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METHOD OF MANUFACTURING SYNTHETIC SUTURES AND THE LIKE

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This invention relates to improvements in methods for manufacturing synthetic suture material and similar products comprising an integral mass of fibers which occur in animal parts, as for instance, animal tendons or sinews, such as beef tendons.

One method of producing filaments or threads comprising such animal fibers involves the steps of suspending the fibers, whether in their elementary condition or after cutting thereof to selectively controlled lengths, as described in the pending application of Hall, Hollihan and Morehead, Serial No. 630,686, filed November 24, 1945, in an organic or inorganic acid, extruding the suspension into a coagulating and/or dehydrating medium, raising the pH on the thus formed filaments by treating them in an aqueous buffering system and thereafter drying the buffered filaments simultaneously with stretching thereof.

Stretching of the buffered filaments concomitantly with their drying is an essential step of the process, and I have found that in order to obtain final filaments or threads having the most desirable properties as respects tenacity and extensibility, it is necessary to stretch the filaments about 14 to 16% during the drying step, which is equivalent to subjecting the filament bundle to a tensioning load which varies in accordance with the size of the filament, from about 70 gms. for a 200 denier filament to about 200 to 250 gms. for a 1000 denier filament, as measured by any standard strength-testing device. I have discovered, further, that in order to produce filaments capable of accepting the required stretch during drying without rupture at the weaker portions which inevitably occur along the filament length, it is important to avoid excessive swelling of the filaments when the pH on the acidic filaments is raised by treating them with a buffering solution. Thus, excessive swelling of the filaments in the buffer system has been found to reduce the capacity of the filaments to withstand, at all portions along their length, the stresses and strains developed therein when they are stretched during drying.

The acidic filaments invariably swell when they are subjected to the action of alkaline solutions, but I have found that if the extent of the swelling is controlled so that the buffered filaments are swollen to about twice their normal (dry) size, the filaments accept a stretch of 14 to 16% during drying without rupture, and the final filaments are characterized by high tensile strengths and extensibilities.

The object of the present invention, therefore,

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is to provide a method for raising the pH on the acidic filaments while controlling the extent of swelling of the filaments during buffering thereof.

This and other objects are achieved by treating the acidic filaments with an aqueous alkaline solution which, under the conditions of treatment, has a limited swelling action on the filaments such that the buffered filaments are swollen to only about twice their normal (dry) size after withdrawal thereof from the buffering medium.

One buffer system which has been suggested for use in treating the acidic filaments comprises an aqueous solution of ammonium hydroxide and ammonium chloride. It has been found that all solutions of ammonium hydroxide and ammonium chloride are not satisfactory for use in treating the acidic filaments from the point of view of controlled swelling of the filaments and ability of the buffered filaments to withstand stretching to the required 14 to 16% without rupture during drying thereof. I have found that both dilute and highly concentrated solutions of the ammonium compounds have a pronounced swelling action on the filaments and that the filaments thus swollen have a markedly decreased capacity to undergo stretching without rupture. I have discovered, however, that there is an optimum concentration of the ammonium hydroxide and ammonium chloride in the buffering solutions at which the pH on the filaments is raised while at the same time the filaments are swollen only to a minimum controlled extent which does not prevent their accepting a stretch of about 14 to 16% without rupture. Thus I have determined that when the dry acidic filaments are immersed in water to which has been added about 6 to 6.5 cc. of concentrated ammonium hydroxide and about 1 to 1.2 grams of ammonium chloride, per liter, for about eight minutes the filaments leaving the buffering medium are swollen to a size which is only about twice their normal (dry) size. The term "concentrated ammonium hydroxide" is used here in its usual sense to define an aqueous solution containing approximately 28% NH_3 by weight and of sp. gr. 0.90. (Handbook of Chemistry, Lange, p. 1165, 1944; Talbot's Quantitative Chemical Analysis, 1939, p. 284; Qualitative Chemical Analysis, Prescott and Johnson, p. 618). In contrast to this comparatively slight swelling of the filaments when they are buffered in aqueous media containing the ammonium compounds in the optimum selectively con-

trolled concentrations in accordance with this invention, the extent of swelling of the filaments increases markedly when the ammonium hydroxide and ammonium chloride are added to the water in conecntrations either materially lower or higher than about 6 to 6.5 cc. and 1 to 1.2 grams, respectively, per liter. When the acidic filaments were immersed in buffer systems consisting of aqueous solutions of ammonium hydroxide and ammonium chloride in concentrations ranging from about 0.63 cc. to 0.107 gram up to about 6.3 cc. and 1.07 grams, respectively, the filaments after only a few minutes immersion in the solution were swollen to a size which was about three times their normal (dry) size, while at concentrations of the ammonium hydroxide and ammonium chloride appreciably greater than about 6.3 cc. and 1.07 grams, respectively, the filaments were swollen to a size as much as five times normal size.

When the filaments comprising the integral mass of fibers occurring in animal parts are buffered by treatment with the buffering systems comprising dilute or highly concentrated solutions of ammonium hydroxide and ammonium chloride, and swollen to the extent described above, that is from three to more than five times normal (dry) size, the filaments, regardless of size, cannot be subjected to a tensioning load corresponding to the tension required to impart a stretch of from 14 to 16% thereto without rupturing very readily at their weaker portions. In order to avoid frequent rupture of the filaments and permit continuous handling thereof, it was necessary to subject them to a lower stretch equivalent to a lower tensioning load, which resulted in final filaments having correspondingly reduced tenactity and extensibility.

On the other hand, filaments which had been buffered by immersion in an aqueous medium containing about 6.3 cc. of ammonium hydroxide and about 1.07 gms. of ammonium chloride, per liter of water, could be stretched from about 14 to 16% without rupture, and in all cases were actually capable of withstanding a tensioning load considerably greater than that required to impart the desired stretch thereto. For example, the tension required to impart a stretch of 14 to 16% to a 1000 denier filament corresponds to a tensioning load of only about 200 to 250 gms., whereas the filaments were found capable of withstanding a tensioning load as high as 500 grams. The ability of the comparatively slightly swollen buffered filaments to withstand tensioning loads higher than are required to impart the desired stretch thereto provides, in effect a safety factor which guards against rupture of the filaments at their weaker portions which are less well-adapted, inherently, to withstand the stretching stresses and strains. The filaments buffered in accordance with this invention can be dried and simultaneously stretched practically to the rupture point without actually rupturing, and the final dried and stretched filaments are characterized by high tensile strengths and extensibilities.

The acidic filaments or threads comprising the integral mass of animal fibers may be manufactured in any suitable manner. For example, the starting material, which may be a commercially practicable animal sinew or tendon, as a beef tendon, may be subjected to a mechanical teasing operation to separate the fibers therefrom the conditions of separation being such that the fiber structure is not impaired, and the fibers with or without cutting to obtain shorter fibers of controlled length, may be suspended in a suitable acid or acidic substance to obtain a suspension of the fibers in the desired concentration. The fibers may be suspended in such substances as aqueous solutions of lactic, formic, phosphoric, malonic or hydrochloric acid, potassium or sodium bisulfate, potassium bioxalate or potassium tetraoxalate. The suspensions may then be extruded into a coagulating and/or dehydrating bath consisting of acetone or a similar liquid of low viscosity. Alternatively, the starting material, such as beef tendon, may be hardened by treatment with dry ice and then sliced to reduce the length of the fibers, care being taken to maintain the fiber structure. The slices or shavings thus obtained may then be suspended in the acid or acidic substance and the suspension extruded into acetone or the like to form continuous filaments. However the acidic filaments are obtained, in accordance with this invention, after thorough drying of the filaments leaving the coagulating bath, the pH on the filaments is adjusted to the alkaline side by treatment thereof with an alkaline solution to which has been added about 6 to 6.5 and preferably about 6.3 cc. concentrated ammonium hydroxide and from 1 to 1.2 and preferably about 1.07 grams of ammonium chloride per liter of water, and which exerts only a controlled limited swelling action on the filaments. Usually the treating period is of short duration of the order of from 5 to 10 minutes. The extent to which the filaments are swollen by the aqueous alkaline solution is not appreciably influenced by the temperature of the solution and temperatures within a practical working range may be used. Preferably, the temperature of the solution is maintained at about 23 to 28° C.

After immersion in or thorough washing with the buffering solution, the filaments, which are in only relatively slightly swollen condition, may be dried and simultaneously stretched by passing them through a drying zone such as a heated tube or the like, between a pair of godets rotating at controlled relative speeds such as to stretch the filaments from about 14 to 16%. The filaments can be stretched without rupturing and can be continuously advanced over the godets and passed from the second godet to a take-up device or to another treating stage, such as a chroming or tanning stage, as the case may be.

It will be understood that modifications may be made in the procedure specifically exemplified without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. Method for the manufacture of threads and the like comprising an integral mass of fibers which occur in animal sinews, tendons, and the like, which comprises suspending the fibers in an aqueous acid solution, extruding the suspension into a non-basic coagulating and dehydrating medium to form acidic filaments, withdrawing and drying the thus formed acidic filaments and raising the pH on the filaments while swelling the fibers to approximately twice their normal dry size by treating them with water to which has been added from about 6 to 6.5 cc. of concentrated ammonium hydroxide and from about 1 to 1.2 grams of ammonium chloride, per liter, and thereafter drying the filaments while stretching them from about 14 to 16%.

2. Method for the manufacture of threads and the like comprising an integral mass of fibers which occur in animal sinews, tendons, and the

like, which comprises suspending the fibers in an aqueous acid solution, extruding the suspension into a non-basic coagulating and dehydrating medium to form acidic filaments, withdrawing and drying the thus formed acidic filaments and raising the pH on the filaments while swelling the fibers to approximately twice their normal dry size by treating them with water to which has been added about 6.3 cc. of concentrated ammonium hydroxide and about 1.07 grams of ammonium chloride, per liter, and thereafter drying the filaments while stretching them from 14 to 16%.

3. Method for the manufacture of threads and the like comprising an integral mass of fibers which occur in animal sinews, tendons, and the like, which comprises suspending the fibers in an aqueous acid solution, extruding the suspension into a non-basic coagulating and dehydrating medium consisting of an organic solvent, to form acidic filaments, withdrawing and drying the thus formed acidic filaments and raising the pH on the filaments, while swelling the filaments to approximately twice their normal dry size, by treating them with water to which has been added from about 6 to 6.5 cc. of concentrated ammonium hydroxide and from about 1 to 1.2 grams of ammonium chloride, per liter, and thereafter drying the filaments while stretching them from about 14 to 16%.

4. Method for the manufacture of threads and the like comprising an integral mass of fibers which occur in animal sinews, tendons, and the like, which comprises suspending the fibers in an aqueous acid solution, extruding the suspension into a non-basic coagulating and dehydrating medium consisting of acetone to form acidic filaments, withdrawing and drying the thus formed acidic filaments and raising the pH on the filaments, while swelling the filaments to approximately twice their normal dry size, by treating them with water to which has been added from about 6 to 6.5 cc. of concentrated ammonium hydroxide and from about 1 to 1.2 grams of ammonium chloride, per liter, and thereafter drying the filaments while stretching them from about 14 to 16%.

5. Method for the manufacture of threads and the like comprising an integral mass of fibers which occur in animal sinews, tendons, and the like, which comprises suspending the fibers in an aqueous acid solution, extruding the suspension into a non-basic coagulating and dehydrating medium consisting of acetone to form acidic filaments, withdrawing and drying the thus formed acidic filaments and raising the pH on the filaments, while swelling the filaments to approximately twice their normal dry size, by treating them with water to which has been added about 6.3 cc. of concentrated ammonium hydroxide and about 1.07 grams of ammonium chloride, per liter, and thereafter drying the filaments while stretching them from about 14 to 16%.

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