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METHOD OF FABRICATING PLIABLE POLYFILAMENTOUS PLASTIC STRANDS

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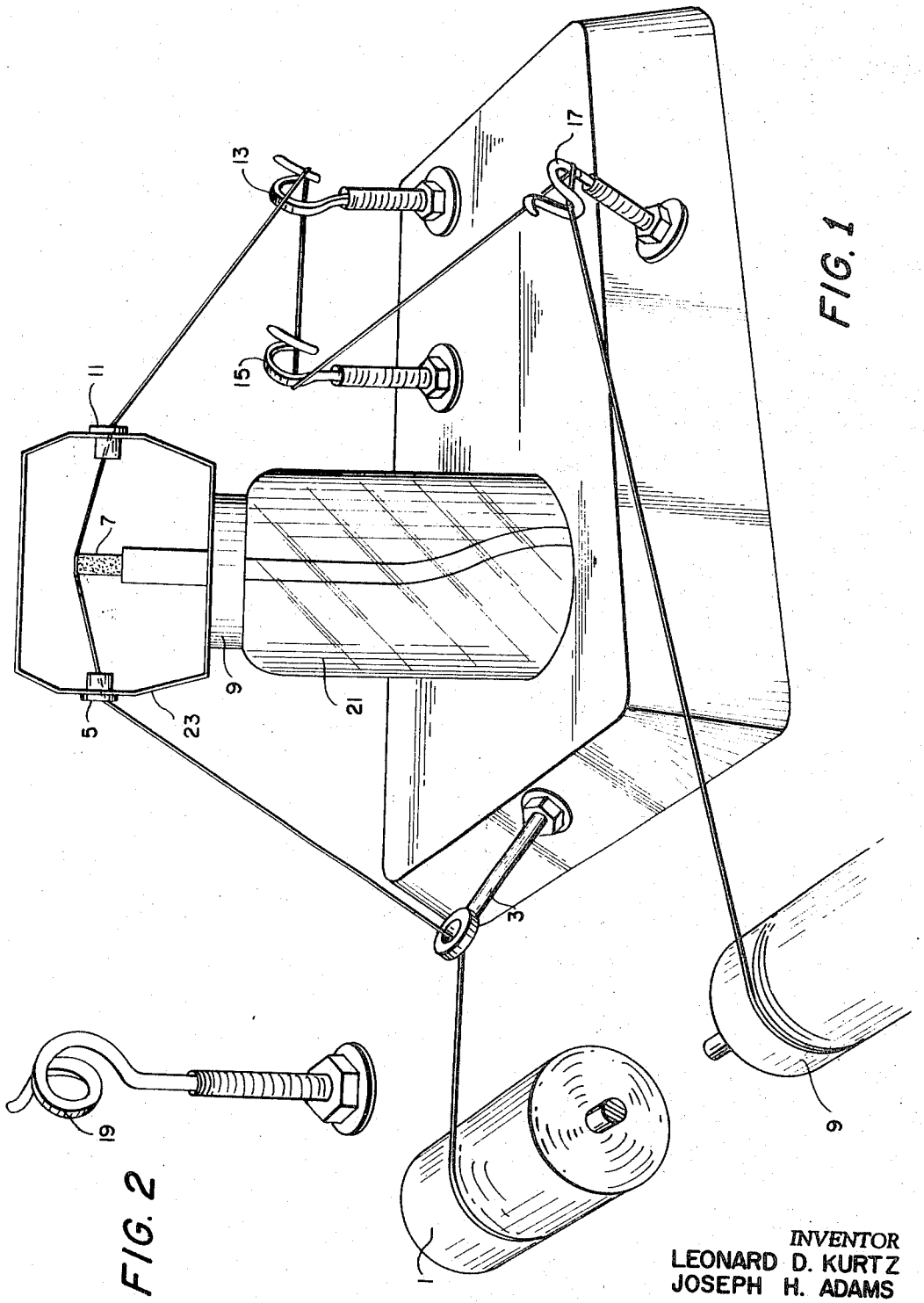

FIG. 1

FIG. 2

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METHOD OF FABRICATING PLIABLE POLYFILAMENTOUS PLASTIC STRANDS

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Continuation of application Ser. No. 78,174, Oct. 2, 1970, which is a continuation of application Ser. No. 828,495, May 28, 1969, both now abandoned. This application Nov. 14, 1972, Ser. No. 306,217
The portion of the term of the patent subsequent to Aug. 21, 1990, has been disclaimed
Int. Cl. A61l *17/00;* B29c *17/02*
U.S. Cl. 264—131 4 Claims

ABSTRACT OF THE DISCLOSURE

Polyfilamentous polyester sutures of improved softness and pliability are fabricated by impregnating the sutures with a lubricating oil, followed by stretching the sutures at the heat setting temperature. The sutures are next cooled, followed by flexing under tension by passing the sutures around a plurality of sharp edges. The sutures are then contacted with a solvent for the lubricating oil. Finally, the sutures are impregnated with polytetrafluoroethylene particles.

This is a continuation of Ser. No. 78,174 filed Oct. 2, 1970, now abandoned, which is in turn a continuation of Ser. No. 828,495 filed May 28, 1969, now abandoned.

This invention relates to an improvement in the fabrication of pliable plastic polyfilamentous strands such as pliable sutures.

Plastic strands, for example, braided or twisted polyethylene terephthalate threads, have certain physical and chemical properties superior to naturally occurring materials for many applications. Polyfilamentous polyethylene terephthalate threads, for example, are suitable for use as surgical sutures because of the high tensile strength and inertness thereof. However, the thread is very stiff relative to, for example, silk of equal tensile strength and/or dimension and this lack of pliability causes the knotting characteristics of the thread to be quite poor for surgical use. To this end, various methods have been disclosed in the art for modifying the lubricity and pliability of plastic threads such that the knotting properties are similar to those of silk threads.

Moreover, to make the polyfilamentous strand suitable for use, including surgical use, it has been necessary to reduce the elasticity and memory (tendency to return to original length) of the plastic polyfilamentous strand by hot-stretching the strand.

A method has now been discovered which provides a polyfilamentous plastic strand of improved softness and pliability. In accordance with the invention, a polyfilamentous plastic strand is first impregnated with an oil or lubricating viscosity and then hot-stretched while maintaining the strand at least at the heat-setting temperature thereof. The hot-stretched strand is then permitted to cool and the impregnated strand is found to possess a greater pliability and softness than non-treated strands.

In a preferred embodiment of the invention, further pliability and softness is endowed the polyfilamentous strand by subjecting it after cooling to repeated flexion in order to cause relative movement between adjacent filaments of the strand. By this embodiment of the invention, there is produced an unusually soft and pliable strand. Although the role of the lubricating oil is not entirely understood, it is believed that the presence of the oil before hot-stretching reduces the tendency of

adjoining filaments of the strand to adhere or cohere and also to promote the breaking or loosening of adhered or cohered filaments upon flexing.

By the term "polyfilamentous plastic strand" as used herein and in the appended claims is meant a unitary structure of a plurality of plastic filaments and includes plastic monofilaments and polyfilaments which have been twisted, braided, entangled, spun and the like. Illustrative of such strands are braided and twisted threads, sutures, strings and rope, spun and continuous synthetic filament yarns, etc.

The oils employed in the method of the invention are oils of lubricating viscosity, stable toward the high hot-stretching temperatures to which the polyfilamentous strand is subjected and include mineral and synthetic oils. Generally, such oils have viscosities from about 35 to 250 SUS at 210° F. In the case of polyfilamentous surgical sutures, the oil selected for the impregnation should, of course, be physiologically inert.

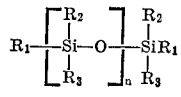
The mineral oils may be solvent extracted or solvent refined mineral oils obtained in accordance with conventional methods of solvent refining petroleum lubricating oils. The base oil from which these lubricating fractions are obtained may be derived from paraffinic, naphthenic, asphaltic or mixed base crudes.

Synthetic oils which may be used include those of the ester type, for instance, the complex esters, diesters, monoesters and polyesters, prepared from aliphatic aromatic acidic and alcoholic compounds. Various useful ester base oils are disclosed in United States Pat. Nos. 2,499,983; 2,499,984; 2,575,195; 2,575,196; 2,703,811; 2,705,724; and 2,723,286. Generally, the synthetic base oils consist essentially of carbon, hydrogen and oxygen, i.e. the essential nuclear chemical structure is formed by these elements alone. However, these oils may be substituted with other elements such as halogens, e.g., chlorine and fluorine. Some representative components of ester lubricants are ethyl palmitate, ethyl stearate, di-(2-ethylhexyl) sebacate, ethylene glycol di-laurate, di-(2-ethylhexyl) phthalate, di-(1,3-methylbutyl) adipate, di-(2-ethylbutyl) adipate, di-(1-ethylpropyl) adipate, diethyl oxylate, glycerol tri-n-octoate, dicyclohexyl adipate, di-(undecyl) sebacate, tetraethylene glycol-di-(ethylene hexoate), dicellosolve phthalate, butyl phthallyl butyl glycolate, di-n-hexyl fumarate polymer, di-benzyl sebacate and diethylene glycol bis(2-n-butoxy ethyl carbonate). 2-Ethylhexyl-adipate-neopentyl glycyl-adipate-2-ethylhexyl is a representative complex ester.

Preferred synthetic oils are the silicone oils of lubricating viscosity. The silicone oils 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 purpose 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 used 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-chlorophenyl 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:



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 is an integer of at least 2. Such silicones are also referred to in the literature as organo polysiloxanes.

Impregnation of the polyfilamentous strands may be effected in any convenient manner, for instance, by simply immersing the strand in the oil 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.

The hot-stretching step of the invention comprises stretching the strand at a temperature above its glass transition temperature, 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 strand such that the strand is stretched, for example, up to its breaking point. Elongation of over 10% and particularly from about 20% up to about, but not including, the breaking point are suitable to reduce the elasticity and 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 various plastic materials. For instance, in the case of polyesters of terephthalic acid, a temperature of 320° F. or above will suffice, although temperatures of about 390° F. to 450° F. are preferred.

The flexion to which the strand is subjected after cooling in the preferred embodiment of the invention may be accomplished, for instance, by subjecting the strands to repeated flexion as described in U.S. Pat. No. 3,257,702 hereby incorporated by reference. Alternatively and preferably, the flexion may be induced by passing the impregnated strand under tension after hot-stretching and cooling over a plurality of sharp edges, each edge being positioned to effect at least about a 30° change in direction of the passing strand. Treatment of the hot-stretched strand in this manner induces a consistent flexing uniformly throughout the entire strand. There is consequently provided a strand of particularly improved softness and pliability since no area of this strand escapes flexing. In addition, the improvement of the invention offers reproducibility advantages since it enables repeated preparation of strands of like softness and pliability. Furthermore, the improved method of the invention permits easy adjustment of the degree and the rapidity of flexion applied so as to enable optimization of conditions with respect to whatever type strand is being flexed.

The edge over which the strand is passed may be any suitable element having a relatively sharp edge. By "sharp edge" as used in the specification and claims is meant an edge that provides a sharp flex to the strand over which it is passed in accordance with the methods of the invention that breaks free or loosens adhering or cohering filaments of the strand. Thus, the edge of the element, over which the strand is passed, should not be so sharp as to cause severing, cutting or abraiding of the strand; nor should the edge have a radius of curvature so large as not to provide the desired sharp flex. Included within the sharp edges contemplated by the method of the invention are sharp angular edges which can be considered as having essentially a zero radius of curvature and cylindrical elements having a very small radius of curvature of say up to $\frac{1}{32}$ inch as is found in edges having a diameter of up to $\frac{1}{16}$ inch. The sharp edged-elements over which the strand is passed may be constructed out of any suitable solid, hard material resistant to wear such as steel, ceramic and the like. The number of edges in the series over and around which the strand passes will vary depending upon the nature of the particular polyfilamentous strand, the tension applied, and the rate at which the strand is drawn around the elements. Use of too many edges in the series, however, should be avoided since an excess of edges will often cause the strand to break. A series of three edges has been found to provide satisfactory results.

Any arrangement of the edges that provdes the desired degree in change of direction can be employed. Although an arrangement which gives a 30° change of direction as the strand passes around each edge provides sufficient flexion, an arrangement which effects at least about a 90° change is preferred. The rate at which the strands are passed around the edge is not critical and during passage the strand may be drawn either partially around or completely around each of the elements as long as it is passed over the flex-inducing edge. The strands should be under sufficient tension as they are passed over the edges in order to induce the desired flex. Any tension which keeps the strand taut without breaking the strand can be employed. Tensioning devices known to the art may be used for this purpose, if desired. The drawing of the strand may be accomplished manually or, if desired, any suitable automatic or mechanical means may be employed. It may be necessary to repeat the passage of the thread around the plurality of edges to achieve the desired degree of softness and pliability.

The oil of lubricating viscosity may be removed from the final product, if desired, by any of the techniques well known to the art. For example, the oil may be conveniently removed by washing the product with a suitable solvent for the oil. The particular solvent selected will depend upon the lubricating oil employed. For instance, in the case of the silicone oils and ester-type synthetic lubricants, suitable solvents include, for example, 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. In the case of mineral lubricating oils, on the other hand, the aromatic solvents including benzene, xylene, toluene and the like are satisfactory.

If desired, the strand may also be subjected to any of the conventional treatments known in the art. For instance, the polyfilamentous strand may be provided with polytetrafluoroethylene to improve knotability and flexibility as described in U.S. Pat. Nos. 3,390,681 and 3,322,-125.

The following examples are included to further illustrate the present invention. In the examples, reference is made to the attached figures wherein:

FIG. 1 is a perspective view of an apparatus for effecting the flexing in accordance with the invention and,

FIG. 2 is an enlarged perspective view of one of the sharp edged-elements employed in the apparatus of FIG. 1.

Example I

A five/zero polyethylene terephthalate thread is immersed in silicone fluid ("Dow Corning 710") a polyphenylsiloxane having an average molecular weight of 2600, approximately 20 silicon atoms per molecule, and a phenyl to methyl ratio of 1.0 for approximately one minute. The excess silicone fluid is wiped off the thread and the thread is stretched at approximately 390° F. to an elongation of approximately 50%. The hot-stretched thread is drawn from a supply **1** and manually threaded through an introductory guide **3**, entrance opening **5**, over the wick **7** of applicator indicated generally as **9**, through exit opening **11**, and around guides **13**, **15** and **17**, respectively, in the manner illustrated in FIG. 1. The thread is then attached to take-up spool **9**. The guides, each containing a sharp ceramic edge shown for instance in FIG. 2 as **19**, are arranged in a manner which will effect at least a 90° change of direction of the passing thread at each edge. The applicator **9** is composed of a container **21** provided with wick **7** and a guide structure **23** provided with the aforementioned entrance opening **5** and exit opening **11**. The wick **7** is immersed in a cooling medium such as water. When take-up spool **9** is rotated, the hot-stretched thread is pulled over wick **7** of the applicator **9** where it is cooled by the application of the liquid cooling medium and then over the sharp edges of guides **13**, **15** and **17**.

Example II

Thread softened according to Example I is gathered into a skein and immersed in an aqueous solution of Teflon. Du Pont blend 2510, containing water and about 58% by weight of Teflon (polytetrafluoroethylene) particles having an average particle size of 0.5 micron diluted with water to a 1/25 concentration, are used. Triton X–100, an alkylaryl polyether alcohol having the general formula $R—(OCH_2—CH_2)_n—OH$ wherein R is an alkylaryl radical and *n* is an integer from 5 to 100 or more. (Rohm and Haas) and agitation are used to keep the well dispersed.

The skein of thread is kept immersed in the Teflon dispersion for 15 minutes to permit the particles of Teflon lubricant to permeate into the interstices of the thread. While the immersion time can vary widely, it has been found that 15 minutes is adequate for skeins weighing up to 50 pounds as determined by measuring the amounts of Teflon picked up after final processing. Excess Teflon is then removed to provide a thread which is extremely pliable and has knotting characteristics substantially identical to that of silk sutures.

It is claimed:

1. A method for fabricating hot-stretched polyfilamentous polyester sutures of improved softness and pliability which comprises thoroughly impregnating a braided polyester suture having an elastic memory with a lubricating oil which is physiologically inert and is inert to said polyester suture, stretching the impregnated suture while maintaining the suture at the heat-setting temperature above its glass transition temperature to reduce the elastic memory thereof, cooling the stretched suture, passing the cooled suture under tension that holds the suture taut around a plurality of sharp edges, each edge being fixed and positioned to effect at least a 30° change in direction of the passing suture so as to induce consistent flexing uniformly throughout the entire suture, contacting the stretched suture with a solvent for said oil to remove said oil from the suture and impregnating the suture with polytetrafluoroethylene particles having a size sufficiently small to enter into the interstices of said braided suture.

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

3. The method of claim **1** wherein the lubricating oil is silicone fluid.

4. The method of claim **1** wherein each edge is the sharp edge of a guide pin.

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28—75 R; 117—7, 138.8 F, 139.5 A, 161 UZ; 128—335.5; 264—233, 237, 290 T