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METHOD OF TREATING POLYVINYL ALCOHOL FILAMENTS AND TREATED FILAMENT

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This invention relates to filaments of polyvinyl alcohol and to an improved process of treating them.

Although polyvinyl alcohol filaments, particularly of the mono-filament type are susceptible of many uses, emphasis herein has been placed on their use for suturing because of the exacting requirements involved.

Because of its inertness to body reaction, it has been proposed heretofore to use polyvinyl alcohol filaments as a substitute for catgut and silk because sutures made of such materials are often accompanied by stitch abscesses and tissue inflammation. However, polyvinyl alcohol sutures made in accordance with such prior processes are unsatisfactory because of their inability to meet the strength requirements of a good suture, or to retain their strength in the presence of the tissue fluids.

A prerequisite for a good suture is high wet strength. High wet strength is not synonymous with water resistance but on the contrary refers to the strength of the filament after it has had an opportunity of soaking up water. The filaments should become pliable in water without excessive elongation, shortening, or change in thickness. Furthermore, after soaking in water or in the body fluids for one or several days, the filaments should possess adequate strength to resist any strain that body tissues may impose and should not become elastic so as to cause constriction or continuing strain on the tissues. By way of comparison, catgut of good quality exhibits a wet to dry strength ratio of .5 which is adequate. On the other hand, a filament made of polyvinyl alcohol by prior art methods exhibits a wet to dry strength ratio of .2 or less. Such a ratio of wet to dry strength is entirely inadequate for suture use.

In accordance with the present invention, polyvinyl alcohol filaments are provided having a relatively high wet to dry strength ratio, i. e., at least as high, if not higher, than the corresponding ratio for catgut, and having a tensile strength substantially in excess of that exhibited by catgut whether wet or dry. For instance, catgut of good quality must possess a tensile strength in the neighborhood of 2 grams per denier to satisfy U. S. P. standards. Polyvinyl alcohol filaments made by the improved process exhibit a tensile strength as high as 5 grams per denier when dry and 3 grams per denier when wet, which is a wet to dry strength ratio of .6. When it is considered that, for material of the specific gravity of polyvinyl alcohol, 1 gram per denier is equivalent to

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a tensile strength of 18,000 pounds per square inch, a filament possessing a tensile strength of 90,000 pounds per square inch when dry and 54,000 pounds per square inch when wet (i. e., after soaking at least twenty-four hours in water) has advantages which are manifest.

In accordance with the present invention, it has been found possible to control at will the wet strength of polyvinyl alcohol filaments through the medium of a heat treating process, the critical factor of which is the moisture content of the polyvinyl alcohol during the period of heating. To be more specific, the filament is first extruded, properly conditioned for stretching, and then stretched to give proper orientation of the molecules. Thereafter, the stretched filament is adjusted to a given moisture content and then heated under conditions which maintain the moisture content substantially intact or at least prevent the escape of too much water. With this procedure, filaments may be produced having high tensile strength and a high wet to dry strength ratio, the tensile strength and wet to dry strength ratio depending upon the moisture entrapped in the filaments during the heat conditioning step.

The improved process contemplates the preparation of a spin mix of polyvinyl alcohol which is suitable for extrusion through a spinneret. Polyvinyl alcohol of medium or high viscosity resulting from a medium or high degree of polymerization is preferred, although with careful handling polyvinyl alcohol of a lower degree of polymerization may be used. Generally speaking, the strength of the finished filament is greater the greater the degree of polymerization or viscosity of the polyvinyl alcohol, but this factor is by no means as important as the subsequent process steps. Polyvinyl alcohol as free as possible from all impurities is preferred.

Polyvinyl alcohol is prepared commercially by the saponification of the corresponding acetate. It is supplied in two grades, A and B, the former containing about twenty-five percent of the acetate, and the latter about one or two percent. Where the percentage of acetate is large, it preferably should be removed if suitable filaments are to be obtained. The commercial grade B polyvinyl alcohol containing the lower percentage of acetate may be used in the process, but even this is improved by the removal of the acetate present.

One method of treating the polyvinyl alcohol to remove the small amount of acetate that may be present as well as other possible contaminat-

ing agents which might be objectionable in a suture, comprises saponifying the polyvinyl acetate in the polyvinyl alcohol with alcoholic potash followed by washing with hot alcohol. This procedure serves to render both commercial types of polyvinyl alcohol suitable for spinning. Specifically and merely by way of example, approximately 225 grams of polyvinyl alcohol containing a small amount of acetate is covered with approximately 900 cc. of ethyl alcohol containing about 3 grams of potassium hydroxide. The mixture is agitated or stirred while heating under a reflux condenser for about two hours after which the alcoholic potash is filtered off and fresh warm alcohol added to the solids. The mixture is just neutralized with acetic acid and filtered again. The filter cake is thoroughly washed with warm alcohol, recovered and dried in air at room temperature. If the commercial grade of polyvinyl alcohol containing the higher percentage of acetate is to be treated, the quantity of potassium hydroxide used is increased accordingly.

The purified polyvinyl alcohol in finely divided form has added to it a proportion of water in amount suitable to yield a mixture which is a firm elastic solid at room temperature but which softens sufficiently for extrusion at about 100° C. In this connection it might be stated that polyvinyl alcohol hydrolyzed with alcoholic potash as described above is definitely superior to the commercial product because it imbibes the water more slowly and does not lump, thus facilitating a more uniform mixing of the water throughout the mass of the spin mix. A spin mix prepared from medium viscosity polyvinyl alcohol preferably should contain about 50% polyvinyl alcohol and 50% water. A mix prepared from the high viscosity polyvinyl alcohol is more easily extruded if the proportion of water in the mix is increased to about 55%.

The spin mix is preferably prepared by atomizing the water into a weighed quantity of polyvinyl alcohol, keeping the latter which is in the form of a finely divided solid or powder in motion by thorough stirring. With the water added, the mix is in a moist crumbly solid state. For good filaments the moisture content should be uniform throughout the particles of polyvinyl alcohol and this may be insured by suitable aging, as by sealing the solid mix in a container overnight or longer if necessary. After aging and while still in the sealed container, the mixture is autoclaved for about two hours at the temperature of steam at 12 to 15 pounds gauge pressure. Autoclaving is resorted to merely to maintain a proper temperature and prevent local overheating. Any other method of heating giving equivalent results would suffice, such as immersing the sealed container which contains the spin mix in an oil bath heated to the proper temperature. This heating step melts the mixture and acts to expel from the mix such air as may have been entrapped therein, the air appearing in the form of a layer of foam above the clear bulk. If desired, this operation could be assisted by partially evacuating the sealed container before heating.

As hereinafter set forth, it may be desirable to incorporate in the mix certain other ingredients to impart specific properties to the finished filaments. Such ingredients may be introduced into the spin mix either in solution with the water which is added or they may be mixed dry with the polyvinyl alcohol prior to the addition of water, depending upon their solubility behavior.

When the spin mix is ready for extrusion, it is placed in a container provided with a spinneret nozzle of the desired cross section. For a spin mix of the character previously alluded to, it has been found that best results are obtained by maintaining the polyvinyl alcohol at a temperature of 90° C. during the spinning operation, and heating the spinneret by suitable jacketing, to raise the filament as it is extruded to a temperature of about 100° C. These temperatures are given merely by way of example, and may be somewhat higher or lower depending upon the viscosity of the polyvinyl alcohol spin mix.

The polyvinyl alcohol mix is extruded into air at room temperature. It leaves the spinneret in the form of a filament which is preferably deposited on a roller or belt driven so as to conduct the filament away from the spinneret at a suitable rate of speed. This speed in conjunction with the diameter or dimensions of the spinneret orifice determines the diameter or dimensions of the filament at this stage of the process. For instance, if the desired size of the filament corresponds to the size of the spinneret orifice, the traveling belt or roller would be operated to conduct the filament away from the spinneret at the rate the filament is extruded. However, because the size of the spinneret affects the ease of spinning, it is preferred to use an orifice having an area corresponding to a circle 1 mm. in diameter and increase the surface speed of the roller or belt above the speed at which the filament is extruded so as to attenuate the filament by traction to the desired size. Where the size of the filament is regulated by drawing as just described, it may be found helpful to incorporate in the spinning equipment both a tension indicator and a gauge to indicate continuously the filament size.

After extrusion the polyvinyl filament is processed in a manner to increase its tensile strength and pliability. This is accomplished by stretching the filament while plastic to effect orientation of its molecules or aggregates while under strain but the plasticity must not be so great as to permit the molecules or aggregates to move past each other, thereby relieving the strain or permitting them to return to a random arrangement. The greater the orientation, the greater the increase in filament strength, but this introduces the problem of elongating the filament to a degree necessary to produce maximum orientation without breakage.

According to this invention the polyvinyl alcohol filaments are elongated under conditions adapted to produce maximum tensile strength but which for all practical purposes will reduce breakage to a minimum. It has been found that the ultimate strength of a polyvinyl alcohol filament at the tube of stretching depends upon the materials in the polyvinyl alcohol and the degree of moisture present during the stretching operation. The degree to which the filaments should be elongated may be determined from a chart which can be prepared for the type of spin mix under consideration. While such a curve may be prepared by plotting elongation at break as ordinates against moisture content, it has been found that comparisons may be made directly only if filaments are of uniform size. With increasing diameter, somewhat greater elongation occurs, but variation in size are very nearly compensated by determining an "elongation index" which is plotted against moisture content. This index factor for all practical purposes corrects for variations

in diameter and is calculated according to the following formula:

Elongation index=

$$\frac{\text{Elongation in multiples of original length}}{\text{Sq. root of wt. in gms. per 100 cm.}}$$

A typical curve for a given polyvinyl alcohol mix is illustrated in the accompanying drawing. As will be observed, the curve rises as the moisture decreases beyond that required for extrusion and then gradually changes direction through a smoothly rounded part, dropping as the moisture is reduced to a range where the filament ceases to be plastic. Depending upon the ingredients in the filaments, it has been found that the most favorable moisture content for maximum elongation is generally between 25 and 35 percent.

Having determined the moisture content that will give the best elongation characteristics it will be a simple matter to elongate the filaments to a point just short of breaking and thereby provide for a filament of maximum tensile strength.

The adjustment of the moisture content of a polyvinyl alcohol filament to a value suitable for best elongation is most effectively brought about by slow conditioning in an atmosphere of high relative humidity. Experimentally this can be accomplished most conveniently by extending the conditioning over a period of several days in a chamber above crystals of Glauber's salts. More practically from a commercial standpoint, the filament may be exposed in dry air until the portion adjacent its outer surface is relatively too dry while the central portion is still relatively too moist. The filament in that condition may then be passed through a conditioning chamber nearly saturated with water vapor (as over saturated sodium sulfate solution) to permit equalization of the moisture throughout the mass.

With the filament properly conditioned, it is stretched to give it the proper degree of elongation and then wound on a reel to insure that the elongation will be retained. The elongation obtainable in filaments made from a good quality of polyvinyl alcohol is commonly between 400 and 600 percent, and the cross-sectional area will be reduced to about one-eighth or one-tenth the cross-sectional area of the filament as it is originally spun.

Filaments stretched in the manner just described and air dried retain their length if maintained quite dry, but on immersion in water or even on subjection to moist air, immediately begin to soften, shortening almost to their original length and becoming very weak. Mere heating of the filament to reduce its permeability to moisture is not sufficient. A filament thus processed may have a high dry strength but when wet its strength is reduced to the neighborhood of about .2 gram per denier and it becomes worthless through swelling and shortening. Applicants have discovered, however, that if the heating is carried out in the presence of moisture, i. e., with moisture actually entrapped in the filaments, not only will dry strength be increased, but wet strength will be increased as well. Indeed, as stated at the outset, polyvinyl alcohol filaments have been made in accordance with the instant process having a tensile strength as high as 5 grams per denier when dry and 3 grams per denier when wet, a dry and wet strength corresponding respectively to 90,000 pounds per square inch and 54,000 pounds per square inch.

The best results have been obtained where the moisture content during the heat conditioning

process is between about 6 and 12 percent. If the moisture content is too low, the heat has insufficient effect in developing an increase in wet strength. On the other hand, if the moisture content is too high, there is a tendency for the filament to soften and break at the high temperature at which it must be processed. The required temperature will depend upon the duration of the heating period wherefor the selected upper limit for moisture content will depend upon the temperature chosen for the heating step.

During the heating period, contraction of the filament must be guarded against. For this reason, it is preferred that the moisture content be regulated while the filament is in its stretched condition, and after the filament has come to equilibrium with the desired moisture content, it is heated under conditions which will prevent shrinkage or contraction as well as the escape of moisture. Any suitable method may be used to moisture condition the filament while maintaining it stretched. For example, the reel on which the stretched filament has been wound may be placed in a conditioning chamber having an atmosphere adjusted to give the filament the required moisture content after a condition of equilibrium has been reached. Suitable chamber conditions for the purpose may be obtained by adjusting the temperature in the chamber to 40° C. while a current of air which has previously been bubbled through a saturated calcium chloride solution at room temperature, is caused to pass around the filament. Equilibrium is fully reached only after conditioning for one to several days, depending on the filament size. However, for filaments of sizes most commonly used for sutures it has been found that overnight conditioning brings the moisture content within the range required. After the filament reaches the proper moisture content it is heated under conditions which will neither allow the escape of moisture from the filament nor permit it to absorb more moisture. By way of example, such conditions will be satisfied if the reel on which the stretched moisture-conditioned filament is wound is immersed in a container and covered with a high boiling inert and anhydrous liquid and the container sealed leaving just enough space above the liquid to allow for its expansion when brought to the temperature at which the heating process is carried out. Naphtha which is dry and free from acid and which has a boiling point just above 160° C. is suitable for the purpose although any dry, inert heating medium, i. e., one in which water is not appreciably soluble, may be used in its stead.

Any suitable means may be employed for heating the bath containing the filament, the time and temperature of heating being adjusted according to the moisture content. With a moisture content adjusted to about 8 percent, filaments of high dry and wet strength have been prepared by heating the bath at 180° C. for a period of four hours. A longer period of time at temperatures of 140° C. and 160° C. will produce similarly good filaments and these lower temperatures will permit a higher moisture content in the filament without detriment and with some improvement in wet strength. For any given temperature the quality of the filament improves as the heating period continues until an optimum condition is obtained after which little or no change will take place in the filament either from the standpoint of improving or detracting from its quality.

Generally speaking, it has been found that maximum strength is obtained where the filament comprises pure polyvinyl alcohol. However, other materials may be added to the mix prior to extrusion where the quality imparted by such materials outweighs any sacrifice that may be made in tensile strength. For instance, in the case of sutures, one or another of the sulfonamides such as sulfanilamide up to say 5% may be incorporated into the spin mix and fortunately, in the case of these agents, without any appreciable detriment in the tensile strength of the finished filament. The sulfonamide carried into the suture tract by a polyvinyl alcohol suture will act to inhibit the growth of bacteria in the suture tract and thus assist in the prevention of stitch abscesses. In this connection, however, it should be noted that sutures made of pure polyvinyl alcohol are surprisingly free of any tendency to form stitch abscesses; indeed, in this respect, such sutures are markedly superior to catgut or silk sutures currently in use.

In some phases of surgery, a suture predominating in color is desirable. Furfural in the presence of an alkalinizing agent such as urea or morpholine or both will impart to a polyvinyl alcohol filament a jet black color which appears in the filament after it has passed through the final heating stage. The furfural, urea, and morpholine are incorporated in the spin mix, and merely by way of example, a formula which gives an excellent black color to the filament is as follows:

	Grams
Polyvinyl alcohol -----	100
Furfural -----	2.5
Urea -----	3.1
Morpholine -----	1.0
Water -----	93.4

While the invention has been described in connection with polyvinyl alcohol filaments suitable for sutures, it will be understood that their use is not thus limited and that filaments made from polyvinyl alcohol in accordance with the present invention may be used in all cases where their particular properties indicate they will be of service.

In some instances it may be desirable to use polyvinyl alcohol strands in very large sizes as for tennis racket strings, in which case it may be preferred to provide a string of multiple strands rather than the mono-filament heretofore described. One method of making such a strand consists in combining a suitable number of stretched filaments of the smaller sizes into a bundle of the required size, bonding the bundle into what is essentially a mono-filament by coating with a size of polyvinyl alcohol dissolved in water and heat-treating the bonded filament in the manner described before. Alternatively, the small mono-filaments may be grouped into bundles and coated with the polyvinyl alcohol size prior to the stretching process and the stretched units heat treated by the improved process herein set forth. The advantage of the alternative method resides in the fact that the bonding size is oriented by stretching the same as the filament and therefore will contribute to the strength of the composite mass in proportion to its percentage weight.

While the invention has been described merely by way of example, many modifications thereof may be made without departing from its spirit. It will be understood, therefore, that the inven-

tion is to be limited only by the prior art and the scope of the appended claims.

We claim:

1. The process of treating a polyvinyl alcohol filament to improve its tensile strength, which includes stretching the filament, conditioning it to a moisture content in the range 6% to 12%, and heating it for at least four hours within the temperature range 140° to 180° C. without permitting any substantial variation either in its degree of stretch or in its moisture content.

2. The process of treating a polyvinyl alcohol filament to improve its tensile strength, which includes stretching the filament, conditioning it to a moisture content in the range 6% to 12%, and heating it without permitting any substantial variation either in its degree of stretch or in its moisture content, the duration of the heating period being from four to eight hours, and the temperature of heating being in the range 140° to 180° C.

3. The process of treating a polyvinyl alcohol filament to improve its tensile strength, which includes stretching the filament, conditioning it to a given moisture content in the range 6% to 12% and heating it totally immersed in an anhydrous medium for at least four hours within the temperature range of 140° to 180° C. without permitting any substantial variation either in its degree of stretch or in its moisture content.

4. The process of treating a polyvinyl alcohol filament to improve its tensile strength, which includes stretching the filament, conditioning it to a given moisture content in the range 6% to 12% and heating it totally immersed in an anhydrous liquid sealed from the atmosphere for at least four hours within the temperature range of 140° to 180° C. and without permitting any substantial variation in its degree of stretch or in its moisture content.

5. The process of treating a polyvinyl alcohol filament to improve its tensile strength, which includes stretching the filament, conditioning it to a given moisture content in the range 6% to 12% and heating it totally immersed in a high boiling, inert anhydrous liquid sealed from the atmosphere and which is free from acid, for at least four hours within the temperature range 140° to 180° C., and without permitting any substantial variation in its degree of stretch or in its moisture content.

6. The process of treating a polyvinyl alcohol filament to improve its tensile strength which includes conditioning the filament to a moisture content permitting substantially maximum orientation by stretching, stretching the filament just short of the breaking point, reconditioning the filament while in stretched condition to a moisture content in the range of 6% to 12%, and heating it for at least four hours within the temperature range 140° to 180° C., without permitting any substantial variation either in its degree of stretch or in its moisture content.

7. The method of making a multi-filament unit of polyvinyl alcohol which includes bonding a plurality of polyvinyl alcohol filaments together by a polyvinyl alcohol size, stretching the bonded unit, conditioning it to a given moisture content in the range 6% to 12% and heating it for at least four hours within the temperature range 140° to 180° C. without permitting any substantial variation either in its degree of stretch or in its moisture content.

8. The process of treating a medium to high viscosity polyvinyl alcohol filament to improve

its tensile strength, which includes stretching the filament, conditioning it to a moisture content in the range 6% to 12%, and heating it for at least four hours within the temperature range 140° to 180° C. without permitting any substantial variation either in its degree of stretch or in its moisture content.

9. The process of treating a polyvinyl alcohol filament to improve its tensile strength which includes stretching the filament, conditioning it to a moisture content of 8% and heating it for at least four hours at a temperature of 180° C. without permitting any substantial variation either in its degree of stretch or in its moisture content.

10. The process of treating a medium to high viscosity polyvinyl alcohol filament to improve its tensile strength which includes stretching the filament, conditioning it to a moisture content of 8%, and heating it for at least four hours at a temperature of 180° C. without permitting any substantial variation either in its degree of stretch or in its moisture content.

11. An article of manufacture comprising a polyvinyl alcohol filament made in accordance with the process defined in claim 1.

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

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2,236,542	Lukens	Apr. 1, 1941
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2,322,976	Schmitz	June 29, 1943
2,327,872	Dahle	Aug. 23, 1943
2,331,955	Beebe et al.	Oct. 19, 1943
2,339,323	Feld	Jan. 18, 1944
2,346,208	Conaway	Apr. 11, 1944

FOREIGN PATENTS

Number	Country	Date
322,157	Great Britain	Nov. 22, 1929

Certificate of Correction

Patent No. 2,447,140.

August 17, 1948.

ELBERT M. SHELTON ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 4, line 60, for "tube" read *time*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of October, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

its tensile strength, which includes stretching the filament, conditioning it to a moisture content in the range 6% to 12%, and heating it for at least four hours within the temperature range 140° to 180° C. without permitting any substantial variation either in its degree of stretch or in its moisture content.

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