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BENZOIC ACID TREATMENT OF COLLAGEN FIBERS AND CHROME TANNAGE THEREOF

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This invention relates to the processing of collagen fibers to produce a formed leather. The method is particularly adapted for the production of formed collagen sheets where it is desired to chrome tan the collagen sheets. The chrome tanned collagen sheets produced by the method of this invention can be used as a substitute for chrome tanned leather in the manufacture of shoe uppers and for other purposes.

Leather, which consists of chemically modified collagen, is generally available only in the form of sheets of intact animal skin. Manufacturers of leather goods cut pieces of desired shape, size and quality from the sheets of skin and discard the remainder as scrap which is disposed of in relatively uneconomical ways. Differences in quality, thickness and shape of natural leather sheets further add to the difficulties and amount of scrap encountered by fabricators. It has long been recognized that it would be desirable to have methods available for dissolving collagen, the solubilized collagen being susceptible to reconstitution as uniform sheets of leather.

In the production of formed collagen it is desirable to utilize the starting material as completely as possible while obtaining a product which can be used as a substitute for natural leather. The extraction or solubilization of the collagen must be carefully controlled to avoid conversion to gelatin, which is irreversibly denatured, and cannot be repolymerized or reconstituted to the native-like fibrous structure found in leather. It has been found that aqueous solutions of organic acids such as acetic acid and citric acid can be used for the solubilization of collagen. Heretofore, however, it has been difficult to control the extraction, to avoid the formation of substantial quantities of gelatin which cannot be reconstituted. Citric acid is preferable in this respect to acetic acid, but citric acid suffers from the disadvantage that it is not compatible with chrome tanning agents.

It is therefore a principal object of the present invention to provide an improved process for the controlled extraction and solubilization of collagen. A more specific object is to provide a method of the character described which permits a sufficient quantity of the collagen to be converted to a solubilized, reconstitutable state so that the mixture of collagen fibers and solubilized collagen can be formed into sheets, while at the same time substantially avoiding the irreversible conversion of collagen to gelatin. Another object is to provide a method of preparing reconstitutable collagen which permits the collagen upon reconstitution to be subjected to chrome tanning. Further objects and advantages will be indicated in the following detailed specification.

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, 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, native collagen fibers are dispersed in an aqueous solution of benzoic acid, and the dispersion is heated to convert a portion of the fibrous collagen to solubilized, reconstitutable collagen. The acidity of the solution can be readily controlled because benzoic acid has a very limited solubility at the temperatures employed for the extraction. For example, at temperatures ranging from 30 to 65° C., which is the desirable temperature range for the extraction, a 2% concentration by weight of benzoic acid will produce a substantially saturated solution. While fully saturated solutions can be employed, best results are obtained by limiting the benzoic acid concentration to less than 2%. The desirable maximum concentration is believed to be around 1%. At least enough of the benzoic acid should be present so as to promote the solubilization. Preferably in excess of a .1% concentration of the benzoic acid is employed, although the extraction is promoted to some extent by concentrations as low as .05%.

One of the advantages of employing benzoic acid solutions is that relatively moderate temperatures can be used. As the temperature of a fibrous collagen is increased above 65° C. more and more gelatin is formed. Consequently, the temperature should be kept below 65° C. When employing benzoic acid solutions in accordance with the present invention, the extraction can be carried out at a temperature of about 45 to 55° C. while still converting a sufficient proportion of the collagen to solubilized, reconstitutable collagen.

The dispersion of the collagen in the benzoic acid solution is preferably heated until at least 5% by weight of the fibrous collagen is transformed to 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 be varied by adding additional fibers of native collagen to the dispersion either during or subsequent to the heating step.

In one preferred embodiment of the present invention, the dispersion contains from about 10 to 25% solids (fibrous collagen) by weight. To prepare a formable and reconstitutable collagen material in a single step, it is desirable to prepare the collagen dispersion in the form of a thick slurry. The desired condition of the dispersion is that of a doughy pulp. For example, from 15 to 20 parts by weight of collagen fiber may be mixed with from 80 to 85 parts of aqueous benzoic acid to obtain the desired doughy pulp.

In practicing the preferred embodiment of the present invention, the heating step will be terminated while the major portion of the collagen remains in fibrous form. For example, as indicated previously, from 70 to 95% of the collagen will be in its original fibrous form. Optimally, from 10 to 12% of the collagen is solubilized. This quantity has been found to be sufficient to act as a binder in the preparation of formed collagen sheets. It will be understood that the time of heating can be varied considerably, and that the time will usually vary inversely with the temperature. For example, at 50° C., and using a benzoic acid concentration of 0.25%, from 10 to 12% of the collagen can be solubilized with a heating time of only 15 to 20 minutes. Shrinkage of the collagen fibers should be avoided, since this indicates that the collagen is being converted to gelatin rather than to solubilized, reconstitutable collagen. During the heating, the pulp can be observed to see whether shrinkage of the fibers is being avoided, and samples can be taken and subjected to vacuum filtration to measure the percentage 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 my copending 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.

After the collagen has been formed and reconstituted, the sheets or filaments may be tanned with various standard tanning solutions. The formed and reconstituted collagen is particularly adapted for chrome tanning. Not only is the benzoic acid compatible with chrome tanning reagents, but where the collagen fibers have been treated with benzoic acid solutions in accordance with the present invention, the susceptibility of the fibers to chrome tanning is materially increased. It has been found by electron microscopic examination of the benzoic acid treated collagen that the acid opens segments along the fibers, thereby producing reactive sites. The presence of these reactive sites promotes the chrome tanning reaction. For achieving rapid penetration of the collagen sheets and faster fixation of the chrome, it is desirable to employ a chrome tanning reagent containing sodium formate in addition to chromic oxide. For example, an aqueous solution containing 1% chromic oxide and 2% sodium formate is particularly suitable.

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, the dried fiber was dispersed in 0.25% benzoic acid at 50° C. for 15 minutes, while stirring vigorously and keeping the solids content at approximately 20%. After mixing, collagen sheets were rolled to a thickness of 6 mm. while the temperature was maintained at 50° C. The sheets were transported to the cold room (4° C.) and remained there for 30 minutes, after which they were precipitated in a sat./2 $(NH_4)_2SO_4$ bath that was adjusted to pH 8.1 with NH_4OH. After precipitation and reconstitution was complete (about 1 hour) the sheets were washed in running tap water. A strip was removed and tested for thermal shrinkage in a Theis shrink meter, but broke at 62° C. After washing for 2 hours the sheets were exposed to an aqueous chrome tanning solution

(1% Cr_2O_3+2% NaCOOH)

At regular intervals strips of collagen were removed from the tanning bath and shrinkage measurements made. These results are tabulated below.

Effect of Shrinkage Temperature on Chrome Uptake

Exposure in hours:	T_s, ° C.
1	72.5
2	78.5
3	80.0

Exhaustive washing of the sheet before tanning, did not effect the chrome uptake or shrinkage temperature significantly. The salt that is formed during neutralization in the sheets apparently acts as a de-swelling agent during the tanning. The shrinkage temperature can be raised if the collagen is removed from the tanning bath and covered to prevent surface drying. This enhances fixation of the chromium and subsequently will raise the shrinkage temperature.

Electron microscopic examination of the benzoic acid treated collagen revealed a very interesting phenomenon. The acid opened segments along the fiber, thus producing reactive sites which promotes the chrome tanning reaction.

While in the foregoing specification this invention has been described in relation to certain specific embodiments 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 the processing of collagen fibers to produce a formed leather, the steps comprising dispersing native collagen fibers in an aqueous solution of benzoic acid, said solution having a benzoic acid concentration of about .1 to 1% by weight, and heating the dispersion at a temperature within the range of from 30 to 65° C., said heating being continued until at least 5% by weight of the collagen in said dispersion has been converted to reconstitutable, solubilized collagen.

2. In the processing of collagen fibers to produce a formed leather, the steps comprising dispersing native collagen fibers in an aqueous solution of benzoic acid, said solution having a benzoic acid concentration of about .1 to 1% by weight, and heating the dispersion at a temperature of about 45 to 55° C., said heating being continued until at least 8% by weight of the collagen

in said dispersion has been converted to solubilized, reconstitutable collagen.

3. In the processing of collagen fibers to produce a formed leather, the steps comprising mixing discrete fibers of native collagen with an aqueous solution of benzoic acid to form a doughy pulp, said solution having a benzoic acid concentration of about .1 to 1% by weight and said pulp containing from 10 to 25% collagen solids by weight, heating said pulp at a temperature of about 45 to 55° C., said heating being continued until from about 8 to 15% of the collagen is solubilized, and thereafter forming said pulp.

4. In the processing of collagen fibers to produce a formed leather, the steps comprising mixing discrete fibers of native collagen with an aqueous solution of benzoic acid to form a doughy pulp, said pulp containing from 10 to 25% collagen solids by weight, heating said pulp at a temperature within the range from 30 to 65° C., said heating being continued until from about 8 to 15% of the collagen is solubilized, forming said pulp into sheets, reconstituting the solubilized collagen

in said sheets, and subjecting said sheets to chrome tanning.

5. The method steps of claim 4 in which said benzoic acid solution has a concentration of from .1 to 1% benzoic acid by weight, and in which said dispersion is heated at a temperature of about 45 to 55° C.

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