

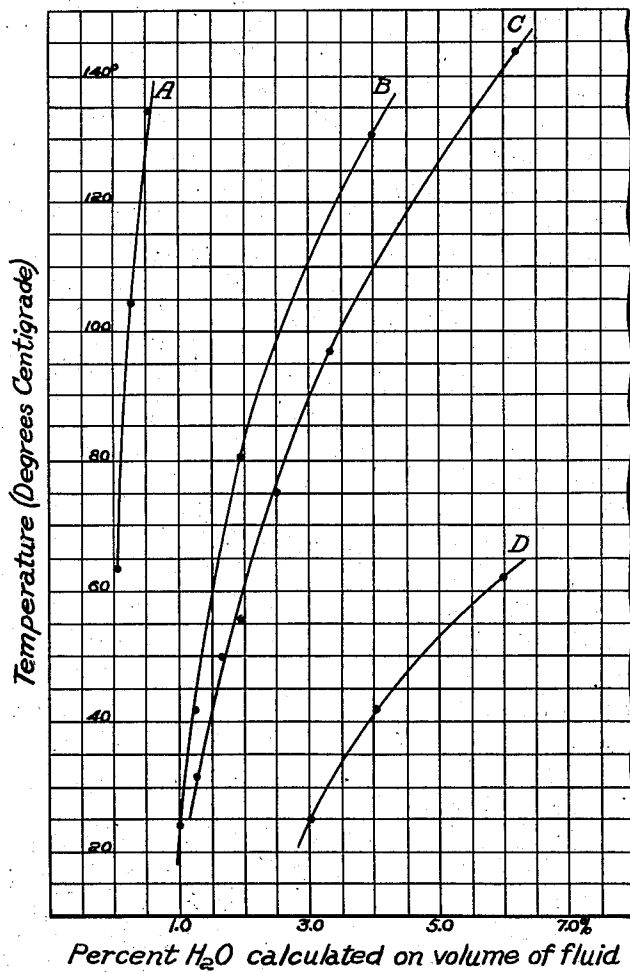
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SYSTEM FOR TUBING SURGICAL MATERIALS

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by

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SYSTEM FOR TUBING SURGICAL MATERIALS

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This invention relates to a system of tubing surgical materials and more specifically to the manufacture of boilable tubed sutures or ligatures.

While the product with which this invention is primarily concerned will be hereinafter referred to as a suture, it will be understood that this term is used, as in manufacturing practice, synonymously with the word "ligature." In addition, in this application the term is used to include sheets or ribbons as well as strands, and the invention deals broadly with a system of tubing surgical products.

Sutures are in many instances supplied to the hospitals and the medical trade in the form of coiled strands of sterile catgut hermetically sealed in glass containers known as suture tubes or ampoules, which tubes contain some type of tubing liquid.

In the preparation of such sutures, high standards of sterility require that the catgut be sealed in sterile form for transportation and storage purposes until brought to the operating room. In order to have the catgut sterile, somewhere in the process of treatment the catgut should be exposed to a high temperature, for example, from 155 to 160° C. for a considerable period.

In addition, surgical practice of high-grade hospitals requires some sort of sterilization or germicidal cleansing of the sealed container in the operating room immediately prior to use, in order to sterilize the exterior of the tube, thus insuring no contamination of the enclosed catgut from this source.

Since hospitals are equipped with heat sterilizers or autoclaves which are used in the sterilization of surgical instruments, swabs and the like, suture manufacturers have supplied tubed catgut sutures which, before the container is broken and the suture removed for use, can be placed in this type of ordinary hospital sterilization equipment, and subjected, along with other surgical accessories, to standard sterilization, normally comprising boiling in water at 100° C. for one-half hour or autoclaving at 121° C. under 15 lbs. steam pressure for one-quarter of an hour. Such sutures are known in the trade as "boilable" sutures, the term implying that the sutures, in the presence of the tubing liquid used therein,

may be subjected to the boiling temperature of water without detriment.

However, such "boilable" sutures, though capable of withstanding, at the hospital, without damage, temperatures equal to or above the boiling point of water, have not, as heretofore provided, been in a condition for immediate surgical use. Their major deficiency is lack of pliability, evidenced by kinks and by harshness, stiffness, and lack of stretchability. With such "boilable" sutures, operating room practice has, therefore, required exposure of the suture, after removal from the tube, to sterile water for a period of time long enough to allow the catgut to absorb sufficient water to soften the catgut, to permit the removal of the kinks and to give the suture characteristics of pliability permitting easy and rapid manipulation and effective knot-tying by the surgeon, and preventing tissue injury in the incision, which might be caused by a harsh or stiff suture.

This water-absorption practice, performed in the operating room—usually by immersion—is a serious obstacle to the provision of proper and uniform sutures, for variations in the temperature of the water or in the length of time of exposure of the suture cause variations in the quality of the product, and the water-absorption step may, if improperly or carelessly performed, ruin the suture. So great are the disadvantages resulting from the necessity of immersing these "boilable" sutures or otherwise exposing them to water prior to use, that sales of this type of suture at the present time amount only to about 20% of total suture sales.

The type of suture which is most largely used does not require water-absorption treatment after the ampoule is broken, since there is included, in the tubing liquid, water in sufficient amount to give the suture its required flexibility and pliability; but, because of the presence of the water in the ampoule, it is not possible to subject these closed ampoules to heat sterilization prior to breaking the ampoule, since exposure of catgut, in tubing fluids of the type heretofore in use containing water, to the standard sterilization temperatures, damages the strength of the suture and may even reduce it to an incoherent jelly-like mass. Accordingly, such su-

tures are called in the trade "non-boilable" sutures. With such "non-boilable" sutures it is customary, by way of sterilization of the ampoule prior to breaking the same, to store the ampoule in an unheated germicidal solution, a treatment which is less certain and effective than sterilization of the exterior of the tube by heat.

Thus the trade has in the past been supplied with two types of suture:

(a) "Boilable"—a suture sealed in an ampoule with a tubing fluid which includes no water, the ampoule being heat-sterilizable but the suture not being pliable without water-absorption prior to use.

(b) "Non-boilable"—a suture sealed in an ampoule with a tubing fluid which includes water, the suture therefore being pliable, but not capable of undergoing standard heat-sterilization in the ampoule without detriment to the suture.

One method used in preparing the "boilable" form of suture is as follows: After the catgut has been subjected to the usual preliminary tanning, polishing and gauging operations, it is placed in an unsealed tube and the entire tube and catgut is subjected to a drying operation to remove any moisture contained in the catgut. The tube is then partially filled with xylene as a tubing fluid and sealed, and thereafter subjected to an oil bath sterilization at about 150° to 160° C. for a period of an hour or more. The drying operation is very carefully performed lest the presence of even a minute quantity of water in the sealed tube cause decomposition of the catgut during sterilization.

A method generally used in preparing the "non-boilable" form of suture is as follows: The catgut, as in the case of the "boilable" suture, is placed in an open tube and completely dried to extract absorbed water. The tube containing the suture is then, prior to sealing the tube, subjected to an oil bath sterilization at about 150° to 160° C. After this open tube sterilization, a certain amount of water is put into the tube, usually in conjunction with ethyl alcohol as a tubing fluid, and the tube is then sealed. This mixture is generally 5% water and 95% ethyl alcohol, but the amount of water is not critical so long as it is sufficient to render the catgut pliable. In this procedure of preparing sutures of the "non-boilable" type, extreme care has to be taken to prevent exposure to bacteria or other pathogenic micro-organisms between completion of the open tube sterilization and sealing, i. e., during filling of the tube, and such an ampoule cannot be subjected to heat sterilization at the hospital prior to use.

The present invention has for its chief object the provision of a "boilable" or heat-sterilizable suture ampoule, in which the suture is pliable and ready for immediate surgical use when removed from the ampoule, without preliminary water immersion or other water-absorption treatment. The terms "sterilizable" or "boilable" are here meant to connote the capacity to be subjected to the temperature of the boiling point of water for an acceptable sterilization period without substantial damage to the suture.

This invention may be viewed as accomplishing the result of making the heretofore known "boilable" suture pliable, or of making the heretofore known "non-boilable" suture sterilizable by heat in the usual hospital auto-clave or by water-boiling.

The invention is based upon the discovery that if water in limited amount be placed in an am-

poule containing a catgut suture, together with certain types of organic substances in proper proportions, water is retained in the suture at normal room temperatures, in sufficient quantity to give the suture the requisite pliability and flexibility, and yet the suture is not disintegrated or damaged when the ampoule is subjected to heat-sterilization at such elevated temperatures, either 100° C. or about 120° C., as are ordinarily employed in water-boiling or in hospital auto-claves.

In practicing the invention, the manufacturer's sterilization step may be performed either by the closed tube method or by the open tube method.

When the closed tube method is used, the sealed ampoule containing the tubing fluid, water and the suture, is subjected to oil bath sterilization at a temperature of 150-160° C. If this closed tube method of sterilization be adopted, the organic substance used in the tubing fluid must be of such character, and of such proportion with relation to the water present in the ampoule, as to prevent disintegration of the suture at this relatively high temperature.

If, on the other hand, the manufacturer's sterilization step be performed by the open tube method, the sterilization, at a temperature of 150-160° C., is carried out before the tubing fluid has been supplied to the tube. Since the temperature to which the sealed ampoule is to be subjected subsequently by a doctor or at a hospital prior to use is only 100° C. to 120° C., different organic substances or different proportions of organic substances with relation to the water content of the ampoule, may then be adequate to prevent damage to the suture during such subsequent sterilization.

It has been found that tubing fluids made in accordance with any one of the following formulae, when used in ampoules sterilized by the closed tube method, give satisfactory results, when, as in the usual practice, a sixty-inch length of any standard size suture is tubed in a 7 cc. capacity tube filled approximately one-half full with tubing fluid.

	Cubic centimeters
1. Diethyl carbonate.....	100.0
Water.....	1.2
2. Diethyl carbonate.....	81.0
Isopropanol.....	19.0
Water.....	1.0
3. Diethyl carbonate.....	84.3
Ethyl lactate.....	15.7
Water.....	1.0
4. Diethyl carbonate.....	84.3
Butyl lactate.....	15.7
Water.....	1.0
5. Diethyl carbonate.....	84.3
Ethyl hydroxy butyrate.....	15.7
Water.....	1.0
6. Ethyl acetal glycolate.....	100.0
Water.....	1.4
7. Ethyl acetal glycolate.....	84.3
Methyl lactate.....	15.7
Water.....	1.3
8. Iso-propyl acetate.....	84.3
Ethyl glycolate.....	15.7
Water.....	1.0
9. n-Hexanol.....	100.0
Water.....	1.0
10. Diacetone alcohol.....	100.0
Water.....	1.0
11. Ethyl n-valerate.....	100.0
Water.....	1.0
12. n-Butyl ether.....	100.0
Water.....	0.8

The figures contained in the foregoing formulae represent volume at 70-80° F.

Examples of formulae which have been found suitable for use as tubing fluids in accordance with this invention when the manufacturer's sterilization is conducted by the open tube method, the 150° C. sterilization thus being performed before the tubing fluid is added, are the following, all amounts being by volume at 70-80° F.

	Cubic centimeters
13. Diethyl carbonate.....	46
Ethyl lactate.....	4
Water..... 1.0-1.4 (1.2 cc. preferred)	
14. Ethyl lactate.....	100
Water..... 2.0-6.0 (4.0 cc. preferred)	
15. Ethyl acetate.....	46
Ethyl lactate.....	4
Water..... 1.0-1.4 (1.2 cc. preferred)	
16. Diethyl carbonate.....	50
Water..... 1.0-1.3 (1.1 cc. preferred)	
17. Diethyl carbonate.....	46
Isopropanol.....	4
Water..... 1.0-1.3 (1.2 cc. preferred)	
18. Diethyl carbonate.....	46
Acetone.....	4
Water..... 1.0-1.3 (1.2 cc. preferred)	
19. Ethyl acetate.....	50
Water..... 1.0-1.3 (1.1 cc. preferred)	
20. Diethyl carbonate.....	45
Ethyl glycolate.....	6
Water..... 1.0-1.3 (1.2 cc. preferred)	
21. Diethyl carbonate.....	45
Ethyl-hydroxy butyrate.....	10
Water..... 1.0-1.3 (1.2 cc. preferred)	
22. Ethyl propionate.....	45
Ethyl glycolate.....	5
Water..... 1.0-1.3 (1.2 cc. preferred)	
23. Diethyl carbonate.....	50
Butyl lactate.....	12
Water..... 1.0-1.3 (1.2 cc. preferred)	
24. 2 ethyl hexanol (octyl alcohol).....	50
Isopropanol.....	10
Water..... 1.0-1.4 (1.2 cc. preferred)	
25. Methyl n amyl ketone.....	35
Ethyl acetate.....	2
Isopropanol.....	6
Water.....	.65
26. Methyl n amyl ketone.....	50
Water.....	.8
27. Acetonyl acetone.....	45
Water.....	.9

As stated, the amount of tubing fluid supplied to any ampoule may be about half the volume of the tube, for example, 3½ cc. of tubing fluid for a 7 cc. capacity tube, but, in any case, each tube after sealing should contain a water-to-organic fluid proportion corresponding to the proportion set forth in the particular formula which is used. If the suture and tube have not been completely dried prior to the addition of the tubing fluid, the amount of moisture which the suture and tube together contain before the addition of the tubing fluid should be treated as a part of the water content in order to give a final water-to-organic fluid proportion in the sealed tube corresponding to the proportion required by the formula used. In fact, in some cases the proportion of water required by a formula may all be present in the catgut, so that no additional water need be added as a part of the tubing fluid.

As indicated by the formulae hereinbefore given, it is often desirable to use a mixture of tubing fluids. One reason for so doing is based upon the mechanical difficulty of distributing

water in many tubing fluids useful in the practice of this invention sufficiently uniformly at normal room temperatures so that ampoules may be successively filled from a large supply, with each ampoule receiving an equal and correct percentage of water. For instance, in the case of formula 1, which is diethyl carbonate alone, for uniform water distribution the supply should be held at a slightly elevated temperature (say 45-50° C.) during the tube filling. But the ampoules may be filled from a supply at room temperature if solubilizing agents such as the substances listed second in certain of the formulae are included in small proportion.

While I am unable to state with certainty the reason for the successful sterilization in the presence of water, I view the result as involving, in the preferred form, the action of a reversible equilibrium system which is set up within the tube, and in which the limited amount of water present is distributed between the catgut and the organic tubing fluid, which is a solvent for the water; and in this system the distribution of water is materially affected by temperature changes, causing water to shift in the direction of the tubing fluid with rising temperature, and to shift in the direction of the catgut with falling temperature. The theory of the presence of such an equilibrium system must be supplemented by the assumption that the organic substances which are used as the tubing fluid, or as a portion thereof, have the property of causing such an amount of shift in the system that, with rising temperatures, practically all absorbed water is extracted from the catgut, but, upon return to normal room temperatures, a similar amount of water is restored to or re-absorbed by the catgut, having been given up by or taken away from the tubing fluid.

This assumption is supported by the fact that if sutures are tubed in accordance with certain of the foregoing formulae and removed from the ampoules while the ampoules are at an elevated temperature, the sutures are lacking in flexibility and pliability, whereas if they are removed after the temperature of the ampoules has fallen from the elevated temperature to room temperature, the sutures are flexible, stretchable and pliable. This at least indicates that at the elevated temperature, water has been removed from the sutures, but is restored to and re-absorbed by the sutures upon reaching the lower temperature.

In any event, the system set up is such that whether water is shifted from the catgut to the tubing fluid or not, during temperature rise the water is held in association or union with the tubing fluid in such manner as to prevent destructive attack of the water upon the catgut, but is again available for plasticizing the catgut upon fall of the temperature to substantially normal room temperature.

Materials, in order to be useful as tubing fluids for the purposes of this invention, must conform to certain requirements:

1. The material must be stable under increasing temperatures at least to 100°, 120° or 150° C. (according to which method of preparation is used).

2. The material must be chemically inert or inactive to catgut over the range from normal room temperature to 100°, 120° or 150° C. (according to which method of preparation is used), at least for periods of time equivalent to normal sterilization periods.

3. The material must have the characteristic

of operating to inactivate the water at elevated temperatures so that the presence of the material in the ampoule prevents destructive decomposition of the catgut, throughout a range from normal room temperature to at least 100° C., by water present in the tube and available to the catgut at normal room temperature in an amount sufficient to render the catgut pliable upon removal from the tube.

Among the organic substances which have properties rendering them suitable for use in accordance with this invention are esters, alcohols, ketones, ethers and aldehydes of the following types:

Esters:

Ethyl acetate
Iso-propyl acetate
n-Amyl acetate
Ethyl propionate
n-Propyl propionate
Ethyl n-butyrate
Ethyl n-valerate
Methyl n-caproate
Di-ethyl carbonate
Di-propyl carbonate
Di-butyl carbonate
Ethyl glycolate
Methyl lactate
Ethyl lactate
Iso-propyl lactate
Butyl lactate
Ethyl hydroxy butyrate
Ethyl acetal glycolate
Propyl crotonate

Alcohols:

n-Butyl alcohol
Amylic alcohol
n-Hexyl alcohol
Cyclohexanol alcohol
Octyl alcohol (2 ethyl hexanol)
Diacetone alcohol

Ketones:

Di-n-propyl ketone
Acetone
Acetonyl acetone
Methyl-n-amyl ketone

Ethers:

n-Butyl ether

Aldehydes:

n-Butyl aldehyde
Iso-butyl aldehyde
n-Heptyl aldehyde
n-Valer aldehyde

The materials listed all have more than three, and, in most cases, not over seven carbon atoms to the molecule.

A method which I have found useful in determining the suitability or lack of suitability of different organic materials for use in accordance with this invention is the following:

A mixture of the organic fluid to be tested, with a predetermined percentage of water, is sealed in a small glass tube, in quantity sufficient partly to fill the tube. The tube is heated to a temperature slightly higher than the temperature at which all trace of water, as indicated by cloudiness in the fluid, disappears. The tube is then allowed to cool slowly in a water bath, until a separate water phase is noted by the first appearance of a cloud in the fluid. The temperature at which this takes place is noted and the percentage of water used represents, for test purposes, the "solubility of water" in that fluid at that temperature.

By repetition of this experiment with different percentages of water, the "solubility of water" in the particular fluid under test at various temperatures may be plotted, thus revealing a solubility curve extending through the range of temperature from normal room temperature to 140° C. or more.

The accompanying drawing illustrates the solubility curves of four substances, determined by the above test. In this drawing, the abscissae represent percentage of water calculated on volume of organic fluid and the ordinates represent temperature in degrees centigrade. Curve A represents the solubility of water in xylene, a tubing fluid heretofore used for "boilable" sutures. Curve B represents the solubility of water in amyl acetate. Curve C represents the solubility of water in diethyl carbonate. Curve D represents the solubility of water in ethyl acetate. The curves of amyl acetate, diethyl carbonate and ethyl acetate, i. e., curves, B, C and D, are given as typical of the substances previously listed as suitable for use in accordance with this invention, the solubility of water in these substances ranging from borderline materials, such as amyl acetate and ethyl-n-butyrate—the former, as shown in the curve B, dissolving about 1% by volume of water at 25° C., and only about 2% at 75° C.—to compounds having curves of less slope, such as diethyl carbonate, which, as shown by curve C, dissolves about 1% of water at 25° C., and about 2.5% of water at 75° C., or such as ethyl acetol glycolate or ethyl acetate—the latter, as shown by the curve D, dissolving about 3% at 25° C., 6% at 60° C., and a still greater percentage of water above 60° C.

An organic fluid which, as determined by the above test, dissolves a minimum amount of water at room temperature, increasing to about 2% at least by volume at 75° C., is of practical value for the purposes of this invention insofar as water dissolving capacity is concerned. Materials which possess a capacity of increasing the amount of water dissolved by at least 0.1% by volume of the fluid with each 5° rise in centigrade temperature and possess a water dissolving capacity of approximately 2% at least at 75° C., are suitable from the standpoint of solubility of water therein.

As shown by the curve A, xylene does not fall within this category; for, while xylene dissolves only a minute quantity of water at room temperature, the solubility percentage does not increase sufficiently rapidly, and does not increase to anywhere near 2% at 75° C., as required in materials suitable for use in accordance with this invention.

Of all the materials listed, herein, the preferred substances are those which, consistent with other necessary properties, have solubility curves of the least slope with increasing temperature plus a minimum water dissolving capacity at room temperature. The latter factor is important because the less the amount of water dissolved by the fluid at normal room temperature, the more readily will the catgut absorb the water contained in the tube at normal room temperature. Thus, substances which have a solubility curve of the type C are to be preferred to those having a curve similar to curve D, despite the fact that the curve D is of less slope. Similarly, given two substances with similar slopes, the substance having the least water dissolving capacity at room temperature is to be preferred.

It should be clearly understood that determina-

tion of water solubility by the above described test is a wholly empirical method for the determination of the practicability of substances for use in accordance with this invention. For example, the fact that, as measured by the above test, diethyl carbonate dissolves more than 1% of water at 25° C., does not mean that when a catgut suture is immersed in a mixture of 100 parts of diethyl carbonate and 1 part of water at 25° C., the association of the water with the diethyl carbonate is so strong as to prevent absorption of an amount of this water by the catgut. Likewise, the fact that, as measured by the above test, diethyl carbonate dissolves more than 4% of water at 120° C., does not mean that when a catgut suture is immersed in a mixture of 100 parts of diethyl carbonate and 4 parts of water, the association of the water with the diethyl carbonate as the temperature rises will be so strong as to prevent detrimental attack by water on the catgut at 120° C. In other words, while the "solubility" test is one test for determining the suitability of a fluid, it does not determine the proportion of water that may be safely used with that tubing fluid.

In fact, it has been found that, with catgut, in using ethyl acetate, the maximum percentage of water which may be safely included when the tube is to be subjected to a temperature approaching 160° C. is from 1.2 to 1.4% of the volume of ethyl acetate; that in using diethyl carbonate the maximum percentage of water is from 1.0 to 1.2% of the volume of the diethyl carbonate; and that in using amyl acetate the maximum percentage of water is from 0.8 to 1.0% of the volume of amyl acetate present, despite the fact that each of these substances dissolves water in an amount more than 2% at temperatures above 100° C. as measured by the above test. The above maximum percentages, however, relate only to the closed tube type of manufacture, that is, wherein the tube containing catgut and fluid is to be subjected to a temperature approaching 160° C. With open tube manufacture the maximum percentage of water which may be included in an ampoule with these substances may be substantially greater. But, even with these maximum percentages, with water present in the range from 0.8 to 1.4% of the volume of the 3½ cc. of tubing fluid, the amount of water present in the ampoule will be from 0.0280 to 0.0490 gram, which may be from about 10% to 22.5% of the combined catgut-water content of the ampoule, assuming the catgut weights from 0.17 to 0.26 gram. These percentage relations are of the order of the percentage of water in catgut suitable to insure pliability, the higher the percentage the more the pliability up to about 20 to 25%. Higher water percentage is undesirable because of its adverse effect on the tensile strength of the catgut.

I have found that when standard sutures are tubed with 3½ cc. of tubing fluids made in accordance with the foregoing formulae, subsection of the ampoule to the temperatures ordinarily used in heat sterilizers or auto-claves in hospital practice does not deleteriously affect the quality of the suture, and that the suture is satisfactory as regards flexibility, pliability and other qualities, without any water absorption treatment upon removal of the suture from the ampoule at normal temperatures. This is particularly true in the case of #0 catgut in which the pliability of a standard sixty inch length of suture tubed in accordance with this invention does not differ noticeably from that of the ordinary "non-boilable" #0 catgut suture. In the larger sizes of

suture, such as the #1 or #2 catgut, the pliability of the same standard sixty inch length suture tubed in 3½ cc. of tubing fluid in accordance with the formulae given is somewhat less than that of the ordinary non-boilable sutures of these sizes, but it is still within the range of pliability acceptable to the surgeon. Where considerations of tube size are not important, it is evident that the organic substance included for the purposes of this invention can be included in greater amount (i. e. more than 3½ cc.) so that a greater percentage of water relative to the weight of the catgut can also be included without acting to hydrolyze the catgut at the elevated temperatures—always with the limit that in excessive quantities the substance may by remote dispersion impair the availability of the water for absorption by the suture at normal room temperatures.

Other materials besides those which operate to secure the results of this invention may be included as a part of the tubing fluid so long as these substances do not deleteriously affect the catgut throughout the range of temperature contemplated for the manufacturer's, doctor's or hospital sterilization, so long as the proper proportion of water to the fluid acting in accordance with this invention is maintained and so long as the amount of water in the tube is sufficient to render the catgut pliable at room temperatures.

For the purposes of this invention, it is essential that the suture at any time upon removal from the sterilized tube be in a condition for immediate surgical use, without other operation than the usual manual stretching to remove temporary kinks arising from the reeling. For surgical use the suture must have a straight pull tensile strength exceeding 25,000 pounds per square inch, and should have an increment of initial permanent plastic flow stretch upon removal from the tube equivalent preferably to at least 3% and not less than 1½% of its length, to permit reeling kinks to be removed by manual stretching. In addition, it is desirable that the suture have, upon removal, as low a modulus of elasticity as is consistent with adequate tensile strength, and permitting, in the small sizes, preferably, a total plastic stretch in the order of 6-10% of the length of the suture upon removal from the ampoule. Sutures tubed in the above described manner will come well above the minimum limits of strength and pliability, even after re-sterilization, and will tie down easily with a tight knot.

Principles to be borne in mind in the practice of this invention include the following:

1. The lower the temperature to which the suture, in the presence of the tubing fluid, is to be subjected, the greater the proportion of water which may be safely included in the tubing fluid.
2. The greater the proportion of organic substance to water in the tubing fluid, the greater will be the protective action of the organic substance against damage to the suture during sterilization at elevated temperature.
3. It is desirable, in order to give the suture proper pliability and flexibility, that the weight of the water contained in the catgut at the time of use shall be about 15% of the dry weight of the catgut.

As examples of materials which are not satisfactory when used as the dominant fluid, regardless of their particular water-holding capacity, there can be mentioned:

- (1) Organic fluids which in and of themselves destructively decompose catgut during steriliza-

tion, so that the catgut becomes unusable (ethyl alcohol, methyl alcohol);

(2) Chlorinated esters which give off lachrymose fumes on heating;

(3) Certain dibasic acid esters which decompose upon heating, building up gas pressures which make their use dangerous (diethyl malonate, ethyl acetal-acetate).

Practical experience leads me to believe that diethyl carbonate is the most satisfactory all-purpose fluid when used in accordance with formula 1 as a 3½ cc. fluid with a 60-inch length of any regulation size catgut from #000 to #3.

The term "catgut suture," as used in the appended claims, is used to include sheets or ribbons, as well as strands, of surgical materials which have peptide linkages and are plasticized by water at normal room temperatures, but are attacked by water at sterilization temperatures, including animal tissues such as catgut, kangaroo tendons, amniotic or allantoic membranes such as described in Patent No. 2,135,399 to Johnson, dated November 1, 1938, and synthetic polymers having the same or different molecules, such as polymers of casein and formaldehyde.

References in the appended claims to "water dissolving capacity" are to be understood as referring to the solubility of water in the fluid as measured by the test above set forth.

I claim:

1. The method of sterilizing a catgut suture which is pliable by reason of an absorbed water content, comprising heating said suture to sterilization temperatures in a sealed enclosure in the presence of a tubing fluid having the capacity in the amount present by volume relation to the total sealed-in water content of said enclosure, of extracting sufficient of the absorbed water from the catgut at elevated temperatures to prevent destructive hydrolysis of said catgut by said water content during sterilization while not materially impairing the availability of said extracted water for re-absorption by said catgut as the temperature of said sealed enclosure returns to normal room temperatures, said tubing fluid being stable and substantially inert chemically to said catgut over a temperature range from normal room temperatures to said sterilization temperatures.

2. A boilable catgut suture ampoule containing hermetically sealed therein a catgut suture together with a sealed-in water content always absorptively available to the catgut at normal room temperatures in quantity sufficient to render said catgut pliable and ready for immediate surgical use without additional water absorption upon removal of said catgut from said ampoule at normal room temperatures, and a sealed-in organic tubing fluid substantially inert to catgut at temperatures ranging from room temperatures to 120° C. included in an amount bearing a predetermined relation by volume to said total sealed-in water content such that the total sealed-in water content does not exceed 2.6% by volume of said tubing fluid and having the capacity in such volume relation of preventing, when said ampoule is sterilized at any temperature up to 120° C., reduction of the tensile strength of said catgut below 25,000 pounds per square inch through decomposition of said catgut by said water content.

3. A boilable catgut suture ampoule containing hermetically sealed therein a catgut suture together with a sealed-in water content always absorptively available to the catgut at normal

room temperatures in quantity sufficient to render said catgut pliable and ready for immediate surgical use without additional water absorption upon removal of said catgut from said ampoule at normal room temperatures, and a sealed-in organic tubing fluid substantially inert to catgut at temperatures ranging from room temperatures to 150° C. included in an amount bearing a predetermined relation by volume to said total sealed-in water content such that the total sealed-in water content does not exceed 1.2% by volume of said tubing fluid and having the capacity in such volume relation of preventing, when said ampoule is sterilized at any temperature up to 150° C., reduction of the tensile strength of said catgut below 25,000 pounds per square inch through decomposition of said catgut by said water content.

4. As a new article of manufacture, a sterilizable catgut suture ampoule containing hermetically sealed therein a reversible equilibrium system comprising a catgut suture, a liquid organic solvent for water, and water distributed between said catgut and said solvent, said organic solvent having an increasing water dissolving capacity with rising temperature, being stable and substantially inert chemically to catgut over a temperature range from normal room temperatures to sterilization temperatures and bearing a predetermined relation by volume to said water such that the distribution of said water between said catgut and said solvent is subject to material variation with changes in temperature shifting in the direction of the organic solvent with rising temperature and shifting in the direction of the catgut with falling temperature, a substantial amount of water in said system being absorbed in said catgut at temperatures in the range of normal room temperatures, whereby said catgut is pliable and ready for immediate surgical use without additional water absorption upon removal of said suture from said ampoule at said temperatures, and the amount of water absorbed in said catgut being materially reduced as the temperature of said ampoule rises to sterilization temperature, whereby said ampoule may be sterilized without destructive decomposition of the catgut by water in said system.

5. As a new article of manufacture, a sterilizable catgut suture ampoule containing hermetically sealed therein a reversible equilibrium system comprising a catgut suture, a tubing fluid, and water distributed between said catgut and said tubing fluid, the weight of said water being equivalent to at least 10% of the combined weight of the catgut and the water, said tubing fluid being stable and substantially inert chemically to catgut over a temperature range from normal room temperatures to sterilization temperatures and bearing a predetermined relation by volume to said water such that the distribution of said water between said catgut and said tubing fluid is subject to material variation with changes in temperature, shifting in the direction of the tubing fluid with rising temperature and shifting in the direction of the catgut with falling temperature, a substantial amount of water in said system being absorbed in said catgut at temperatures in the range of normal room temperatures, whereby said catgut is pliable and ready for immediate surgical use without additional water absorption upon removal of said suture from said ampoule at said temperatures, and the amount of water absorbed in said catgut being materially reduced as the temperature of said ampoule

risers to sterilization temperature, whereby said ampoule may be sterilized without destructive decomposition of the catgut by water in said system.

6. As a new article of manufacture, a sterilizable catgut suture ampoule containing hermetically sealed therein a reversible equilibrium system comprising a catgut suture, a tubing fluid, and water distributed between said catgut and said tubing fluid, the volume of said water being within the range from about 0.8% to about 2.6% of the volume of said tubing fluid, the weight of said water being equivalent to at least 10% of the combined weight of the catgut and the water, said tubing fluid being stable and substantially inert chemically to said catgut over a temperature range from normal room temperatures to sterilization temperatures, and the distribution of said water between said catgut and said tubing fluid being subject to material variation with changes in temperature shifting in the direction of the tubing fluid with rising temperature and shifting in the direction of the catgut with falling temperature, a substantial amount of water in said system being absorbed in said catgut at temperatures in the range of normal room temperatures, whereby said catgut is pliable and ready for immediate surgical use without additional water absorption upon removal of said suture from said ampoule at said temperatures, and the amount of water absorbed in said catgut being materially reduced as the temperature of said ampoule rises to sterilization temperature, whereby said ampoule may be sterilized without destructive decomposition of the catgut by water in said system.

7. A boilable catgut suture ampoule containing a catgut suture, water, and as a tubing fluid, diethyl carbonate, the water being in proportion within the range of only about 0.8% to about 2.6% by volume of the diethyl carbonate.

8. A boilable catgut suture ampoule containing hermetically sealed therein a length of catgut, a total sealed-in water content in excess of $\frac{1}{2}$ of 1% by weight of said catgut exposed to said catgut, and diethyl carbonate in an amount by volume exceeding 40 times the volume of total sealed-in water content.

9. A boilable catgut suture ampoule capable of sterilization without destructive decomposition of an enclosed catgut suture comprising a container having hermetically sealed therein a catgut suture, water, and as a tubing fluid therefor, diethyl carbonate, the total sealed-in water content of said container not exceeding 2.6% by volume of the diethyl carbonate, but by weight exceeding 10% of the combined weight of the catgut suture and water content.

10. A boilable catgut suture ampoule capable of sterilization at a temperature exceeding 120°

C. without destructive decomposition of an enclosed catgut suture comprising a container having hermetically sealed therein a catgut suture, water, and as a tubing fluid therefor, diethyl carbonate, the total sealed-in water content of said ampoule being by volume within the range of about 0.8% to about 1.2% of the volume of the diethyl carbonate, and by weight exceeding 10% of the combined weight of the catgut suture and water content.

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