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SHAPED ARTICLE AND METHOD OF
PRODUCING IT

Arthur Cresswell, Stamford, Conn., assignor to
American Cyanamid Company, New York, N. Y.,
a corporation of Maine

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The present invention relates to filaments, threads, strands and tapes, hereinafter sometimes referred to as "shapes" or "strands." The invention further relates to such shaped articles consisting essentially of regenerated collagen and to methods of producing them.

The invention is particularly concerned with the manufacture of such strands from collagen or collagenous material.

The shapes produced by the present invention are particularly useful as surgical sutures or ligatures and have a decided advantage over those articles normally produced from intestinal material known as "catgut." The present collagenous shapes may be produced in unlimited lengths, are uniform throughout their length as to size, strength, toughness, and capacity for indirect or heat sterilization. Any desired degree of tannage may be given such sutures or ligatures in the usual variety of tanning baths.

Collagen is a protein which is an ingredient of the hide, skin, fasciata and muscles of vertebrates and occurs therein as fibrous matter, along with a multitude of other substances such as hair, elastin and other insolubles from which the collagen must be separated before it can be successfully used according to the present invention.

Collagen is itself insoluble in water but it may, upon suitable treatment in water and at an elevated temperature, be converted to gelatin. While gelatin and collagen are both protein, yet they are dissimilar and are not equivalents. It is well known that gelatin is soluble in water which is not true of collagen.

Throughout the present specification and claims, where the words "collagen" or "collagenous material" are used, it is to be understood that the material thereby designated is to be completely differentiated from gelatin as the two materials are not at all interchangeable in carrying out the purposes of the invention.

Broadly speaking, the invention contemplates the extrusion of a collagen solution through a small orifice followed by coagulation of the extruded filament. Such threads may be made of any desired size or shape and either coagulated or cohered in such shape or spun, twisted or woven together in multi-filament form for larger threads or shapes. Such strands and tapes, due to their manner of manufacture, may be produced in unlimited lengths, the dimensions of which are remarkably uniform throughout their length.

Such strands may be tanned by the usual methods employed in the tannage of leather, and sutures prepared therefrom may be made in vary-

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ing degrees of absorbability by living tissue, all as is well known in the suture art.

Animal hides or skins are, by and large, the most readily available source of collagen. It is desirable in using this source of material that unlimited hides be chosen. These may be fresh or green-salted calf skin, kip skin or other hides which are comparatively low in elastin content. Kip skin is preferred because the collagen therefrom is of an optimum viscosity as compared to that of calf skin. These are fleshed and unhaired down to the clean corium which is that lamination of the animal hide containing the greatest proportion of collagen. If green-salted hides are used, the hides should be soaked before this treatment and also allowed to remain in the soaking liquid after cleaning until substantially salt free.

After cutting the corium into strips or small pieces for convenience in handling, the corium is covered with a dilute solution of an organic acid preferably, though not necessarily, in the pH range of from 2 to 4. Any organic acid is satisfactory although from 0.05 to 0.10 N formic acid or 0.5 to 1.0 N acetic acid are preferred. Any other concentration of other organic acids may be used.

The corium is thus allowed to swell for from sixteen to twenty-four hours in the acid solution at temperatures between 10 and 30° C. In this swelling, the hide imbibes from one to three times its own weight of liquid but by maintaining the temperature at this point below 30° C., gelatin forming conditions are definitely avoided.

Following the swelling, the excess liquid is drained off and the swollen corium mechanically disintegrated, for example, by a meat grinder, shredder or other form of sub-dividing mechanism which will break down the collagen fibers to the point where dissolution will be facilitated. In the mechanical disintegration step, heat may be developed due to friction and it is, therefore, important that the necessary steps be taken to maintain the material during this operation at temperatures below 30° C.

At this stage and if the mechanical disintegration has been fine enough, practically all of the collagen will have gone into solution. Where this collagen solution is highly concentrated, it will gel at 35° C. or below. Therefore, to separate the dissolved collagen from the insolubles, it may be desirable to warm it slightly until fluidity has been reached. This will certainly be at a temperature no higher than 60° C. While warming to this temperature, if mechanical agitation is carried on, any last traces of undissolved collagen will dissolve and the whole may then be centri-

fused and filtered to remove fibers, elastin, hair fragments and other insoluble matter. The filtrate will be a clear heavily concentrated solution of collagen.

While the preferred source of collagen is the corium as this involves handling a material of maximum collagen content with minimum insolubles, yet as a matter of fact, due to the distribution of collagen throughout the animal hide, it may be desirable to disintegrate the entire hide followed by collagen solution in dilute organic acid and the separation of the insolubles. Such a process while varying in the last step in the removal of an excessive amount of insolubles, does extract substantially all the collagen available.

The concentration of the collagen in its solution may be adjusted to a desired content appropriate for spinning by the addition of a further amount of the dilute organic acid solution such as that used for swelling and solution. It is preferred that the spinning solution contain from 5 to 15% collagen although solutions of lower or higher collagen concentration may be used.

Before spinning, it is desirable to deaerate in order that there may be no thread interruption due to the passage of air bubbles through the jet orifice. Therefore, by maintaining the collagen solution at a temperature slightly above that at which it will gel and applying a vacuum or partial vacuum, the air contained in the solution may be removed. The warm solution may then be pumped by any suitable means to a spinnerette, that used in the rayon industry for this purpose being eminently satisfactory, and then immersed in a coagulating bath.

This type of extrusion, that is, from solution, is to be distinguished from the method such as extrusion of a pulp of swollen collagen, not in solution and skin containing insolubles. Such a method is distinctly disadvantageous as large sized orifices are required and the filaments resulting therefrom are non-uniform as to size, strength and the like due to the non-uniformity of collagen content.

Strong salt solutions have been found satisfactory as coagulating baths, such as a 35% to saturated solution of ammonium sulfate with sufficient free ammonia to maintain a pH of 7.8, which is an isoelectric point of collagen. The free ammonia is useful for the purpose of neutralizing the organic acid introduced by the spinning solution. Another satisfactory bath is one containing 25% by weight of magnesium sulfate, buffered with triethanolamine to a pH of 7.8. Regardless of the particular coagulant used, it is highly desirable that the bath be maintained at from 20° to 30° C.

It has been found that collagen solutions of the concentrations above mentioned may be extruded into a coagulating bath as above described from spinnerettes with orifices of from 50 microns to 1 mm., but preferably from 75 to 250 microns in diameter. The filament or thread may be passed over a plurality of revolving wheels commonly called godets which have increasing peripheral speeds so that a stretch is imparted to the filament or thread. Following this, the filament or thread may be taken up by a revolving spool which may or may not impart a further stretch. Satisfactory filaments have been spun as above from a spinnerette with orifices measuring 110 microns in diameter to a finished filament at the rate of 80 meters a minute. At this rate, the jetted material remains in contact with the coagulating bath for less than one second.

Adhering coagulants may then be washed from the filament or thread by passing the same in contact with water at a temperature below that at which softening will occur such as less than 20° C. The washed filament or thread may then be dried in air heated to from room temperature to 60° C. However, the lower the temperature the less damage may occur to the treated material.

Where a multi-filament strand is desired, a multi-hole spinnerette may be used. When spinning onto spools, the resulting strand is washed, dried and then twisted. It is also possible to twist the strand while spinning by collecting the strand in a centrifugal pot as commonly practiced in viscose rayon pot spinning.

Single or multi-filament strands may be tanned in baths commonly used for the tannage of surgical sutures from gut to determine the degree of body absorption which would be characteristic of the finished article.

It has been noted that when the wet filaments from the coagulating bath are twisted together to form a strand and permitted to remain in contact with each other without drying, a coalescence or cohesive action occurs which tends to make a unitary strand out of the filaments. Thus, if a large single coherent strand is desired to be made from a number of smaller filaments, it is only necessary to spin the desired number of filaments with the coagulating bath, arrange them in contact with each other and keep them wet until coalescence occurs. Thus any size or shape of strand or tape may be secured.

By using suitable godets, any desirable degree of stretch may be imparted to the spin filaments. Of course, the degree of stretch will determine in large measure the degree of fiber orientation in the finished filament, thread or strand. Reasonably satisfactory orientation has been obtained through stretching a filament to an extent equal to 700% by using a combination of godets having increasing peripheral speeds.

This application is a continuation-in-part of copending application Serial No. 527,339, filed March 20, 1944, now abandoned.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and restricted solely by the scope of the appended claims.

I claim:

1. A shaped article consisting essentially of regenerated collagen free from fibers and any other material insoluble in a dilute aqueous solution of an organic acid.

2. A shaped article consisting essentially of regenerated collagen free from fibers and any other material insoluble in a dilute aqueous solution of an organic acid in the range of pH 2 to 4.

3. A shaped article consisting essentially of coalesced filaments of regenerated collagen free from fibers and any other material insoluble in a dilute aqueous solution of an organic acid.

4. A method of making a regenerated collagenous shape which includes the steps of dissolving collagen from collagenous material in a dilute aqueous solution of an organic acid removing all insolubles including fibers from said solution while maintaining the temperature of said solution above its gelling point but below a temperature at which substantial conversion to gelatin occurs, extruding the thus heated solution into a

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coagulating bath and removing the coagulated shape therefrom.

5. The method of claim 4 in which the concentration of collagen in the extrusion solution is from 5% to 15%.

6. A method of making a regenerated collagenous shape which includes dissolving collagen from collagenous material by soaking and swelling said collagenous material in an aqueous solution of an organic acid at a pH of substantially 2-4, mechanically disintegrating said swollen collagenous material in said dilute aqueous solution of an organic acid, removing all insolubles including fibers from said solution while maintaining the temperature of said solution above its gelling point but below a temperature at which substantial conversion to gelatin occurs, extruding the thus heated solution into a coagulating bath and removing the coagulated shape therefrom.

7. The method of claim 6 in which the coagulated shape is stretched after extrusion to 700%.

8. The method of claim 6 in which the collagenous material is animal corium.

9. The method of claim 6 in which the collagenous material is corium from kip skin.

10. A method of making a regenerated collagenous strand which includes dissolving collagen from collagenous material by soaking and swelling said collagenous material in an aqueous solution of an organic acid at a pH of substantially 2-4, mechanically disintegrating said swollen collagenous material in said aqueous solution of an organic acid, removing all insolubles including fibers from said solution while maintaining the temperature of said solution in the range of substantially 35°-50° C., extruding the thus heated solution into a coagulating bath and removing the coagulated strand therefrom.

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11. The method of claim 10 in which the collagen solution is deaerated before spinning.

12. A method of making a collagen multi-filament suture strand which comprises extruding a fiber-free, aqueous organic acid solution of collagen maintained at a temperature above its gelling point but below a temperature at which substantial conversion to gelatin occurs, through a multi-holed spinnerette into a coagulating bath, removing the thus spun filaments from the bath and washing and drying said filaments while held apart from each other and then twisting the filaments into a strand.

13. The method of claim 12 in which the collagen solution is dissolved in an aqueous organic acid solution having a pH of substantially 2-4, the concentration of collagen being 5-15% and the solution being deaerated before spinning.

ARTHUR CRESSWELL.

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