, the proportion of zein used being such as to give a viscosity of about from 10 poises to 1,000 poises, and spinning the dispersion in a liquid coagulating acid medium containing a strong mineral acid and an organic acid.

3. The process of forming fibers comprising treating zein with an aldehyde, cold mixing the treated zein with an aqueous alkali metal hydroxide to produce a dispersion having a pH range of about from 11 to 12.8, the proportion of zein used being such as to give a viscosity of about from 10 poises to 1,000 poises, and spinning the dispersion in a liquid coagulating acid medium containing a strong mineral acid and an organic acid.

4. The process of forming fibers comprising mixing powdered zein with water to form a paste, slowly mixing therewith an aqueous solution of an alkali metal hydroxide, the while maintaining the mixture cold, to produce a dispersion having a pH range about from 11 to 12.8, the proportion of zein used being such as to give a viscosity of about from 10 to 1000 poises, and spinning the dispersion in a liquid coagulating acid medium containing a strong mineral acid and an organic acid.

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(References on following page)

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,245,975	Satow	Nov. 6, 1917
1,316,854	Ostenberg	Sept. 23, 1919
2,156,929	Swallen	May 2, 1939
2,192,194	Kajita et al.	Mar. 5, 1940
2,237,832	Kajita et al.	Apr. 8, 1941
2,331,434	Sitzler	Oct. 12, 1943

Number	Name	Date
2,342,994	Atwood	Feb. 29, 1944
2,358,219	Dickson et al.	Sept. 12, 1944
2,364,792	James	Dec. 12, 1944
5 2,429,214	Biehn et al.	Oct. 21, 1947

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OTHER REFERENCES

Ind. & Eng. Chem., March 1941, pages 394-398, article by L. C. Swallen, Zein—A New Industrial Protein.
Ser. No. 96,470, Ferretti (A. P. C.), published Apr. 27, 1943.