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[54] **METHOD OF MAKING PLIABLE, DYED AND BRAIDED POLYESTER SUTURES**

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[52] **U.S. Cl.** .... **87/1,** 28/75 R, 57/164, 117/138.8 F, 117/139.5 CQ
[51] **Int. Cl.** **D06p 7/00,** D04c 1/12
[58] **Field of Search** ...... 57/153, 164, 140 R, 140 C; 87/1, 23; 28/74 R, 75 R, 76 R, 75 WT; 117/138.8 R, 138.8 F, 139.5 CQ, 139.5 CF, 138.8 B, 139.5 R, 7

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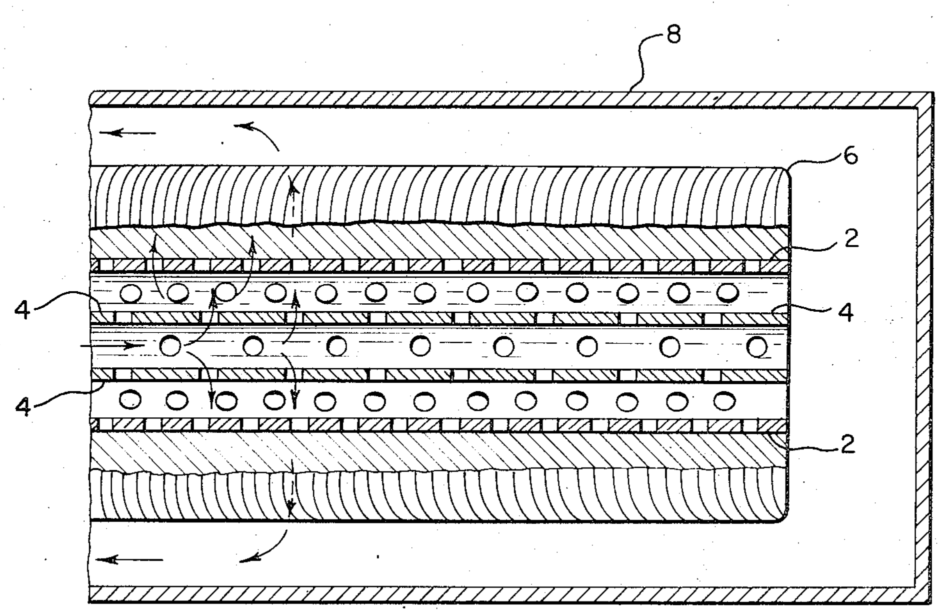
[57] **ABSTRACT**

Fabricating a pliable, dyed and braided polyester thread which comprises winding a polyester strand loosely around a perforated hollow dyeing element, passing dye under pressure through the winding of said polyester strand, hot-stretching the dyed strand to reduce the elastic memory thereof, coating the hot-stretched strand with a liquid, film-forming material adherent but substantially inert to said polyester strand braiding a plurality of said coated filaments into a braided thread, and removing said film-forming material.

7 Claims, 2 Drawing Figures



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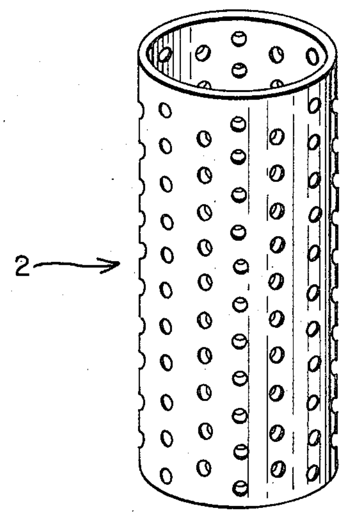

FIG. 1

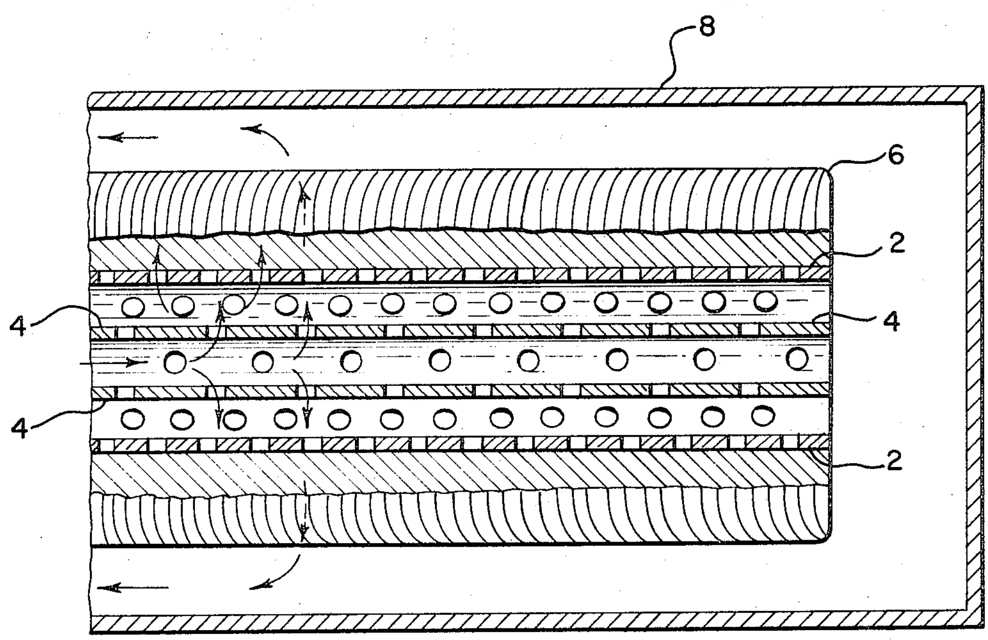

FIG. 2

METHOD OF MAKING PLIABLE, DYED AND BRAIDED POLYESTER SUTURES

The present invention relates to an improved method for the preparation of braided sutures of dyed and hot-stretched synthetic polyester filaments or strands.

There are several synthetic fibers which have been proposed for use as sutures, amongst which are polyester fibers. Polyester fibers have been found to possess certain physical and chemical properties superior to natural fibers such as silk fibers that render them particularly suitable for use as surgical suturing material. The shortcomings of synthetic fibers, however, is that they are relatively stiff compared to naturally occuring fibers. Consequently, in order to minimize this stiffness, it has been found necessary to prepare a polyfilamentous thread as opposed to a single filament thread. The monofilament fiber has a cross-section which cannot be varied, i.e., the cross-section is frozen and in a fixed relationship to adjacent cross-sections. Polyfilamentous materials, on the other hand, can have displacement of the fibers, thus accomodating the stress of curvature.

Polyfilamentous synthetic filaments although exhibiting improved flexibility compared to synthetic monofilaments, are still quite stiff relative to silk. In U. S. Pat. No. 3,379,091 to Leonard D. Kurtz, there is described a method of preparing polyfilamentous synthetic materials such as polyesters of improved softness and flexibility by hot-stretching individual fiber components before braiding them into the polyfilamentous threads. When a dyed product, such as a surgical suture, is desired to be prepared, the dyeing step in this process must be effected before the hot-stretching operation because hot-stretching causes the synthetic fibers to lose their affinity for satisfactory dye absorption.

Nor is the method of U. S. Pat. No. 3,379,091 free from criticism, however, when the dyeing of the polyester filament is effected by "pressure dyeing," that is, the dyeing process wherein the polyester filament to be dyed is first wrapped loosely around a perforated tube or its equivalent and the wrapped filament then dyed by passing the dye under pressure through the wrapped polyester filament. When a polyester filament is pressure dyed in this manner, hot stretched and passed onto the braiding machine for braiding, the dye tends to come off the fibers and deposit on elements of the braiding machine. Accumulations of such deposits eventually come off the braider as "louses" which fall onto filaments being braided thereby ruining the product.

This problem is peculiar to braided polyester suture fabrication wherein the fiber is pressure dyed as opposed to say dyeing the fiber as, for instance, by dipping the fiber in a loose form such as a skein. No dye deposit problem has been experienced in the latter operation. Without being bound by any theory as to the cause of the dye deposit problem it is believed that the tightly wound polyester fiber acts as a filter and small particles of dye under the pressure of the dyeing step are filtered out by the wound fiber where they attach. Then when this fiber is subsequently passed onto the braider after hot-stretching the attached dye particles abrade off, accumulate on the machine and eventually, as aforementioned, come off as "louses."

It is an object of the invention, therefore, to provide a method of preparing pliable braided polyester sutures, pressure dyed before hot-stretching which eliminates or substantially alleviates the dye deposit problem normally experienced when such filaments are subsequently braided.

It is another object of the invention to remedy the aforementioned problem without adversely affecting the pliability and flexibility characteristics of the final product.

These and other objects of the invention are obtained by winding a polyester strand loosely around a perforated hollow dyeing element, passing dye under pressure through the winding of polyester strand, hot-stretching the dyed strand to reduce the elastic memory thereof, coating the hot-stretched strand with a liquid, film-forming material adherent but substantially inert to said polyester strand, braiding a plurality of said strands into a braided suture and removing said film-forming material.

The liquid film-forming materials contemplated for use in the present invention are those which form adherent films on the polyester strand. The liquid film-forming materials allow the loose particles and dyes to come off the polyester strand without aggregation during the braiding operation. Deposition of the loose dye and scuff occurs onto the braiding maching but in the liquid film-forming material which prevents aggregation and formation of the "louse." The film-forming liquids should be substantially inert to the polyester and substantially non-absorbable thereby.

A variety of suitable film-forming liquids will readily come to the mind of those skilled in the art and include materials such as surface active or wetting agents, oils of lubricating viscosity, antistatic agents and the like. A particularly suitable film-forming liquid for use in the present invention are silicone oils of lubricating viscosity. Silicone oils of lubricating viscosity which can be employed in the method of the invention are liquid organic siloxane polymers in which the siloxane structure, —Si—O—Si—, occurs successively along the polymer chain and in which the major number of residual valences of the silicone atoms are not satisfied by the substitution thereon of monovalent organic essentially hydrocarbon radicals such as aromatic and aliphatic radicals. For the purposes for which such silicone oils are used in the present invention, the aliphatic substituents of the polymers are preferably low molecular weight alkyl radicals (i.e., those not having more than about 5 carbon atoms per radical) such as methyl, ethyl and butyl radicals, and the aromatic substituents are preferably phenyl, halogen-substituted phenyl radicals, and alkyl-substituted phenyl radicals in which the alkyl group is halogenated. The aromatic siloxane polymers are preferably those in which a major proportion of the silicone atoms are bonded to aliphatic radicals such as methyl radicals, and in which the remaining number of organic radicals are aromatic radicals. Typical examples of specific silicone oils which may be use are the dimethyl siloxane polymers having a viscosity of at least 10 centistokes at 25° C. (77° F.) and preferably a viscosity of at least 20 centistokes at 25° C. Such methyl-substituted siloxanes are commercially known as the Dow Corning Silicone Type 200 fluids and are mixtures of polymers of the homologous series of trimethyl end-blocked dimethyl siloxane polymers having a viscosity at 25° C. ranging up to about 12,500 centistokes. Other suitable siloxane polymers which may be used in accordance with the present invention are the aliphatic- and aromatic-substituted siloxane polymers such as the methyl phenyl siloxane polymers of medium aromaticity commercially available as Dow Corning DC-550 silicone oil, and those containing a low ratio of phenyl to methyl groups commercially available as Dow Corning DC-510 silicone oils. Further examples of suitable aliphatic- and aromatic-substituted siloxane polymers are the methyl phenyl siloxanes in which the phenyl radical is substituted with halogen such as in methyl-p-bromophenyl siloxane polymer, methyl-p-chlorphenyl siloxane polymer, methyl-m-trifluoromethyl phenyl siloxane polymer and methyl 3,4-dichlorophenyl siloxane polymer. It is within the scope of the present invention to employ any admixture of the above-mentioned silicone oils as an ingredient of the presently described novel compositions.

It is to be understood that the term "siloxane polymer" as used herein includes silicone oils having the following general formula:

$$R_1-\left[\begin{matrix} R_2 \\ | \\ Si \\ | \\ R_3 \end{matrix}-O-\right]_n\begin{matrix} R_2 \\ | \\ Si \\ | \\ R_3 \end{matrix}-R_1$$

wherein R_1, R_2 and R_3 are the same or different hydrocarbon radicals such as straight or branched chain alkyl, aryl, alkaryl, arylalkyl, halogen-substituted aryl or halogen-containing alkyl-substituted aryl radicals and n in an integer of at least 2. Such silicones are also referred to in the literature as organo polysiloxanes.

Dyes suitable for use in the method of the invention have been determined and are well recognized in the suture dyeing art. Generally, the dyes may be defined and classified as oil-soluble or oil-solvent soluble, water-insoluble azo, quinoline, anthraquinone, thio-indigo and isoxanthene dyes. It is intended that the dyes contemplated by the present invention embrace F. D. A. approved dyes.

Illustrative of dyes that may be used in the method of the invention are:

D & C Green No. 6 (1,4 di-p-toluido anthraquinone)
[Phtalocyaninato (2-)] copper
D & C Blue No. 9
1 xylylazo-2-naphthol
1-phenyl-azo-2-naphthylamine
1-o-tolyl-azo-2-naphthylamine
1-p-phenyl-azo-phenylazo-2-naphthol
1-xylylazo-xylylazo-2-naphthol
1-(o-nitro-p-tolylazo)-2-naphthol
1-(o-chloro-p-nitrophenylazo)-2-naphthol
2-(2-quinolyl)-1,3-indandione
1-hydroxy-4-p-ptoluianthraquinone
5,5'-dichloro-3,3'-dimethyl-thio-indigo
o-[p-β,β'-Dihydroxy-diethylanino)-phenylazo] benzoic acid

The dyeing of the polyester strands may be effected by any of the well known pressure dyeing methods and techniques of the art wherein dye under pressure is passed through windings of the strands about perforated hollow dyeing elements. Generally the perforated dyeing elements are in the form of a hollow tube or cone and can be of metal such as aluminum, stainless steel, etc., or synthetic polymeric plastics.

The hot-stretching step of the invention comprises stretching the strand at a temperature above its glass transition temperature, to the softening point thereof which will permit a change in configuration without the

introduction of internal stresses. Conveniently, the strand may be heated to its softening point. Tension is applied to the heated filament such that the filament is stretched, for example, up to its breaking point. Elongation of over 10 percent and particularly from about 20 percent up to about, but not including, the breaking point are suitable to reduce the elastic memory of the strand sufficiently. The temperature necessary to reduce or eliminate elasticity and memory is called the heat-setting temperature which is known for the various polyesters. For instance, in the case of polyesters of terephthalic acid, a temperature of 320° F. or above will suffice, although temperatures of about 390° to 450° F. are preferred.

Coating of the polyester strands with the liquid, film-forming material may be effected in any convenient manner, for instance, by simply immersing the strand in the liquid for a short period of time sufficient to saturate and thoroughly impregnate and coat the strand. Ordinarily, complete saturation is effected in a matter of minutes.

As aforementioned, removal of the liquid film-forming material from the braided thread may be effected by any of the techniques well known to the art such as washing the product with a suitable solvent for the film-forming material. Solvents for silicone oil, for instance, include the alkyl and aryl monoethers of alkylene glycols such as ethylene glycol, propylene glycol, etc. Illustrative of these solvents are those of the "Dowanol" series.

After extraction of the liquid, film-forming material from the braided thread, the thread may be water-washed in any convenient manner and then while still wet impregnated with inert, insoluble synthetic polymeric particles small enough to penetrate into the interstices of the polyfilamentous thread. The inert, polymeric particles may be any of those known in the art for endowing polyfilamentous strands with improved softness, knottability and flexibility such as those disclosed in U. S. Pat. Nos. 3,390,681 and 3,322,125, hereby incorporated by reference. Other suitable inert, insoluble synthetic resins which can be used for this purpose include polyolefins such as polyethylene, polypropylene and the like; diolefins such as polymers of butadiene and isoprene; polystyrene; polyamides and silicone waxes such as are disclosed by U. S. Pat. No. 3,187,752, hereby incorporated by reference. A particularly preferred particle is polytetrafluoroethylene (Teflon). Aqueous dispersions of these materials such as aqueous dispersions of Teflon described in Berry, U. S. Pat. No. 2,478,229, are suitable to incorporate the particles into the thread. Saturated aqueous dispersions are particularly suitable. Ordinarily, the inert particles employed will have a particle size of up to 1 micron.

The following example is included with reference to the drawing to further illustrate the present invention wherein FIG. 1 shows a perforated dye tube and FIG. 2 shows a dye tube with thread wound thereon in a pressure dye machine.

EXAMPLE

A surgical polyester (polyethylene terephthalate) suture is prepared as follows:

Eight filaments of drafted 40 denier polyethylene terephalate are twisted and taken up on twister bobbins. The twisted thread is transferred from the twister bobbins and wound around a perforated stainless steel dye tube **2** shown in FIG. **1**. The perforated dye tube is 6 ½ inches long and has an outside diameter of approximately 2 inches. The perforated dye tube containing approximately 6 oz. of wound thread **6** is then fitted onto the perforated shaft **4** of a pressure dye machine shown as **8** in the manner diagramatically illustrated in FIG. **2**. The heating fluid of the dye machine is raised to a temperature of approximately 280° F. and the fluid passed through the wound thread under pressure as indicated by the arrows in FIG. **2** for approximately an hour to shrink the thread. The shrunken thread is then loosely wound onto another perforated dye tube and the tube with the winding of thread is refitted onto shaft **4** of the dye machine. The wound threads are then dyed by passing under pressure in the same manner as the heating fluid in the shrinking operation an aqueous solution of D & C Green No. 6 dye at a temperature of approximately 270° F. The dyed thread is then transferred onto a twister bobbin and in a twist texturing machine given two final twists while hot-stretching the thread 20 – 25 percent of its original length at a temperature of 450° F. The resulting hot-stretched thread is transferred onto a soft package dye tube and the tube with the winding of thread immersed in a vat of silicone fluid ("Dow Corning 710"). Eight threads thus prepared are then braided on a New England Butt braider. The braided thread is washed with "Dowanol" (dipropylene glycol monomethyl ether) after which it is water-washed and dried.

No localized deposits of dye or polymer are found on the resulting braided thread and examination of the braiding machines show no aggregation of dye or polymer accumulations which would cause "louse" formation. The procedure is repeated and several hundred braid polyester sutures are prepared by the same procedure. All the braided threads continue to be free of localized dye and polymer deposits and the braiding machine show no aggregation of dye and polymer accumulations.

It is Claimed:

1. A method of fabricating a pliable, dyed and braided polyester thread which comprises winding a polyester strand loosely around a perforated hollow dyeing element, passing dye under pressure through the winding of polyester strand, hot-stretching the dyed strand to reduce the elastic memory thereof, coating the hot-stretched strand with a liquid, film-forming material adherent but substantially inert to said polyester strand, braiding a plurality of said coated filaments into a braided thread, and removing said film-forming material.

2. The method of claim **1** wherein the polyester is polyethylene terephthalate.

3. The method of claim **1** wherein the liquid, film-forming material is silicone fluid of lubricating viscosity.

4. The method of claim **3** wherein said silicone fluid is removed by washing the braided thread with a solvent.

5. The method of claim **4** wherein the solvent is dipropylene glycol monomethyl ether.

6. The method of claim **4** wherein the hot-stretching is conducted at a temperature in the range of from the glass transition temperature thereof to the softening point thereof to elongate the strand in the range of a minimum of 20 percent based on its pre-stretched length, to just below the breaking point.

7. The method of fabricating a pliable dyed and braided polyethylene terephthalate thread which comprises winding a polyethylene terephthalate strand loosely around a perforated hollow dyeing element, passing dye under pressure through the winding of polyethylene terephthalate strand, hot-stretching the dyed strand to reduce the elastic memory thereof, said hot-stretching being conducted at a temperature in the range of from the glass transition temperature thereof to the softening point thereof to elongate the strand in the range of a minimum of 20 percent based on its prestretched length to just below the breaking point, coating the hot-stretched filament with silicone fluid of lubricating viscosity, braiding a plurality of said coated polyethylene terephthalate strands into a braided thread and then removing the silicone fluid by washing the braided thread with a solvent.

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