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METHOD OF PREPARING FORMED COLLAGEN
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This invention relates to a method of preparing formed collagen. More particularly this invention relates to a method wherein native fibrous collagen can be formed into uniform sheets, filaments, molded bodies, and the like. The sheets and filaments are adaptable for use as substitutes for natural leather.

In prior attempts to prepare sheets, filaments, and the like from native collagen, it has been extremely difficult to obtain a product of satisfactory quality while fully utilizing the starting material. The present invention provides for the achievement of this objective.

In practicing the method of the present invention, the preferred starting material is native collagen which has been reduced by mechanical means to the form of discrete fibers. This can be accomplished in various ways. For example, the native collagen can be subjected to a preliminary treatment in a paper beating machine in much the same way as cellulose is treated to form a fibrous pulp. If desired, the beaten collagen can be dewatered, and stored prior to use in the present process. It will be understood that in preparing collagen fibers from animal hides, such as cattle hides, that the grain layer and the flesh layer are preferably separated from the corium, which is the collagen-containing layer.

In accordance with the present invention, an aqueous pulp of collagen fibers is heated at a substantially neutral pH. The pulp should be in the form of a soft pasty mass. In one preferred embodiment, discrete fibers of native collagen are mixed with sufficient water to form a doughy pulp containing from 10 to 25% solids by weight. Since the pulp is to be heated at a substantially neutral pH, there will normally be no need to add any acidic or basic reagents to the pulp.

Preferably, the doughy, substantially neutral pulp of fibrous collagen is heated at a temperature within the range from 40 to 65° C. It is desirable to control the heating step to solubilize a portion of the collagen without appreciably shrinking the collagen fibers. At the temperature where appreciable shrinkage begins to occur, as can be determined visually and by a standardized test procedure, the collagen in the fibers begins to melt and to be extracted into the solution as gelatin rather than as reconstitutable collagen. At temperatures above 62° C., this undesirable conversion may occur to some extent, and at temperatures above 65° C., it is almost certain to occur to an objectionably large extent. When the temperature of the heating is too low, the desired conversion to reconstitutable collagen proceeds too slowly. On the basis of present knowledge, it is believed that the optimum temperature of heating is within the range from 54 to 62° C. At temperatures within this range there is little fiber shrinkage and formation of gelatin. At the same time, however, the conversion of a portion of the fibrous collagen to solubilized but reconstitutable collagen is facilitated.

It is preferred to terminate the heating step while the major portion of the collagen remains in fibrous form. If the pH is below 5.0 or above 8.0, it is difficult to control the heating step, and it is therefore desirable to avoid pronounced acidic or basic conditions during the heating. Optimum results are believed to be achieved at a pH within the range from 5.5 to 7.0.

To achieve the benefits of the present invention, the heating should be continued until at least 5% by weight of the fibrous collagen in the pulp is transformed to

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solubilized collagen. Best results are believed to be obtained when from 8 to 15% by weight of the collagen is solubilized, although higher percentages up to 30% may be achieved under certain conditions. The relative proportions between the solubilized collagen and the collagen fibers can also be varied by adding additional fibers or native collagen to the pulp during or subsequent to the heating step.

In one preferred embodiment, the pulp will contain 12 to 18% solids and will be at a pH of approximately 6.0. This pulp is then heated at a temperature of 55 to 60° C. until 10 to 12% of the collagen has been solubilized. In this particular embodiment, the desired solubilization can usually be obtained in approximately one hour. It will be understood, of course, that the time of heating can be varied considerably, and that the time will usually vary inversely with the temperature. During the heating, the pulp can be observed to see whether the shrinkage of the fibers is being avoided, and samples can be taken and subjected to vacuum filtration to measure the percent of collagen which has been solubilized. The solubilized collagen will pass through the filter, which upon being separated from the water by drying, can be compared on a weight basis with the dried insoluble residue.

Following the heating step the doughy pulp is formed into the desired shape. This may be done by various procedures. For example, the pulp may be extruded to form sheets or filaments. In this procedure, the dough is forced under pressure through a die. In accordance with known procedures, if sheets are desired the die will provide a horizontally extending slit corresponding to the desired width of the sheet. For filaments, the die will provide one or more orifices corresponding in diameter to the diameter of the filaments. Upon being extruded, the dough can fall upon a moving conveyor belt which is timed to permit the continuity of the sheets or filaments to be maintained. By this procedure, uniform sheets or films of any desired thickness may be produced. The thickness will usually correspond to that of natural leather. The diameters of the filaments can also be varied as desired. For some purposes, it may be advantageous to form the collagen dough in a mold to produce solid or hollow bodies.

The forming or extrusion step is preferably carried out while the pulp is still at an elevated temperature. For example, temperatures of 35 to 55° are suitable, and particularly good results are obtained at a temperature of around 50° C. In this step, the temperature is not particularly critical providing the dough is sufficiently fluid to permit it to be satisfactorily formed by extrusion or other forming procedure.

Following the forming step, the sheets may be fixed or set by subjecting them to chilling. In this step, the temperature of the sheets should usually be reduced below 20° C. More specifically, temperatures in the range of 2 to 10° C. are suitable. The chilling may be accomplished in various ways, such as by passing the sheets over chilled rollers.

The formed collagen produced in the manner described above can be subjected to further processing steps in order to improve its appearance, strength, and other properties. For example, the sheets may be subjected to "needling." In this procedure, the porosity of the sheets is increased by pressing a die or roller providing a plurality of needles against the sheets. As described in co-pending application, Serial No. 141,956, filed October 2, 1961, entitled "Method of Increasing Strength of Formed Collagen," the formed and set collagen may be subjected to the action of a protein precipitating agent, such as an aqueous solution of ammonium sulfate. For example, the sheets or filaments may be passed through a bath of half saturated aqueous ammonium sulfate having a pH

of around 6.0. As an alternative, the ammonium sulfate solution may be injected into the formed collagen at spaced intervals. This procedure is believed to increase the strength of the formed collagen by encouraging the precipitation of the solubilized collagen. The sheets or filaments may also be subjected to other procedures which are well-known in the processing of leather. For example, the sheets may be tanned with various standard tanning solutions, such as an aqueous solution containing 1% chromic oxide and 2% sodium formate.

The following example provides a more specific illustration of the method of this invention. The starting material was native collagen fibers which had been prepared from the corium layer of fresh unlimed cattle skins by mechanically subdividing the corium into discrete fibers by means of a paper beater. The corium was treated in an aqueous slurry in the beater, and the resulting fibers were subsequently dewatered and dried to provide the starting material. In the experiment, 60 grams of the collagen fibers were dispersed in 240 cc. of water. The pH was 6.0 and the solids concentration was 20%. The temperature of the water was raised to 50° C. before the fiber was metered in. Heating was continued until a maximum of 60° was reached at which time blending was started. Blending was continued during the entire heating period of one hour. At the conclusion of the heating, the doughy pulp was formed into a sheet by a hand rolling procedure. The sheet was cold set at 4° C. for ten minutes, and then immersed in a bath of half saturated ammonium sulfate (pH 6.0). After one hour the sheet was examined and found to be exceedingly strong. The sheet was then tanned according to standard procedures, using a chrome tanning reagent.

While in the foregoing specification this invention has been described in relation to certain specific embodiment thereof and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

I claim:

1. In a method of preparing formed collagen, the steps comprising mixing discrete fibers of native collagen with water to form a doughy pulp, said pulp having a substantially neutral pH, heating said pulp at a temperature within the range from 40 to 65° C. to solubilize a portion of the collagen therein without appreciably shrinking said fibers, continuing said heating until at least 5% by weight of the collagen in said pulp has been solubilized while the major portion of the said collagen remains in fibrillar form, and thereafter forming said pulp.

2. In a method of preparing formed collagen, the steps comprising mixing discrete fibers of native collagen with water to form a doughy pulp, said pulp having a pH above 5.0 but below 8.0 and containing from 10 to 25% solids by weight, heating said pulp at a temperature within the range from 40 to 65° C. to solubilize a portion of the collagen therein without appreciably shrinking said fibers, continuing said heating until from 8 to 30% by

weight of the collagen in said pulp has been solubilized, and thereafter forming said pulp.

3. In a method of preparing formed collagen, the steps comprising mixing discrete fibers of native collagen with water to form a doughy pulp, said pulp having a pH of from 5.5 to 7.0 and containing from 10 to 25% solids by weight, heating said pulp at a temperature of from 54 to 62° C., continuing said heating until from 8 to 15% by weight of the collagen in said pulp has been solubilized while the major portion of the said collagen remains in fibrillar form, and thereafter forming said pulp.

4. In a method of preparing collagen sheets, the steps comprising heating an aqueous pulp of collagen fibers, said pulp having a substantially neutral pH and being in the form of a soft pasty mass, said heating steps being controlled to transform at least 5% by weight of the fibrous collagen in said pulp to solubilized collagen without appreciable shrinkage of the collagen fibers, terminating said heating step while the major portion of said collagen remains in fibrous form, extruding the heated pulp to a predetermined form, and chilling the formed collagen.

5. In a method of preparing formed collagen, the steps comprising heating an aqueous pulp of collagen fibers, said pulp having a pH above 5.0 but below 8.0 and being in the form of a soft pasty mass, said heating step being controlled to transform from 8 to 30% by weight of the fibrous collagen in said pulp to solubilized collagen without appreciable shrinkage of the collagen fibers, terminating said heating step while the major portion of said collagen remains in fibrous form, extruding the heated pulp to a predetermined form, and chilling the formed collagen.

6. In a method of preparing collagen sheets, the steps comprising heating an aqueous pulp of collagen fibers, said pulp having a pH of from 5.0 to 7.0 and being in the form of a soft pasty mass, said heating step being controlled to transform from 8 to 15% by weight of the fibrous collagen in said pulp to solubilized collagen without appreciable shrinkage of the collagen fibers, extruding the heated pulp to form sheets, and chilling said sheets.

7. In a method of preparing collagen sheets, the steps comprising heating an aqueous pulp of collagen fibers, said pulp having a pH of from 5.5 to 7.0 and being in the form of a soft pasty mass, said heating step being controlled to transform at least 8 to 15% by weight of the fibrous collagen in said pulp to solubilized collagen without appreciable shrinkage of the collagen fibers, said heating being carried out at a temperature of substantially from 54 to 62° C. and being terminated while the major portion of said collagen remains in fibrous form, extruding the heated pulp to form sheets, and chilling said sheets.

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