This invention relates to sutures of poly (glycol terephthalate) dyed with indigo. Sutures of poly (glycol terephthalate) will be referred to throughout the rest of this specification by the registered trademark Dacron, used by the Du Pont Company for their polyester fiber. This is a typical poly (glycol terephthalate) fiber, but the invention is not limited to the use of fibers from this source. These sutures have many advantages, including high tensile strength, inertness to tissue, and the like. The Dacron fiber, as purchased, is white or colorless, and there has been a demand for colored sutures. It has been proposed to dye Dacron sutures by means of oil soluble dyes in an organic solvent, such as dimethyl formamide. This is described in U.S. Pat. 2,909,177. The present invention is directed to a process of dyeing Dacron sutures with the vat dye, indigo, natural or synthetic, from baths which do not contain organic liquids and hence do not tend to dissolve or soften the Dacron.

Vat dyes, such as indigo, have many valuable characteristics, notably extreme fastness, inertness, non-toxicity, and the like. However, it has been found that ordinary vat dyeing techniques are not satisfactory for dyeing sutures of Dacron with indigo. Several requirements are necessary. First of all, the dyeing procedure must not injure the Dacron suture by reducing its tensile strength or knot strength. Secondly, the dyed suture must not crock or bleed when in contact with tissue or tissue fluids. Thirdly, it is very desirable that the dyeing be uniform.

Dacron sutures must not have high capillarity, or at least the capillarity must be rigidly controlled so that excessive absorption of fluids from body tissues will not take place. This prevents transfer of infection. A preferred method for doing this is by coating the suture with a thin coating of silicone rubber. The use of silicone coating for non-absorbable sutures is described in U.S. Pat. 3,187,752.

It has been found that a coating of silicone rubber not only reduces the capillarity of the suture, but it also improves its handling properties and knot tying characteristics. Sometimes sutures are used in deep recesses of the body to approximate tissues or to ligate blood vessels. When they are used in deep recesses longer sutures are required than when they are used near the surface. If, for example, a deep lying blood vessel is to be ligated, the center portion of the suture is looped around the vessel and the knot is started at the remote ends of the suture. The suture ends are drawn apart to move the knot down to the vessel. As one suture strand is pulled over the other until the knot is set abrasive action results which can cause the knot to chatter during run-down or the suture to fray.

Silicon coating of sutures minimizes or eliminates chattering or fraying. The coating allows the strands to glide over each other and at the same time offers protection against abrasion. No problem is presented with white Dacron sutures which can be handled in the same manner as other materials, such as for example silk; however, in the present invention, as will be brought out hereinafter, a dyeing at lower pH arises if the ordinary silicone treatment is carried out under the conditions which are standard for other materials and for white Dacron sutures. Ordinarily, silicone rubber contains a small amount of a peroxide catalyst, such as benzoyl peroxide, which is used to effect the initial polymerization of the silicone to produce commercial solutions of satisfactory viscosity.

When non-absorbable sutures such as silk or white Dacron art coated with a silicone rubber, it is standard procedure to increase the concentration of the peroxide catalyst so that the coating sets more rapidly and has greater resiliency. However, too high a concentration of peroxide catalyst reacts adversely with the indigo producing a dull, unlevel greenish-blue color instead of full deep, level shades of blue that are desired. Therefore, in addition to the requirements for the dyeing step itself, there are certain critical limitations on catalyst content in the silicone rubber treatment step of the suture.

Indigo has been dyed on cellulosic materials by two different general methods: One, a highly alkaline method in which high alkalinity is obtained with sodium hydroxide and the dyeing is from the sodium leuco of the vat dyestuff, which is yellow in color; two, lower alkalinitities (pH values less than 7) in which the indigo is reduced to its white hydrogen leuco, sometimes referred to as “vat acid.” Neither of these procedures is useful for dyeing sutures of Dacron. The first procedure, while capable of producing a good blue color, adversely affects the characteristics of the suture, such as tensile strength and the like. The second process does not adversely affect the properties of the suture, but neither does it dye it. There has, therefore, been a need for a process of dyeing the sutures with the yellow sodium leuco under conditions which do not injure the suture and which include dyeing on the slightly acid side, for example near a pH of 5, which is comparable to the pH for vat acid dyeing. The effectiveness of the dyeing, however, requires certain very definite conditions.

For best results, the dyeing must be at high temperatures, preferably at the boiling point of water. It is believed that the penetration of the sodium leuco into the Dacron suture is a thermally influenced process. A second factor is that there must be in the vat sufficient sodium ion so that the sodium leuco of the indigo is formed. This is entirely apart from the pH at which the dyeing takes place, because this latter is determined by a balance of the reducing agent, sodium dithionite, Na₂S₂O₄, which will be referred to throughout the specification by the common designation in the art of hydroxulfite, and whatever alkali is present. In other words, at the same pH the indigo might be present as its hydrogen leuco or as its sodium leuco, depending on the sodium ion concentration, and the latter is an essential feature of the present invention.

It has been found necessary to take care that the sutures are completely submerged in the dye bath until the penetration by the sodium leuco is complete. This requirement necessitates maintaining the dye bath volume regardless of the actual weight of sutures being dyed, which is quite a different situation than that in ordinary vat dyeing where chemical amounts are based on the weight of the material being dyed. Usually when carrying out the
process of the present invention the sutures are dyed in skein form, care being taken to tie the skeins sufficiently loosely so that the individual sutures are contacted adequately by the dye bath on all sides during the dyeing. It is also possible to dye by package dyeing procedures, but care shall be taken that the packages be sufficiently loosely wound so that imperfect dyeing at the point where the material crosses in the package is not encountered. This problem, which is usually referred to in the art as the cross-over problem is somewhat more severe with Dacron sutures than with the vat-dyeing of other materials, such as for example cotton yarn, which is more porous and can absorb the dye bath effectively. The Dacron sutures, of course, are not porous as far as the individual filaments are concerned and so somewhat greater care must be exercised if the present invention is conducted in a packaged dyeing procedure. While greater care is necessary, it is well within ordinary dyeing skill, and therefore the process of the present invention can be carried out using package dyeing techniques.

The problem of peroxide catalysts concentration in the silicone coating step, which has been referred to above, is a concentration problem, and in general in the present invention the peroxide catalyst, such as benzoyl peroxide, should not be present in concentrations which substantially exceed about 3%. As the commercial silicone rubber usually contains about 2% to 2.5% of benzoyl peroxide, it is normally desirable to effect the silicone coating step with the added benzoyl peroxide, and then a separate procedure. However, if the benzoyl peroxide content of a particular batch of silicone rubber is unusually low, it is permissible to add small amounts of benzoyl peroxide, care being taken that the amounts added do not produce a concentration substantially in excess of 3%. If this concentration is substantially exceeded, the color of the dyed suture becomes greenish blue and of low color intensity and such sutures are less visible in the presence of blood and do not show up well in contrast to tissue.

The dyeing procedure utilizes a well known step to avoid crocking and to produce deep colors. Thus, when the Dacron sutures are first dyed with a sodium leuco and the color developed by oxidation, there may be insufficient penetration of the dye into the Dacron fibers and it is a common procedure in the dyeing art to again reduce, the so-called reduction procedure, and then again oxidize. Full, deep shades of blue are produced which have not been practical hitherto with indigo. Crocking is also reduced and, of course, the silicone coating which follows also helps to prevent any undesired crocking.

The invention will be described in greater detail in conjunction with the following specific example, in which the parts are by weight unless otherwise specified. The example is a typical one and uses typical equipment, but this invention is not limited to the exact details therein set forth so long as the process requirements which have been set out above are met.

**EXAMPLE**

A steam heated, stainless steel tank is used which can handle 90 gallons of bath (747 lbs. of water). Up to 21 lbs. of Dacron sutures can be dyed at one time, and all quantities of chemicals set out below are expressed as a percentage of the weight of water instead of a percentage of the weight of the fiber dyed, as in most conventional dyeing procedures. Skeins of braided Dacron sutures are supported by a stainless steel rack which holds the skinned Dacron submerged during the dyeing procedure; the skeins should be sufficiently loosely tied to permit the dye bath to attack and penetrate all sides of the entire skein.

The skinned Dacron is scoured with 0.5% detergent (40% flake-sodium linear alkylarylsulfonate) flakes, for 30 minutes at the boil. A small amount of anti-foaming agent (10% emulsion of dimethyl poly siloxane) is added to prevent the bath from boiling over. The bath is then drained from the tank and 90 gallons of cold water added, the temperature is raised to 70°-80° C, and the sutures rinsed in this hot water bath for 10 minutes, followed by draining, as set out above, and raising the skews out of the bath.

The rinse bath is drained and 90 gallons of cold water added. 49 grams of D&C Blue #6 (indigo) is pasted with a dispersing agent (sulfated fatty acid) and then is added to the cold water in the dye tank, the bath is stirred until a uniform dispersion is obtained, a small amount of anti-foaming agent is added, and the temperature of the dye bath then raised to about 70° C. 0.35% sodium hydrosulfite is added, the bath being maintained between 70° and 80° C, the above noted D&C Blue #6 is C.I. Vat Blue 1 having Colour Index No. 7300, reference; Colour Index, 2nd Edition, 1956, vol. 4, page 4217, published by The Society of Dyers and Colourists, Yorks., England.

Technical grade sodium hydrosulfite 90% Na₂S₂O₄ is used. Care must be taken to protect the hydrosulfite in storage from moisture and from atmospheric oxidation. If the salt is excessively exposed it will deteriorate. Loss in potency of the hydrosulfite will require additional amounts than those indicated to be added during the dyeing cycle.

The tank is covered, and after a short wait 0.014% of sodium hydrosulfite is added, followed, after a short wait, with an additional 0.57% of sodium hydrosulfite in a sodium carbonate solution. The temperature of the bath is then raised to 100° C. and the skinned Dacron lowered into the boiling dye bath. The tank should be covered to prevent surface oxidation. At this point the dye bath is yellow, which is the color of the sodium leuco of indigo. A 250 ml. sample of the dye bath is then removed and the pH is taken at this stage. The temperature of the bath is then raised to 70° C. The pH should be between 5 and 5.5 when measured on a Macbeth pH Meter Model 1051 using a glass electrode. If the color of the dye bath is not yellow at this step, allow the temperature of the bath to drop to 95°-98° C. Add an additional 0.57% sodium hydrosulfite to the dye bath and raise the temperature to the boil. This step may be necessary if the sodium hydrosulfite has lost potency. The Dacron skews are boiled for about 15 minutes, raised above the tank and rotated, then lowered again and boiled for an additional 15 minutes. The skews are raised again and, the dye bath is then drained from the tank, which is refilled with 90 gallons of cold water, 1.25% of sodium perborate, technical grade, and 0.014% of glacial acetic acid are stirred in, and the temperature raised to 70°-80° C. A small amount of anti-foaming agent is then added. The bath is raised to the boil and the Dacron skews are directly introduced into the oxidizing bath at the boil. After 15 minutes the skews are raised, moved on the rack to straighten out any crocked skews, and again lowered and boiled for 15 minutes. The skews are then raised, the tank drained, refilled with water, the temperature raised to 70°-80° C., and the skews returned and rinsed in the hot water bath.

After rinsing, the skews are raised, the tank is again drained and refilled with cold water and heated up and 0.5% of soap flakes added with a small amount of anti-foaming agent. The skews are re-introduced, the bath heated up to 100° C. and boiled for 15 minutes. After 15 minutes the skews are raised, moved on the rack to straighten out any crocked skews, and boiled for 15 minutes. The tank is again drained and refilled with cold water. The water is heated up and the hot water rinses, as described above is repeated.

The dyed skews are then releuced by repeating the treatment with sodium hydrosulfite and sodium hydroxide described above. If the color of the dye bath is not green at this step, allow the temperature of the bath to drop to 95°-98° C. and add an additional 0.57% sodium hydrosulfite to the releuco bath and raise the temperature to the boil. Again, this step may be necessary be-
cause the hydrosulfite has lost potency. The bath is then drained, refilled with cold water, and the oxidizing step repeated, followed by a second soaping and boiling in water. The dyed Dacron sutures are then dried in an oven at 100°-110° C.

The dyed Dacron sutures are coated with silicone rubber by preparing a coating bath of the silicone rubber and xylene containing from 2% to 2.5% benzoyl peroxide, adjusting the viscosity with xylene to 5 seconds at 23° C. on a Ford fixed orifice viscometer cup having a 9/64" orifice. The Dacron sutures are wound on spools or cops on a coating machine and drawn through a reservoir and then through a suitable wiper to wipe off excess silicone rubber. The coated strands are then passed through three curing ovens in series, the first one being maintained at 100° C., the second at 130° C., and the third at 165° C.; each oven is 36" long. The strands are kept taut while passing through the curing ovens to prevent contact with the oven sides. Coating speed will vary somewhat with the size of the suture, for example 12'/min. for the size group 6/0-2/0 and 9'/min. for the size group 0-2.

I claim:

1. A process of dyeing poly (glycol terephthalate) sutures which comprises,
(a) dyeing the sutures, substantially at the boil in a dye bath containing indigo and sufficient sodium ion and sodium hydrosulfite to transform the indigo into the yellow sodium leuco and maintain a pH between 4 and 6, and
(b) oxidizing to the blue colored form,

2. A process according to claim 1 in which the dyeing of sutures proceeds in the following steps:
(a) treating the sutures at the boil with the sodium leuco of indigo,
(b) oxidizing
(c) soaping
(d) releucoing
(e) reoxidizing
(f) resoaping

3. The process of claim 1 comprising the additional step of coating the dyed sutures with silicone rubber in the presence of an amount of peroxide catalyst not substantially exceeding 3%.

4. The process of claim 2 comprising the additional step of coating the dyed sutures with silicone rubber in the presence of an amount of peroxide catalyst not substantially exceeding 3%.

References Cited

UNITED STATES PATENTS

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