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3,806,474

HYDROPHILIC POLYESTER URETHANE FOAM

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No Drawing. Continuation-in-part of abandoned application Ser. No. 92,250, Nov. 23, 1970. This application Dec. 27, 1972, Ser. No. 318,730

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5 Claims

ABSTRACT OF THE DISCLOSURE

A sponge is made of a polyester polyurethane having a density of 3 to 4.5 lb./cu. ft., a volume swell in water of 20–50% and a cell size of 100 to 5 cells per linear inch. The sponge is prepared using three different surfactants and has an open cell structure.

This application is a continuation-in-part of application Ser. No. 92,250 filed Nov. 23, 1970 and now abandoned.

The present invention relates to a hydrophilic polyurethane foam in sponge form.

There are many polyurethane foams on the market for use as sponges. However, these sponges do not have the water holding or wiping properties of cellulose sponges. Also they are not hydrophilic.

It is an object of the present invention to provide an improved polyurethane sponge.

Another object is to prepare a polyurethane sponge of improved water holding power.

A further object is to prepare a non-shrinking polyurethane sponge.

An additional object is to prepare a polyurethane sponge having improved wiping properties.

Yet another object is to prepare a polyurethane sponge which is soft when dry.

It has now been found that these and other objects of the invention which will be revealed hereinafter can be accomplished by preparing a polyurethane sponge of specific composition which has the water holding, wiping and other performance properties of a cellulose sponge, but also is soft when dry.

All of the functions of the materials present in the composition are essential. Hence all of the materials must be present or they must be replaced by equivalent materials. The physical properties of the sponge must also be as described, or the performance will not be suitable.

The general description of the foam or sponge is that it must be the reaction product of a prepolymer of toluene diisocyanate with polyethylene oxide and a linear difunctional diethylene glycol adipate polyester. The polyurethane foam should have a density of 3.0 to 4.5 lb./cu. ft., preferably being at least 3.5 lb./cu. ft., it should have a volume swell in water of 20–50% preferably at least 35%, have a mixture of cell sizes ranging from very fine to coarse, i.e. 100 cells per linear inch to 5 cells per linear inch and it must include three specific types of surfactant, preferably in a total amount of 0.2 to 30% based on the polyurethane, to improve the initial wetting of the foam or sponge. The cells are open cells.

The starting polyester preferably has a molecular weight of 1000–3500, most preferably 2000. The polyester as stated in polymerized diethylene glycol adipate.

It is critical that the toluene diisocyanate employed be the mixture of isomers containing 65% 2,4 isomer and 35% 2,6 isomer since when the 80% 2,4 isomer and 20% 2,6 isomer, such as that used in Elkins Pat. 2,965,584 under the trade name Hylene TM, is employed in the formulations of the invention the foam obtained is

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a non-porous, closed cell foam. Such a non-porous foam contains carbon dioxide in the bubbles which gradually leak out and the foam shrinks. In contrast to the foams of the invention the bubbles break but are strong enough to keep the structure (i.e. the foam is permanent) and no shrinkage.

The toluene diisocyanate is reacted with a polyalkylene glycol of molecular weight 500 to 2000 to form a quasi prepolymer. Preferably polyethylene glycol is used (e.g. prepared from ethylene oxide) but there can also be used polypropylene glycol in the same molecular weight range. The toluene diisocyanate is used in an amount sufficient to react with all of the polyalkylene glycol and to have a slight excess of free isocyanate. The isocyanate content of the quasi prepolymer is 3 to 15%.

The quasi prepolymer is then reacted with the polyester and free water to form the open cell foam.

As a foam stabilizer there is preferably used Span 60 which is sorbitan monostearate but there can also be used sorbitan monopalmitate (Span 40) sorbitan monolaurate (Span 20), or sorbitan monooleate (Span 80). These surfactants are sorbitan monoesters of fatty acids having 12 to 18 carbon atoms.

To obtain the desired large bubble formation there is employed Tween 80 which is polyoxyethylene sorbitan monooleate (20 ethylene oxide units) but there can also be employed polyoxyethylene sorbitan monolaurate (Tween 20) polyoxyethylene sorbitan monopalmitate (Tween 40) or polyoxyethylene sorbitan monostearate (Tween 60), in each case there being 20 ethylene oxide units per molecule. These surfactants are polyoxyethylene sorbitan monoesters of fatty acids having 12 to 18 carbon atoms and have 20 ethylene oxide units per molecule.

To facilitate initial wetting there is used a surfactant which does not react with isocyanates and which does not affect foam stability. For this purpose there is employed Igepon AC-78 which is the coconut oil acids ester of sodium isethionate.

A preferred range of proportions is 65 to 180 parts of the quasi prepolymer of the polyalkylene glycol and toluene diisocyanate, 20 to 60 parts of diethylene glycol adipate, 0.5 to 3 parts of the Span 20 or similar material, 0.5 to 3 parts of Tween 80 or similar material and 2 to 20 parts of Igepon AC-78.

To carry out the foaming reaction there can be used any of the conventional basic catalysts employed in polyurethane foam technology, i.e. N-methyl morpholine, N-ethyl morpholine, trimethyl amine, triethyl amine, tributyl amine and other trialkyl amines, 3-diethylaminopropionamide, triethylamine citrate, triethylene diamine, diethylethanolamine, N,N,N',N'-tetraakis (hydroxypropyl) ethylene diamine, N,N'-dimethylpiperazine, N,N-dimethylhexahydroaniline, tribenzyl amine and sodium phenolate. In the above preferred formulation the amine is used in an amount of 0.1 to 4.0 part, but this can be varied.

Likewise tin compounds can be included such as stannous octoate, stannous oleate, dibutyltin dilaurate, dibutyltin diacetate, di-2-ethylhexyltin oxide, octylstannous acid, dibutyltin diethoxide, tributyltin monolaurate, dioctyltin diacetate, dibutyltin maleate, trimethyltin hydroxide, trimethyltin chloride, as well as other tin compounds set forth in Hostettler French Pat. 1,212,252. The amount of tin compound used is not critical and can be varied as is conventional in the art. In the preferred formulation it is 0.01 to 1.0 part. Water is preferably used as the foaming agent and is employed in amounts conventional in the art, e.g., 0.5 to 5.0 parts per 100 parts of polyurethane forming materials.

Unless otherwise indicated all parts and percentages are by weight.

EXAMPLE 3

A typical preferred formulation range is the reaction product of 50-150 parts of polyethylene oxide of 500-2000 molecular weight with 15-30 parts of toluene diisocyanate, 20-60 parts of difunctional diethylene glycol adipate of molecular weight 1000-3500, 0.1-1.0 part of DABCO (triethylene diamine), 0.15-3 parts of N-methyl morpholine, 0.01-1.0 part of a stannous octoate, 0.5-3 parts of Span 20, 0.5-3 parts of Tween 80 and 2-20 parts of Igepon AC-78.

A specific example of preparing a preferred sponge having the above described properties is set forth below:

EXAMPLE 1

The quasi prepolymer from 60 parts of polyethylene oxide having a molecular weight of 1000 with 25 parts of toluene diisocyanate (65% 2,4 isomer, 2,6 isomer), 40 parts of diethylene glycol adipate molecular weight 2000, 1.8 parts of water, 0.5 parts of DABCO, 1.5 parts of methyl morpholine, 0.1 part of stannous octoate, 1 part of Span 60, 1 part of Tween 80 and 10 parts of Igepon AC-78 were mixed to form a foam in the shape of a sponge having a density of 3.5 lb./cu.ft., a volume swell in water between 20-50% and mixed cell sizes ranging from 100 to 5 cells per linear inch. The sponge had the water holding and wiping properties of a cellulose sponge and was soft when dry. The sponge when dry did not shrink upon standing and the cells were of the open type, i.e., when the foam was foamed the bubbles broke but were strong enough to retain the structure of the sponge.

EXAMPLE 2

45.6 g. of a prepolymer made by reaction of 241 grams of Carbowax 1540 (a polyethylene oxide with a molecular weight of 1000, and 125 g. of Hylene TM 65, (a mixed toluene diisocyanate having 65% of the 2,4 isomer, and 35% of the 2,6 isomer).

20.0 g. polyester F-15-22, a diethylene glycol adipate polyester having a hydroxyl number of 55,

0.7 g. H₂O

2.0 g. methyl morpholine

0.2 g. stannous octoate

0.2 g. Span 60

0.5 g. Tween 80

2.5 g. Igepon AC-78, a coconut acid ester of sodium isethionate, made by GAF.

The foam prepared by this formulation had a density 4.7 lbs. per cubic foot and swelled 108% by volume when immersed in water. It had both large and small cells, and formed profuse amounts of lather when squeezed in water. The cells in the foam were of the open cell type.

If the Igepon AC-78 surfactant is replaced with a surfactant such as Triton X-100, the foam collapses during formation. The Igepon AC-78 has no effect in the foam formation, but is released when the foam is wet with water. The Tween 80 is the foam stabilizer, which allows the foam to form. If it is omitted, the foam collapses during formation. The Span 60 creates the large cells. Their size and number depends on the amount added.

The formulation is a partial or quasi prepolymer formulation. If the same composition is run as a one shot foam, the foam is closed cell, shrinks and is unuseable. If the TM-65 is replaced with 80:20 TDI, the foam is closed cell even if a quasi prepolymer formulation is used.

47 g. prepolymer (made from 60 parts of Carbowax 1540 and 34 parts of TM 65)

0.9 g. H₂O

2.0 g. methyl morpholine

0.2 g. stannous octoate

0.5 g. Tween 80

0.1 g. Span 60

2.5 g. Igepon AC-78

This formulation had a density of 3.1 lb./per cubic foot, and swelled 45% by volume in water. The cells of the foam were open cells.

What is claimed is:

1. A linear polyester based polyurethane sponge characterized by having the water holding and wiping properties of a cellulose sponge and also being soft and non-shrinking when dry, said sponge having a density of 3.0 to 4.5 lb./cu.ft., a volume swell in water of 20 to 50% and mixed open cells having cell sizes ranging from 100 to 5 cells per linear inch, and having dispersed through the sponge 3 surfactants, said surfactants being (a) a sorbitan monoester of a fatty acid having 12 to 18 carbon atoms, (b) a polyoxyethylene sorbitan monoester of a fatty acid having 12 to 18 carbon atoms and 20 ethylene oxide units per molecule, and (c) the sodium salt of an ester of sodium isethionate, said sponge having been prepared by reacting the diethylene glycol adipate polyester with the quasi prepolymer of polyalkylene glycol and excess toluene diisocyanate in the presence of said surfactants and water, the alkylene units of said polyalkylene glycol containing 2 to 3 carbon atoms and the toluene diisocyanate containing 65% of the 2,4 isomer and 35% of the 2,6 isomer.

2. A sponge according to claim 1 wherein the polyester has a molecular weight of 1000 to 3500 and the polyalkylene glycol has a molecular weight of 500 to 2000.

3. A sponge according to claim 2 wherein (a) is sorbitan monostearate, (b) polyoxyethylene sorbitan monooleate and the polyalkylene glycol is polyethylene glycol.

4. A sponge according to claim 3 wherein the polyurethane is made from 65 to 180 parts of the quasi prepolymer, 20 to 60 parts of the diethylene glycol adipate polyester and there are present in the sponge 0.5 to 3 parts of (a), 0.5 to 3 parts of (b) and 2 to 20 parts of (c).

5. A process of preparing the sponge of claim 1 comprising reacting a quasi prepolymer of the polyalkylene glycol and toluene diisocyanate with said polyester in the presence of water and surfactants (a), (b), and (c).

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(21) International Application Number: PCT/US83/00495 (22) International Filing Date: 6 April 1983 (06.04.83) (31) Priority Application Number: 387,988 (32) Priority Date: 14 June 1982 (14.06.82) (33) Priority Country: US (71) Applicant: BAXTER TRAVENOL LABORATORIES, INC. [US/US]; One Baxter Parkway, Deerfield, IL 60015 (US). (72) Inventors: BOGGS, Daniel, R. ; 334 W. Jefferson Court, Vernon Hills, IL 60061 (US). McGLOTHLIN, Mark, W. ; 254 Harvest Court, Vernon Hills, IL 60061 (US). (74) Agents: CARUSO, John, A. et al.; One Baxter Parkway, Deerfield, IL 60015 (US).		(81) Designated States: AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), JP, SE (European patent). Published <i>With international search report.</i>
(54) Title: WETTABLE HYDROPHOBIC HOLLOW FIBERS (57) Abstract A bundle (12) of hydrophobic membranes (18) made of hydrophobic plastic containing micropores of less than 10 microns in diameter is treated with an organic solvent containing monoester-type surface active agent to coat the micropores, to permit aqueous liquid to easily flow through the micropores. The coated membranes (18) are not toxic and are particularly compatible with blood, exhibiting very low hemolysis.		

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WETTABLE HYDROPHOBIC HOLLOW FIBERSTechnical Field and Prior Art

Hydrophobic membranes, and particularly microporous membranes, have proven useful in the field of blood handling for oxygenation of blood, and also for the practice of membrane plasmapheresis in which plasma from the blood passes through the membrane for collection, while the cells are retained.

It would be desirable to make use of the known advantageous flow and diffusion characteristics of a hollow fiber design of membrane in which a bundle of hollow microporous hydrophobic fibers carry blood or other fluid, while performing a separation process with respect to the blood, for example, by allowing plasma to pass through the micropores of the fibers. The blood cells, and in some instances high molecular weight components of the plasma, cannot pass through the micropores.

However, in the event that microporous hydrophobic material is used, it is difficult to get blood or any other aqueous solutions to flow through the micropores because of their hydrophobic nature.

In Leonard U.S. patent application Serial No. 901,945, filed May 1, 1978, corona treatment is used to provide a hydrophobic microporous membrane with a hydrophilic outer surface in which the micropores retain their hydrophobic characteristic.

It is taught in Japanese Patent No. 79/153872 to render porous, polypropylene membranes hydrophilic by treatment with a water solution of sodium lauryl sulfate or the like (Chemical Abstracts 92: 148121k (1980)).

U.S. Patent No. 4,087,567 teaches an anticoagulant coating composition suitable for coating the interior surfaces of a blood microsample collection tube such as a



capillary tube, typically made of glass. The coating composition consists essentially of ethylene diamine tetraacetate held in a matrix of polyvinyl pyrrolidone.

However, none of these systems are suitable for the purpose of this invention of rendering hydrophilic with an organic solvent bundles of hollow fibers or other membrane made out of a hydrophobic plastic such as polypropylene, particularly in a manner which is highly compatible with blood, exhibiting very low hemolysis and essentially no toxicity in the doses applied.

Description of the Invention

By this invention hydrophobic membrane, typically containing micropores of less than 10 microns, can be rendered hydrophilic to facilitate the flow of aqueous liquids such as blood therethrough, with a separated material passing through the micropores. This invention is particularly contemplated for use in separation devices containing bundles of hydrophobic, microporous hollow fibers, but the invention is not intended to be limited to such use, but can be used as desired in the medical or other fields for generally improving the flow characteristics of aqueous liquids through narrow flow channels defined by hydrophobic plastic surfaces.

In accordance with this invention, one may apply to the bores of a bundle of hollow fibers made of a hydrophobic plastic such as polypropylene a solution of 0.3 to 14, and preferably 1.9 to 3.2, weight percent of a surface active agent in a volatile organic solvent. The surface active agent consists essentially of a nonionic ester of a carbohydrate moiety and an organic monoacid of 8 to 30 carbon atoms. Thereafter, the hollow fiber is dried to cause the surface active agent to coat the surfaces of the fibers, including their micropores, whereby aqueous liquids can easily flow therethrough.



It has been found that this particular family of surface active agents is particularly compatible with blood, with lower hemolysis, for example, than other candidate surface active agents such as polyoxyalkylene glycol type surface active agents.

It is preferred for the volatile organic solvent to be a Freon-type material, i.e., a fluorochlorocarbon compound of no more than about 3 carbon atoms. The specific surface active agents of this invention exhibit improved solubility in such organic solvent materials. It is also understood that a minor amount of hydrogen may also be present in the fluorochlorocarbon compounds utilized in this invention if desired.

The surface active agents used in this invention also exhibit improvements over surface active agents of the polyoxyalkylene glycol type in that the surface active agents of this invention are more efficient, more easily metabolized, and are subject to lower degree of toxic reaction.

A specific example of the surface active agent of this invention which is preferred is a mixture of monoesters of sorbitan with capric, lauric, myristic, palmitic and/or oleic acids. As a specific example, the mixture may include the following typical weight percentages of monoesters, sold as Span 20 by ICI Americas Inc.: sorbitan caprate 1.1%; sorbitan laurate 43.5%; sorbitan myristate 27.8%; sorbitan palmitate 19.2%; and sorbitan oleate 8.4%. However, other analogous esters can be used, pure or mixed, preferably monoesters of carbohydrates such as sorbitan, glucose, fructose, or other metabolizable carbohydrates of preferably 5 to 6 carbon atoms. The organic monoacids used of 8 to 30, and preferably 10 to 20, carbon atoms, may be any appropriate monoacid which reacts with the carbohydrate moiety to preferably form a monoester,



i.e., one carbohydrate molecule reacted with one monoacid molecule. The acids which may be used include those described above or others such as tridecanoic acid, or mixed acids such as linseed oil acids, to provide an appropriate hydrophobic portion, combined with the hydrophilic carbohydrate moiety to form the desired surface active agent.

The volatile organic solvent utilized preferably is selected from the group consisting of alcohols of no more than 3 carbon atoms, for example, methanol, ethanol, or isopropanol, ethers of no more than 4 carbon atoms, for example diethylether, and fluorochlorocarbon compounds of no more than about 3 carbon atoms, i.e., Freon-type materials such as 1,1,2-trichloro-1,2,2-trifluoroethane.

The fluorochlorocarbon compounds of no more than 3 carbon atoms are preferred because of their high volatility and low flammability. The vapors of the fluorochlorocarbon compounds or other solvents may be recycled for condensation and reuse.

The hollow fibers treated in accordance with this invention may preferably define micropores in their walls of a size of typically no more than a 5 micron and preferably 1 micron mean diameter, and preferably sized to permit blood plasma to flow therethrough, but to prevent the passage of substantial numbers of blood cells therethrough. To this end it is generally preferable for the mean pore size to be no greater than 0.6 micron, and typically no greater than 0.55 micron, down to 0.1 micron. Generally the pores are at least 0.05 micron in diameter.

Generally if the purpose of use of the treated hollow fibers is to separate plasma from blood cells, the size of the pores may be about 0.3 to 0.55 micron. At lower pore sizes, particularly below 0.1 micron, plasma may be fractionated, separating out lower molecular weight components from higher molecular weight components of the plasma.



While the hollow fiber may be made of polypropylene as stated above, it may also be made of any hydrophobic material as may be desired, for example polyethylene, or copolymers containing polypropylene or polyethylene units 5 copolymerized with butadiene, divinylbenzene, styrene, or other units, as well as other hydrophobic plastic materials.

The bore diameters of the hollow fibers are preferably from 0.2 to 0.5 millimeter.

10 Description of the Drawings

In the drawings, Figure 1 is a longitudinal sectional view of a diffusion device in accordance with this invention.

Figure 2 is a greatly enlarged longitudinal sectional 15 view of a single, hollow fiber in accordance with this invention.

Description of Specific Embodiment

Referring to the drawings, Figure 1 shows a diffusion device which can be used as a membrane plasmapheresis 20 device. The overall structure of the device may be in accordance with conventional design for a hollow fiber separation device (e.g., a dialyzer), except as otherwise described herein.

Hollow tubular casing 10 is shown to contain a bundle 25 12 of hollow, hydrophobic fibers made preferably of polypropylene or a hydrophobic copolymer thereof. As is conventional, casing 10 defines manifold end caps 14 surrounding an end mass of potting material 16, through which the individual fibers 18 of bundle 12 penetrate to 30 provide flow communication between inlet 20 and outlet 22 through the bores 24 of hollow fibers 18. This serves typically as the blood flow path through the separation device.



Outlet port 26 communicates with the spaces within bundle 12 but outside of the individual fibers 18, and also manifold spaces 28, 32. In the case of an oxygenator, inlet port 30 can be provided to provide oxygen to manifold space 32, where the oxygen flows between the individual, hollow fibers 18 to collect in manifold space 28 and to pass outwardly through port 26.

In the event that the device is a membrane plasmapheresis device, inlet port 30 is unnecessary, but may be present as a second outlet. The product passing through outlet port 26 is blood plasma, which passes through the wall of hollow fiber 18 from bore 24 to the space between the individual fibers 18, for draining out of outlet port 26, and also port 30, if desired.

Typically, the hollow fibers 18 contain a multitude of micropores 34 which are typically less than 1 micron in size, and are preferably about 0.3 to 0.55 micron in the case of membrane plasmapheresis.

After building of the separation device as shown in Figure 1, substantial difficulties may exist in passing aqueous solutions such as blood through the micropores 34 of hollow fibers 18, because of the natural hydrophobic nature of the material from which they are made. Accordingly, an impure form of sorbitan fatty acid esters (for example, Span 20 sold by ICI Americas) can be mixed in a proportion of, for example about 10 to 16.3 weight percent in a reactor with the balance being 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) and stirred or shaken to dissolve the Span 20 into the Freon material. The mixture is then allowed to stand quietly until it fractionates into two separate fractions. The lower fraction is a solution of Freon 113 and the purified sorbitan monoester mixture (hereafter called sorbitan monolaurate), and is collected for further use.



The collected solution is further diluted with Freon 113 to a sorbitan monolaurate concentration of about 1.9 to 3.2 percent by weight. A bundle 12 of hollow fibers, installed in casing 10 and sealed with sealant 16 in conventional manner, with the end caps 14 off, is positioned to receive the diluted Freon solution of sorbitan monolaurate through port 26, with the solution passing into bores 24 of the hollow fibers through micropores 34. The hollow fibers are then allowed to drain by gravity, centrifuged for final draining, and dried in an oven at about 135° F. Thus a film of sorbitan monolaurate adheres to the surfaces of each fiber 18 including the inner surfaces of micropores 34. Following this, end caps 14 may be applied to the device, and it may be sterilized by treatment with ethylene oxide or other desired sterilization technique.

The resulting device readily receives blood flow in a uniform, complete manner through micropores of the individual fibers 18 for membrane plasmapheresis, or blood fractionation, or for other separation techniques with other aqueous solutions than blood. Such treatment with blood has been shown to be feasible without unacceptable levels of hemolysis or other ill effect.

The above has been offered for illustrative purposes only, and is not intended to limit the scope of the invention of this application, which is as defined in the claims below.



THAT WHICH IS CLAIMED IS:

1. The method of applying a hydrophobic membrane made of hydrophobic plastic, containing micropores of less than 10 microns diameter, a solution of 0.3 to 14 weight percent of a surface active agent in a volatile organic solvent, said surface active agent consisting essentially of a nonionic ester of a carbohydrate moiety and an organic monoacid of 8 to 30 carbon atoms, and thereafter drying said membrane to cause said surface active agent to coat said micropores, whereby aqueous liquids easily flow through said micropores.

2. The method of Claim 1 in which said membrane is a bundle of hollow fibers which define micropores in their walls of a size to permit blood plasma to flow there- through but to prevent the passage of substantial numbers of blood cells therethrough.

3. The method of Claim 2 in which said hollow fibers are made of polypropylene.

4. The method of Claim 2 in which said volatile organic solvent is selected from the group consisting of alcohols of no more than 3 carbon atoms, ethers of no more than 4 carbon atoms, and fluorochlorocarbon compounds of no more than 3 carbon atoms.

5. The method of Claim 2 in which the bore diameter of said hollow fiber is from 0.2 to 0.5 mm. and said hollow fibers define micropores in its wall of no more than 1 micron diameter.



6. The method of Claim 2 in which said surface active agent is a monoester.

7. The method of Claim 6 in which said surface active agent is sorbitan monolaurate.

5 8. The method of applying to the bores of a bundle of hollow fibers made of hydrophobic plastic having micropores less than 10 microns in diameter a solution of 0.3 to 14 weight percent of a surface active agent in a volatile organic solvent consisting essentially of a fluoro-
10 chlorocarbon compound of no more than 3 carbon atoms, said surface active agent comprising a nonionic monoester of a carbohydrate moiety and an organic monoacid of 10 to 20 carbon atoms, and thereafter drying said bundle of hollow
15 bores of said fibers, whereby aqueous liquids easily flow therethrough.

9. The method of Claim 8 in which said hollow fibers are made of polypropylene.

10. The method of Claim 9 in which said hollow fibers
20 define micropores in their wall of less than 0.05 to 0.6 micron mean diameter to permit blood plasma to flow there-through but to prevent the passage of substantial numbers of blood cells therethrough.

11. The method of Claim 10 in which said organic solvent
25 is 1,1,2-trichloro-1,2,2-trifluoroethane.

12. The method of Claim 11 in which said surface active agent is a mixture of sorbitan monoesters, dissolved in a solution concentration of 1.9 to 3.2 weight percent.



13. A membrane made of hydrophobic plastic having micropores of no more than essentially 5 microns mean diameter, said micropores being coated with a film of a surface active agent consisting essentially of a nonionic ester of a carbohydrate moiety and an organic monoacid of 8 to 30 carbon atoms.

14. The membrane of Claim 13 in which said surface active agent is a monoester.

15. The membrane of Claim 13 in which said surface active agent is a mixture of monesters including sorbitan monolaurate.

16. The membrane of Claim 13 which is made of polypropylene.

17. The membrane of Claim 13 which is a hollow fiber defining micropores in its wall no more than 1 micron in diameter and of a size to permit blood plasma to flow therethrough but to prevent the passage of substantial numbers of blood cells therethrough.

18. The hollow fiber of Claim 17 having a bore diameter of 0.2 to 0.8 millimeter and defining micropores in its wall of 0.05 to 0.6 micron mean diameter.

19. A bundle of the hollow fibers of Claim 18.

20. A bundle of hollow fibers made of hydrophobic plastic and having micropores of a mean diameter of 0.1 to 0.6 micron, said micropores carrying a coating of a non-ionic monoester of a carbohydrate moiety and an organic monoacid of 10 to 20 carbon atoms.



21. The bundle of Claim 20 in which said monoester is sorbitan monolaurate.

22. The bundle of Claim 20 in which said hollow fibers define micropores in their walls of a size to
5 permit blood plasma to flow therethrough but to prevent the passage of substantial numbers of blood cells there-through.

23. The bundle of Claim 22 in which said hollow fibers are made of polypropylene.

10 24. The bundle of Claim 23 in which the bore diameter of said hollow fibers is from 0.2 to 0.5 millimeter.

25. A membrane plasmapheresis device made from the bundle of Claim 24.



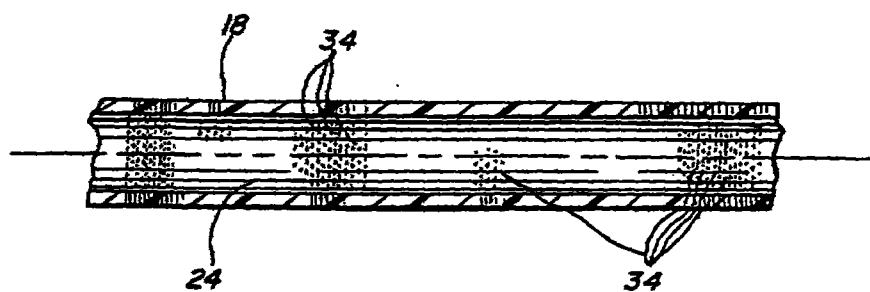
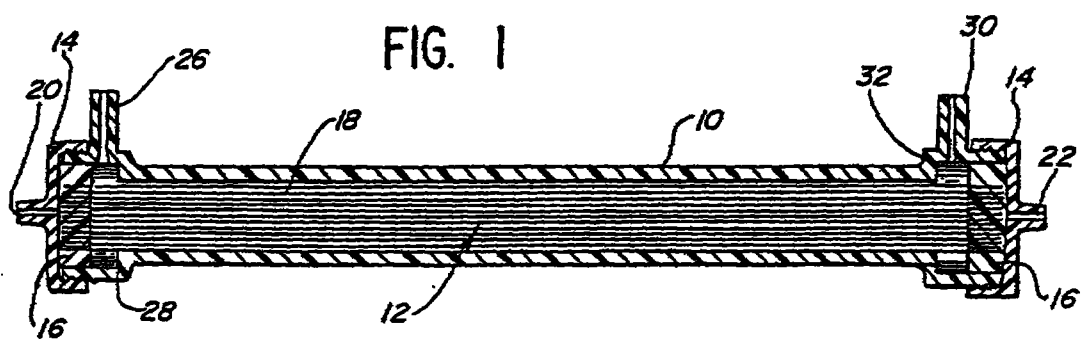


FIG. 2



INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/00495

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. ³ B01D 31/00		
U.S. CL. 210-433.2		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System	Classification Symbols	
U.S.	210/433.2, 500.2, 638, 654, 927 422/48 427/244, 245, 246	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 3,228,876, PUBLISHED 11 JANUARY 1966, MAHON.	2-12 and 17-25
X	US, A, 3,772,072, PUBLISHED 13 NOVEMBER 1973, BROWN, ET AL.	1-25
A	US, A, 4,087,388, PUBLISHED 02 MAY 1978, JENSEN, ET AL.	
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report *	
11 JULY 1983	21 JUL 1983	
International Searching Authority ¹	Signature of Authorized Officer ²²	
ISA/US	FRANK SPEAR	

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