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METHODS OF ALTERING THE SURFACE CHARACTERISTICS OF SOLID RESIN SURFACES AND ARTICLES PRODUCED THEREBY

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This application is a continuation-in-part of my earlier applications Serial No. 220,085, filed Aug. 28, 1962, and Serial No. 230,284, filed Oct. 12, 1962, both now abandoned.

The present invention relates to modification of the lubricity of a plastic surface. More particularly, the invention relates to the modification of the lubricity of a plastic surface comprising polyester, polytetrafluoroethylene or mixtures thereof. Even more particularly, the invention relates to modification of surfaces of threads comprising the aforesaid plastics.

It might often be desirable to modify the lubricity of a plastic surface such that the material is useful for particular applications where the unmodified material could not be efficiently utilized and might not be useable at all.

It is an object of the present invention to provide a process for modifying the surface of a plastic material and to provide materials of modified.

It is a further object of the present invention to provide a process for modifying the lubricity of a surface of polyester, polytetrafluoroethylene and surfaces comprising mixtures thereof and to provide said modified plastics.

It is still a further object of the present invention to provide a process for modifying threads of the aforesaid materials and to provide threads including surgical sutures, so modified.

These and other objects which will be apparent from the following description according to the present invention by depositing particles of a resin having low lubricity on the surface of a resin having a higher or equal lubricity. The resultant structure is thus modified in at least one of the following two ways:

(1) Where the added resin is less slippery, the resultant surface will exhibit the lubricity characteristics of the more slippery substrate and the less slippery coating thus resulting in an overall reduction of lubricity, and

(2) Due to the discrete particulate nature of the coating, which is then melted into the substrate thread, there is a change in "grain" which causes a modification of the apparent lubricity.

While the invention has utility in the modification of plastic surfaces generally, particularly advantageous results inhere from the modification of a particular surface—a thread useful as a surgical suture.

Silk has been universally accepted as a non-absorbable suture. The great majority of surgeons using non-absorbable sutures are best acquainted with the "silk technique."

With the introduction of polyethylene terephthalate (Dacron) fiber (hereinafter termed polyester) as a non-absorbable suture, it was evident that the technique of knotting, so well known with silk, would not apply to the technique required with polyester due to the following factors:

(1) The primary knot of polyester did not hold well and tended to open.

(2) When the first knot slipped upward, there was considerable difficulty using polyester in snugging the first knot back to its original position by the second knot. With silk, the first knot could usually be snugged back without difficulty.

(3) Using the polyester fiber, the knot tended to open

on oscillation. As many as twelve knots had been put in in an attempt to stabilize the knot structure but these would invariably open one at a time. With silk, the knots remain secure under oscillation.

(4) The polyester fiber requires a minimum of four knots (excluding oscillation) for knot security. Silk requires only three. (Knot security is that force necessary to disrupt the knot by pulling on the loops formed by the knot.)

The above disadvantages have weighed heavily against the use of the polyester fiber in place of the standard silk sutures despite certain advantages such as increased strength and decreased reactivity within the tissues achieved with the use of polyester.

In our co-pending applications Nos. 220,085 and 230,284 filed August 28, 1962, and October 12, 1962, respectively, for Teflon (polytetrafluoroethylene) coating polyester fiber as well as impregnating the polyester fiber, attempts have been made to overcome the major disadvantages in the use of the polyester fiber for surgery. Some success is disclosed in those applications as a result of Teflon treatment of the polyester fiber:

(1) The first knot holds its line of approximation like silk.

(2) The second knot can snug the first knot down to its original position.

(3) The knot does not tend to become untied on oscillation.

However, it has been noted that it is necessary to use one knot more than is used with silk in order to get an equivalent knot security.

Investigating the properties of polyester fibers, it was found that there is a common misconception. It was often stated that Dacron is "hard to knot" and that some attempt should be made to roughen the surface. A specially prepared suture has been introduced as a result of this concept. This suture comprises a braided Dacron having a loop on the surface at periodic intervals which attempts to arrest the slide of the Dacron and by this "roughening" of the surface attempts to improve the knotting. As will be shown hereinafter, this is precisely the wrong approach.

The process of knotting must be divided into its components before correct analysis can be made:

(1) A knot fails if it doesn't have the "hand" to lock the fibers of the braid into the new position so that they cannot restore themselves to the original position. "Hand," therefore, gives protection against opening under oscillatory movement.

(2) Another cause of knot failure is due to the lubricity of the surface. It has been found that the surface characteristics of polyester give a more secure knot than the surface characteristics of silk. If the first knot opens slightly along the line of anastomosis, as a rule, the second knot can snug the first knot back to its original position with silk. If the first knot of the polyester fiber slips upward, it is unlikely that the first knot can be snugged down by the second knot. The friction of the surface is too great and the first knot is inhibited from sliding downward.

With a pure Teflon braided suture, even a fourth consecutive knot can snug down all the preceding knots. With silk braided sutures, a second knot can snug down the first knot to a limited extent. With polyester braided sutures, a second knot cannot snug down the first knot, except to a very limited extent.

Also, four simple knots, all squared, with a $\frac{1}{10}$ " ear are required to give knot security with a Teflon impregnated polyester braided suture. Three simple knots, all squared, with a $\frac{1}{10}$ " ear, are required to give the equivalent knot

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security when braided silk is used. Finally, two simple knots, squared, with a $\frac{1}{10}$ " ear, are required to give the equivalent knot security when pure polyester braided sutures are used.

From the above, it is noted that the Teflon impregnated Dacron is not the equivalent to silk in knot security.

The differences in surface characteristics of these three sutures suggested that it would be desirable to decrease the lubricity of the Teflon impregnated polyester.

In my co-pending application Serial No. 230,284 for the Teflon impregnation of polyester fiber, it has been stated that spaces in the braid are filled with Teflon causing the equivalent of a monofilament fiber. It has been found that the concentration of Teflon in the impregnant solution cannot be decreased below a certain concentration without encountering difficulty with the impregnation process. However, this complete impregnation causes too great a lubricity because the proportion of Teflon to polyester on the surface of the Teflon impregnated Dacron is too great.

Two approaches could be made in order to remedy this increase in lubricity on the surface:

(1) The Teflon impregnant could be diluted with polyester so that the fiber would be impregnated with a polyester-Teflon solution of varying concentrations in order to find that particular concentration which might give the equivalent of the silk lubricity.

(2) Or, it might be possible to form a Teflon-impregnated Dacron suture and then attempt to decrease the lubricity of the Teflon.

At the present time there is no feasible way of obtaining a dispersion of polyester which could be used for the impregnating process. The process for making a polyester dispersion can be done but is onerous.

A simpler method has been postulated and found to be effective. According to the present invention, polyester is dissolved in trichloroacetic acid (or other suitable polyester solvent) and the prepared Teflon-impregnated polyester thread is passed through the solution of polyester at a high enough speed to prevent solution of the passing polyester braided thread. The solution of polyester which wets the passing polyester thread deposits a solution of polyester in Trichloroacetic acid on its surface and when dried, deposits the particles of polyester which had been dissolved in the trichloroacetic acid. The problem is then to fuse the polyester particles to the subjacent polyester braid and also, if possible, to implant the polyester particles into the Teflon surface. As is well known, it is postulated that "nothing sticks to Teflon." Therefore, something must be done in order to overcome this property in order to adhere the polyester to the Teflon. This is done in the following manner. While the particles are just lying on the surface of the Teflon impregnated polyester, the thread is passed over rollers under tension. This mechanically impresses the Decron on the surface into the subjacent Teflon and into the subjacent polyester braid, whichever is available. The material is then passed over rollers at a heat necessary to soften the polyester, as in hot-stretching. This process melts and fuses the impressed polyester into the subjacent polyester braid and also smooths it wherever it has pierced the Teflon layer. The net result is an increase in the overall percentage of polyester on the surface compared to the previous percentage of polyester. This increased polyester decreases the lubricity of the surface and approaches that of silk.

The result is spectacularly successful. It is possible to coat almost any desired quantity of polyester and thereby control to a very fine degree the amount of lubricity on the surface, it is actually possible to make the lubricity of the surface closer to polyester than to silk and to actually improve the Teflon impregnated polyester knotting characteristics as compared to silk. Surprising, the smoothness of the surface is not affected as much as might be anticipated. Despite the marked improvement in knotting characteristics, the surface of the Teflon impregnated

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polyester still feels remarkably smooth. It is difficult to differentiate between the modified and non-modified, surface of the Teflon impregnated Dacron. Under magnification, it is noted there is some change in the braiding characteristics. The braid appears to be somewhat roughened and has lost its usual geometrical configuration, undoubtedly due to cross-sealing of the polyester fibers by the impressed polyester particles roughing over it and possibly by the direct action of the solvent on the surface fibers. All in all, the effect is complete control of the knotting characteristics desired.

By the use of polyester particles deposited on the surface of Teflon-polyester, it has been found possible to modify the Teflon-polyester surface to any degree desired. The polyester is pressed, mechanically, into the Teflon. The melting process provides complete entrapment. The resulting Teflon-polyester ratio on the surface can be modified at will. There is complete stability of the final product.

The invention will be more particularly described in the examples which follow. These examples represent specific embodiments and are not to be construed as limiting.

EXAMPLE I

A Teflon coated polyethylene terephthalate thread is prepared according to the specific embodiment disclosed in my co-pending application Serial No. 220,085. This thread consists of polyethylene terephthalate braid which has been coated by passing the thread through an aqueous dispersion of Teflon comprising approximately 50% Teflon by weight having a particle size in the order of 0.5 micron and hot stretched at about 450° F. from 25 to 50% lengthwise to trap the Teflon both on the surface and in the interstices of the thread. Prior to hot stretching, the fiber is dried and excess Teflon removed. The final product contains about 18% Teflon and 82% polyester by weight. In accordance with the present invention, the Teflon coated thread is then passed through a solution of polyethylene terephthalate dissolved in trichloroacetic acid. The thread is passed through the solution at any convenient rate. Slow rates, which might cause excess solvation of the polyester thread material, should be, of course avoided. The coated thread is then air dried. To firmly adhere the coating to the thread, the thread is passed between rollers under pressure to compress the coating of polyester particles into the coated thread. The polyester is thus impressed into subjacent Teflon and Dacron, whichever happens to be in contact with the freshly applied coating. To firmly adhere the polyester particles, the coated thread is next passed over rollers heated to a temperature sufficient to soften the polyester. Temperatures of approximately 450° F. have proven adequate. This step melts and fuses the impressed polyester into the subjacent Dacron and also smooths the thread wherever the polyester particles have pierced the Teflon. The suture thus prepared has a surface of enhanced polyester content and consequently decreased lubricity while essentially retaining its original smoothness.

EXAMPLE II

A Teflon coated polyethylene terephthalate thread is prepared according to the specific embodiment disclosed in co-pending application Serial No. 230,284. This thread is similar to that of Example I except that during the Teflon coating step, the thread is hot-stretched at about 450° F. The coated thread is then passed through rollers which apply pressure to entrap Teflon particles in the interstices of the braided thread. Subsequent treatment according to the present invention is as set forth in Example I, above. The resultant suture has enhanced knotting characteristics due to decreased lubricity.

From the foregoing, it is apparent that a Teflon thread can be modified by treatment according to the present in-

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vention. Thus, a Teflon thread is passed through a solution of polyester in trichloroacetic acid. The rate is not critical due to the absence of polyester in the thread. By proceeding as in the examples, polyester is imbedded in the Teflon thread. The polyesters exemplified such as polyethylene terephthalate, are obtained by reacting an organic polycarboxylic acid, such as terephthalic acid, and an organic polyol, such as ethylene glycol.

Further, polyester itself may be modified according to the present invention. As stated above, the present process does not markedly affect the surface roughness of the substrate. Some roughening, however, occurs, and this slight effect has been found to decrease surface lubricity. In this manner, a polyester substrate can be coated with a coating of the same polyester and heated according to the present invention. The resultant surface contains imbedded particles of polyester imbedded into the polyester substrate.

While the above examples are drawn to the processing of thread, it is readily apparent that plastic surfaces on articles of various configuration may be treated according to this invention. To practice the invention, the surface must be coated in any convenient manner, dried, and the dried coating pressed into the subject material. Any pressure applying means, such as opposed rollers, platens etc. can be used. In addition, the article must be hot-pressed by any convenient means.

I claim:

1. A method of modifying characteristics of a surface consisting essentially of a solid synthetic resin selected from the group consisting of polytetrafluoroethylene, polyester reaction product of an organic polycarboxylic acid and an organic polyol, and mixtures thereof, comprising the steps of contacting said surface with a solution of solid polyester reaction product of an organic polycarboxylic acid and an organic polyol in a solvent to deposit a coating of said polyester on said synthetic resin surface, removing solvent from said coating to provide solid polyester on said surface, and subjecting the solid polyester and subjacent solid resin surface to heat and pressure to adhere said solid polyester to said surface.

2. A method according to claim 1 wherein said surface consists essentially of polytetrafluoroethylene and polyethyleneterephthalate.

3. A method of improving the knotting characteristics of a polytetrafluoroethylene-coated multi-filament polyester thread, said polyester comprising the polymeric re-

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action product of an organic polycarboxylic acid and an organic diol in a solvent to deposit a coating of said polyester on said thread, removing solvent from said coating to provide solid polyester on said thread, and subjecting the solid polyester and subjacent thread surface to heat and pressure to adhere said solid polyester to said thread.

4. A process according to claim 3 wherein said solvent is trichloroacetic acid.

5. A process according to claim 3 wherein said pressure and heat are applied sequentially in that order.

6. A process according to claim 5 wherein the thread is heated to approximately 450° F. during said heating step.

7. A multifilament thread having knotting characteristics similar to those of silk and consisting essentially of a plurality of filaments of a polyester reaction product of an organic polycarboxylic acid and an organic polyol and having polytetrafluoroethylene deposited within the interstices and on the surface of the thread and further having solid particles of a polyester reaction product of an organic polycarboxylic acid and an organic polyol fused to subjacent polyester filaments and imbedded in said polytetrafluoroethylene.

8. A thread is claimed is claim 7 wherein said polyester thread and polyester particles are each polyethylene terephthalate.

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