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W. A. AYRES
ANTICOAGULANT MATERIAL HAVING CHARGED ELECTROSTATIC
SURFACES SUITABLE FOR USE IN PROSTHETIC DEVICES
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3,609,768

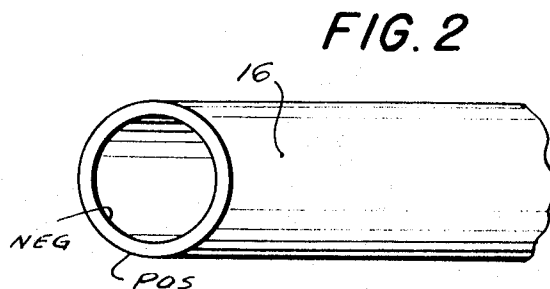
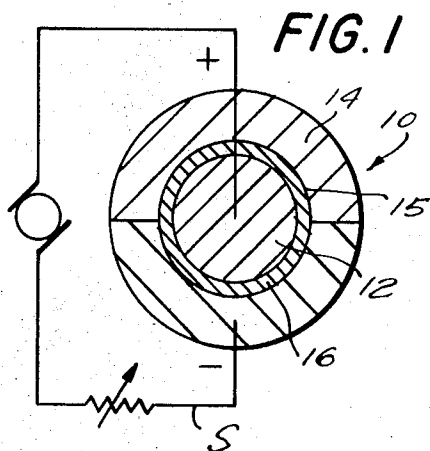


FIG. 5

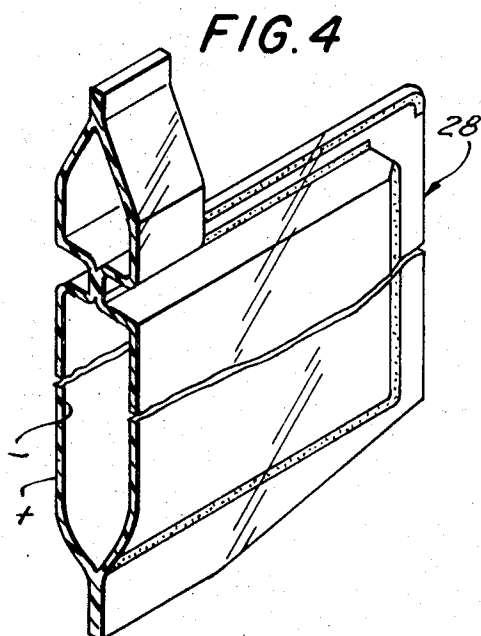
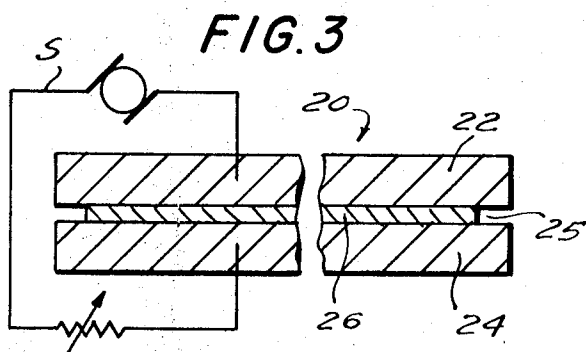
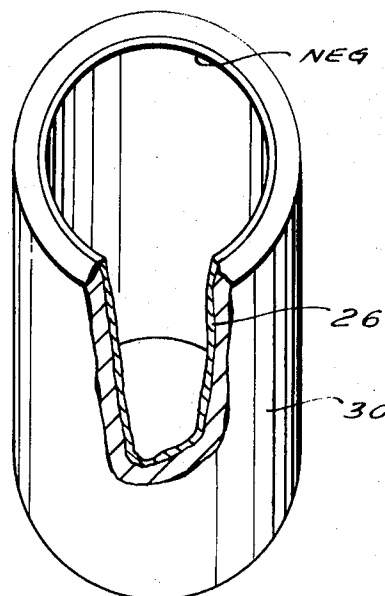
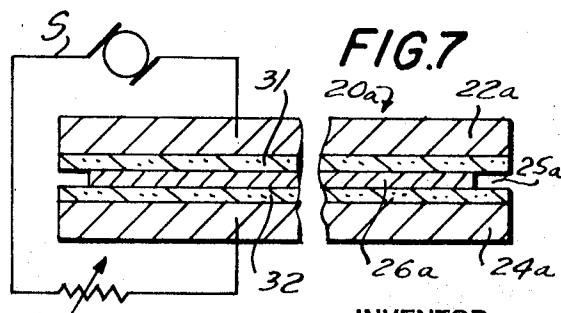
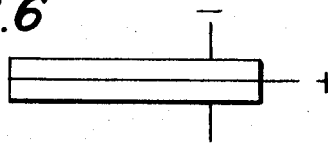


FIG. 6



INVENTOR

WALDEMAR A. AYRES

BY

Kane, Johnson, Kane, Sullivan & Smith
ATTORNEYS

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**ANTICOAGULANT MATERIAL HAVING
CHARGED ELECTROSTATIC SURFACES
SUITABLE FOR USE IN PROSTHETIC
DEVICES**

Waldemar A. Ayres, Rutherford, N.J., assignor to Becton,
Dickinson and Company, Rutherford, N.J.
Continuation-in-part of application Ser. No. 560,653,
June 27, 1966. This application June 16, 1969,
Ser. No. 833,657

Int. Cl. A61f 1/00

U.S. Cl. 3—1

10 Claims

ABSTRACT OF THE DISCLOSURE

An anticoagulant device for confining blood. The device includes a blood engaging wall with a surface for contacting the blood. The wall is formed of a material adapted to have a substantially permanent volumetric charge providing a blood-engaging surface field of not less than approximately 0.3 volt negative.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my previously filed application, Ser. No. 560,653 filed June 27, 1966, now abandoned and incorporates herein by reference the subject matter contained therein.

BACKGROUND OF THE INVENTION

The invention is directed toward anticoagulant materials having surfaces with electrostatic fields and the method of making such a material. Devices envisioned having such a substantially permanent electrostatic field include transfusion and blood storage sets and vascular prostheses whereby the products formed alleviate the coagulation and clotting of blood upon exposure to the charged surfaces without the necessity of chemical anticoagulant additives.

Chemical anticoagulants are known and are used as additives to prevent the coagulation of blood when it is collected and stored in suitable containers. It is common practice for manufacturers to include in blood collection and storage equipment a chemical anticoagulant such as heparin, sodium oxalate, or any other known type of blood anticoagulant.

While chemical anticoagulants are generally effective in preventing coagulation of blood when employing blood collection and storage equipment, there is a limitation upon the use of blood anticoagulants. When blood must be tested for diagnostic purposes, and the anticoagulant is present it may interfere with obtaining accurate results. Also, transfusions of whole blood having anticoagulants therein may adversely interfere with the clotting mechanism of blood. Where vascular prostheses formed of metal or synthetic materials are employed, anticoagulants cannot be utilized effectively because the anticoagulant itself will disperse into the blood and its rate of dissolution cannot be controlled. It is a blood contaminant and may have adverse effects as noted above. Even if anticoagulants could be employed advantageously in vascular prostheses, the amount of anticoagulant which can be applied thereto is necessarily limited and its duration of effectiveness may not be as long as the life expectancy of the subject patient. It has also been reported that where

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anticoagulants are provided or coated on a material, for example, a prosthetic tube for use as an artery or vein, a proteinaceous material in the blood is precipitated over the anticoagulant material thereby forming a layer or film which renders the material ineffective to prevent the clotting and coagulation of blood.

Furthermore, metal or other rigid materials may not be effectively employed for vascular prostheses because the material may corrode or effective healing of the member into which the prosthesis is transplanted may be prevented because of incompatibility between the member and the prosthesis. Also, such a rigid material does not expand or contract in the manner in which a normal artery or vein functions, does not bend with body movements, or does not yield to pressures.

A further problem exists relative to apparatus for storing and pumping of blood, for example, in heart-lung machines. It has been found that such machines cannot be used over long periods of time without changing the blood since the blood will begin to clot and coagulate due to the materials employed for the blood contacting surfaces of the machine.

SUMMARY OF THE INVENTION

Among the primary objectives of my invention is to provide anticoagulant surfaces having a permanent electrostatic field at its surface, to provide an anticoagulant surface in the form of an electret made of an electrostatically aligned material which will prevent the clotting and coagulation of blood without the use of chemical anticoagulant additives. Other objectives include the provision of vascular prostheses which are compatible with the tissues of the body, which will prevent the coagulation and clotting of blood over extended periods of time without employing chemical anticoagulants therewith and which are flexible and elastic. Anticoagulant prosthetic devices and blood storage and collection equipment are also envisioned having surfaces with permanent electrostatic fields and which do not act as contaminants with the blood contained therein. Additionally, a method is provided of making devices having surfaces with a permanent electrostatic field which will prevent the coagulation of blood.

In accordance with my invention, articles or devices made of material having a permanent electrostatic field at its surface, for example, made in the form of an electret, which carry a negative charge of approximately 0.3 volt or more at one or more surfaces thereof, and which will prevent the clotting of blood without the use of chemical anticoagulants. Also, the method of making such devices includes employing a selected material, such as dipole material, which is formed into a predetermined shape and is produced having permanent electrostatic fields at their surfaces by placing the material in an aligning electrical field. The electrical field is of sufficient strength to cause the dipole molecules to become aligned when the selected material is soft or fluid so as to produce a substantially permanent negative field of 0.3 volt in the dipole material. When materials other than dipole materials are utilized, a homocharge may be produced by the electrical field to form a substantially permanent negative surface charge of 0.3 volt in that material. Furthermore, as will be explained in greater detail below, in the use of a dipole material in certain environments a homo-

charge may be produced on the surface in addition to the normally produced heterocharge when the dipole molecules become aligned. As will be noted from the detailed discussion below, the homocharge on or near a given surface under such circumstances will be opposite to the heterocharge at the same surface thereof so that the dominant field will determine the net permanent charge at the surface.

An electret is a body usually having a pair of opposite, permanent electric charges and is often considered as an electrostatic analog to a permanent magnet. Magnets are similar to electrets in that an electret, when cut in half, results in two electrets. Electrets may be formed from materials which are softened or liquefied and then solidified while maintained in a strong directional electret field. In the case of a dipole material, during the liquid or soft state, the dipole molecules of the material are rotated and aligned by the electrical field produced from a suitable source. Solidification of the material while in this field sets the molecules into permanent alignment. The resultant electret has a heterocharge throughout the volumetric cross-section thereof which is caused by the summation of the electrical fields of the aligned molecules. The electrostatic field of the electret extends throughout the cross-section, out through the surface of the electret, and for a short distance into the blood contacting the electret. This field is not a surface charge. This is fundamentally true of the heterocharge, which is produced by the aligned dipole molecules throughout the cross-section. The homocharge is usually much nearer the surface and is believed caused by the embedment of the free electrons or ions, some of which have migrated from the charged electrodes used in making the electrets. The electrets of this invention should be thought of as not having a surface charge (which could be short circuited and nullified by the electrically conductive blood) but be thought of instead as having an electrical field generated within the cross section of the electret and extending out through the surface and a short distance into the blood stream. This is an electrical field at the surface, and we will term this a "surface field." If both heterocharges and homocharges are present, the net polarity of the field will depend upon which is dominant. The preferred type of electret will have heterocharges (aligned molecules) only, and the method of making this type will be described.

An alternative type of electret may have homocharges only, and may be made by any preferred method of embedding free electrons or ions in the electret cross-section, as for example, by electron or ion bombardment. This invention includes any preferred type of material processed so that the electrostatic field originates within its cross-section and extends out through its surface producing a "surface field." In this connection, a dipole material is to be considered as any material including molecules or molecular groups in which the centeroids of the positive and negative charges do not coincide, thereby giving the molecules or molecular group an electric moment.

The material to be permanently charged is placed between the metal plates or other electrodes which together form the electrical field therebetween necessary for the formation of the electret. Either an air gap may be present between the plates and the material to be formed into an electret or a sheet of dielectric material may be placed between each plate and the material to be formed into the electret. As mentioned above, the polarization of the material can consist of heterocharges and homocharges. When sheets of dielectric are interposed between material and electrodes during the formation process, the electret material has a heterocharge. Either a net heterocharge or a net homocharge is usable for this invention if it is of sufficient negative magnitude to produce the resultant voltage to repel the blood cor-

puscles and therefore prevent coagulation, although the heterocharge by itself is preferred.

It has been found that human blood corpuscles carry a negative charge of approximately 0.3 volt. It has also been found that vascular prostheses formed of metals which carry a negative potential greater than 0.3 volt in the electromotive series will prevent the coagulation of blood for a substantial period of time. However, as stated previously, these metals have a tendency to corrode, are inflexible, may be toxic and may not be compatible with the tissues in which they are implanted, thereby retarding or inhibiting healing of the implant with the normal tissue. The presence of any of these factors will limit the usefulness of metal vascular prostheses. A theory has been set forth that the clotting mechanism of blood is triggered when blood and/or arteries, veins or any portion of the circulatory system becomes more positive than 0.3 volt negative. Since unlike charges attract each other, the negative charged clotting components contained in the blood will tend to be attracted to anything more positively charged than minus 0.3 volt and form a clot.

Because like charges repel, it is believed that a vascular prosthesis made of material compatible with the tissues in which it is implanted and which is not adversely affected by blood will prevent the coagulation of blood passed therethrough if the electrical field at the surface of the material is maintained at a negative charge greater than approximately 0.3 volt. Also, it has been reported in medical literature that healthy arteries, veins or other blood tissue interfaces carry a negative surface charge of approximately 0.3 volt. Therefore, when 0.3 volt is used herein, it is to be interpreted as the voltage necessary or useful to prevent coagulation of blood. This unexpected and beneficial result may be achieved with a vascular prosthesis made in accordance with my invention. Such a prosthesis may be employed for extended periods of time without undesirable effects to the subject.

When a suitable material is formed having a permanent negative surface field of 0.3 volt or more and is formed into other devices such as blood storage and collection assemblies, the blood stored therein will be prevented from clotting for extended periods of time without the use of chemical anticoagulants.

It is to be understood that the electrostatic surface field is produced by either the aligning of the dipole molecules of the prosthetic material to form a heterocharge which is in the form of a space charge throughout the material and beyond its surface, or by producing a sufficient homocharge in the form of a space charge throughout the material and beyond its surface which is opposite to the heterocharge at the same surface and of sufficient greater magnitude to provide the desired voltage discussed above. Accordingly, the expression "electrostatic surface field" as used herein should not be confined only to a field available at the surface of the material. Where protein material is deposited by the blood stream on the surface of the prosthetic member, the space charge will extend through this layer and continue to affect the blood at or beyond the blood-protein interfaces of the prosthetic member. However, the surface field does not exclude a prosthetic member where the positive surfaces are placed adjacent each other so that the exterior surfaces both have negative fields to prevent blood coagulation.

Other objects and advantages for forming anticoagulant surfaces having permanent electrostatic surface fields, which may include an electret, and products therefrom, become more apparent from the following description and drawings illustrating preferred embodiments of my invention.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a sectional view illustrating one form of a

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device for forming a tubular prosthesis having an anticoagulant surface charge;

FIG. 2 is a partially perspective view of the prosthesis formed with the apparatus of FIG. 1;

FIG. 3 is a sectional view of another type of apparatus for forming an anticoagulant surface as a sheet or film;

FIG. 4 is a partially perspective and sectional view of an anticoagulant container for blood collection and storage;

FIG. 5 is a partially perspective and sectional view of a rigid cylindrical member having an anticoagulant surface bonded therein;

FIG. 6 is a sectional view of an anticoagulant surface in the form of a laminated sheet or film; and

FIG. 7 is a sectional view of another type of apparatus for forming an anticoagulant surface with the resultant sheet or film having a heterocharge only.

Referring to the drawings and particularly to FIGS. 1 and 2, mold 10 is shown which comprises a cylindrical core 12 positioned within cylindrical tubular member 14 to form annular space 15. Annular space 15 provides a region in which a dipole material or other type of material in liquid or softened state and in tubular form may be positioned around core 12.

A high voltage DC source S is electrically connected: one terminal to core member 12 and the other terminal to cylindrical member 14. Advantageously employing mold 10, one terminal is connected to core member 12 and the opposite terminal is connected to cylindrical member 14 so as to form a prosthetic tubular member 16. The interior and exterior surfaces of tubular member 16 will be formed having produced thereon a charged electrostatic surface opposite to the polarity of each terminal to which the tubular member 16 is connected in the case of a heterocharge and the same as the polarity of each terminal to which tubular member 16 is connected in the case of a dominant homocharge. As shown in FIG. 1, the negative terminal is connected to cylindrical member 14 and the positive terminal is connected to core member 12, thereby producing a negative heterocharge on the interior surface of dipole material 16 and a positive heterocharge on the exterior surface thereof. Naturally in the case of a homocharge the result would be the opposite. It is apparent that by interchanging the terminal connections, the produced surface fields may be reversed. In FIG. 2 the vascular prosthesis suitable for use as an artery or vein, or a tube useful for blood storage and transfusion assemblies is shown formed in accordance with FIG. 1. The exterior surface of tube 16 is produced having a positive electrostatic heterocharge and the interior surface thereof having produced thereon a negative electrostatic heterocharge.

In FIG. 3 mold 20 is formed having upper and lower electrical conducting plates 22 and 24 and is provided with a space 25 for positioning either molten or formed prosthetic dipole material therein. Plates 22 and 24 are similarly connected to a high voltage DC source as shown in FIG. 1. Material 26, accordingly, will be formed having a negative heterocharge for one surface and a positive heterocharge for the other with the corresponding surfaces having a reversed homocharge.

FIG. 4 illustrates a blood collection and storage device 28 having a dominant negative charge produced for the interior surfaces and a dominant positive charge produced for the exterior surfaces.

FIG. 5 is a cylindrical container having a rigid exterior tubular shell 30, formed of any convenient material such as glass, plastic or other suitable material. Material 26, having a permanent dominant negative charge, is bonded in any convenient manner to the interior wall of cylinder 30. The dominant negative surface of the lining material 26 is positioned interiorly of the container for collecting and storing blood.

FIG. 6 illustrates a cross section of sheet or film laminated together in which the dominant charge surfaces of

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each sheet or film of the same polarity are placed in face-to-face contact and are held together by a suitable bonding system, thereby forming a laminated material having upper and lower surfaces of the same dominant polarity.

In FIG. 7, mold 20a is formed having upper and lower electrical conducting plates 22a and 24a and is provided with a space 25a for positioning either molten or formed prosthetic dipole material therein. Plates 22a and 24a are similarly connected to a high voltage DC source as shown in FIGS. 1 and 3. Positioned between plates 22a and 24a and the material are a pair of sheets of dielectric 31 and 32 respectively. Material 26a, accordingly will be formed having a negative heterocharge on one surface and a positive heterocharge on the other.

The electrically chargeable material employed in accordance herewith may be any suitable material for forming an electret which is not adversely affected by and is compatible with blood or tissues in accordance with the invention herein. The material may be, for example, silicone rubber, polyethylene terephthalate, polychlorotrifluoroethylene, polyvinyl chloride, cellulose acetate, or any suitable material having molecular dipole characteristics which is capable of producing a substantially permanent dominant heterocharge or homocharge at the surface in a sufficient amount. Alternatively, if preferred, various non-polar materials, for example polystyrene, polypropylene, etc., can be used as the electret material, where the homocharge only will be created, with the power source connected appropriately to produce the polarity desired at a given surface, as previously explained. Because the heterocharge results from alignment of polar molecules, the use of non-polar molecular material will prevent the formation of the heterocharge.

The following examples illustrate the methods for forming anticoagulant surfaces in the form of a prosthetic device or a blood container:

EXAMPLE 1

A hollow cylindrical tube of dipole material of the type indicated above and of a size suitable for use as an artificial vein or artery is inserted on a metal rod or mandrel of the type indicated in FIG. 1. A metal cylinder which is split for easy assembly and removal after formation of the prosthesis, is placed around the outside of the tube. A high voltage DC source is electrically connected across the metal rod and the split cylinder with the negative terminal connected to the split cylinder. The tube with the rod and split cylinder in place is heated to a point slightly above the softening point of the dipole material and maintained at that temperature, so that the tube is in a plastic condition. While the dipole material is in the softened or plastic flowable state, an aligning electrical field is produced by the high voltage DC apparatus. The electrical field is maintained until the dipole material is solidified. The field is of sufficient strength to align the molecules of the dipole material so as to produce a permanent electrostatic heterocharge at the surface of the tube. Then the metal rod and the split cylinder are removed. The tube, still of a size suitable for use as an artificial vein or artery is found to have a negative charge of at least 0.3 volt at the interior surface of the prosthetic device so that blood when flowing through the tube is prevented from clotting.

EXAMPLE 2

A mold such as shown in FIG. 3 is provided comprising a pair of electrically conductive plates in which one of the plates is provided with a recess to allow casting of a flat plastic sheet of dipole material. After the dipole material has been cast in the mold, the mold is subjected to mild heating to evaporate the solvent from the dipole material. The plates are held in spaced relation to allow the solvent to evaporate from the mold. The plates are electrically connected to a high DC voltage source to produce an aligning electrical field which causes the molecules of the

dipole material to be aligned during the solidification thereof, thereby producing a sheet or film of material having oppositely heterocharged dominant electrostatic surfaces of at least 0.3 volt.

Alternatively, an electrostatically charged sheet or film of dipole material may be made by employing thermosetting resins which may be cured by heat or chemical accelerators rather than employing a solvent system as described in Example 2. Further, a sheet or film of thermoplastic dipole material may be placed within a mold and heated slightly above its softening point in a manner such as described in Example 1 so as to form charged electrostatic fields therein.

Other methods may be employed for forming a sheet material having the same polarity on each surface. For example, the surface of a permanently charged electrostatic dipole material may be softened part way through its cross-section and a reverse electrical field may be applied while the softened portion is solidifying. Another method may be employed by applying an additional coating of the dipole material to an electrostatically charged surface while producing an aligned electrical field of reverse polarity during solidification of the additional coating.

It should be kept in mind that, although, we prefer a dominant heterocharge for creating the surface field of primary concern, an adequate product may be produced having a dominant homocharge which is also of sufficient negative value so as to produce a negative field of 0.3 volt or greater. The fact that the dominant charge is a homocharge rather than a heterocharge does not prevent the functioning of the resultant product.

EXAMPLE 3

Electrodes such as shown in FIG. 7 are provided comprising a pair of electrically conductive plates. Interposed between each metal plate and the flat sheet of thermoplastic dipole material is a sheet of dielectric in place of an air gap which is normally employed, thus forming a three part sandwich with the thermoplastic electret material in the middle, a dielectric sheet below and this three part sandwich is placed between the two electrodes. The dipole material is heated to slightly above its softening point. The plates are electrically connected to a high DC voltage source to produce an aligning electrical field which causes the molecules of the dipole material to be aligned during the cooling and solidification thereof, thereby producing a sheet or film of material having oppositely heterocharged electrostatic surfaces of at least 0.3 volt. The presence of sheets of dielectric material in place of the air gap between the material to be charged and the electrodes during the formation process, substantially eliminates the presence of a homocharge on the resultant electret material. Therefore, the charge in the material forming the electret is a heterocharge only.

It is apparent that many variations may be employed using a dipole material or other materials in the form of an electret as an anticoagulant surface for the prevention of clotting and coagulation of blood. For example, anticoagulant surfaces in the form of electret may be formed by molding the material into a desired configuration, by casting the material from a solvent solution or by dipping a desired configuration into a solvent solution of such material. The electret may be formed by having the electret material fluid by softening through heating, or by having the electret material dissolved in a solvent, or by using chemical constituents which are fluid originally and then react chemically to form a solid. Other solidification means may be by cooling, or by solvent evaporation, as appropriate to the electret material being used.

Also the electret material may be either a single material, or it may be a mixture of materials, as for example particles of barium titanate, calcium titanate, etc., dis-

persed in a binder material such as polyethylene, polypropylene, polymerizable monomers, such as styrene, etc.

Although the invention is useful with regard to the surgical/medical field for providing devices such as transfusion, blood collection and storage equipment, infusion tube assemblies and vascular prosthetic devices, such as arteries, veins, heart valves or the like, it can also be used for solutions which must be maintained at a specific charge so as to prevent precipitation or deterioration thereof.

I claim:

1. An anticoagulant device for confining blood comprising a blood engaging wall with a surface for contacting blood, said wall being formed of a material having a substantially permanent volumetric charge providing a blood-engaging surface field of not less than approximately 0.3 volt negative, said blood engaging wall being an electret.

2. An anticoagulant device for confining blood comprising a blood engaging wall with a surface for contacting blood, said wall being formed of a material adapted to have a substantially permanent volumetric charge providing a blood-engaging surface field of not less than approximately 0.3 volt negative, said blood-engaging wall being an electret in the form of a coating on the surface of said blood-engaging wall.

3. An anticoagulant device for confining blood comprising a blood-engaging wall with a surface for contacting blood, said wall being formed of a material adapted to have a substantially permanent volumetric charge providing a blood-engaging surface field of not less than approximately 0.3 volt negative, said blood-engaging wall being an electret in which the surfaces of the wall are formed having a dominant and negative heterocharge of not less than approximately 0.3 volt.

4. An anticoagulant device for confining blood comprising a blood-engaging wall with a surface for contacting blood, said wall being formed of a material having a substantially permanent volumetric charge providing a blood-engaging surface field of not less than approximately 0.3 volt negative, said device being formed into a vascular prosthesis which includes the surfaces formed by the wall.

5. An anticoagulant device comprising a blood confining wall with at least one surface for contacting the blood, said surface being formed of a dipole material so that at said surface of said material there is a positive homocharge and the substantially aligned dipole molecules have a substantially permanent negative heterocharge with the difference between said heterocharge and opposing homocharge being not less than approximately 0.3 of a volt negative.

6. An anticoagulant device comprising a blood confining wall with at least one surface contacting the blood, said surface being formed of a dipole material with substantially aligned dipole molecules providing a substantially permanent heterocharge of not less than approximately 0.3 of a volt negative.

7. An anticoagulant device comprising a blood confining wall with an interior surface for contacting the blood, said surface being on a dipole material which has a positive homocharge therein and has substantially aligned dipole molecules having a substantially permanent negative heterocharge of not less than approximately 0.3 volt greater at said surface than said homocharge.

8. The invention in accordance with claim 7 wherein said device is a blood storage and transfusion container.

9. The invention in accordance with claim 8 wherein said blood storage and transfusion container has an interior surface which is part of an electret.

10. An anticoagulant device comprising a blood confining wall with at least one surface for containing the blood, said surface being formed of a dipole material so that said surface of said material has a dominant negative field homocharge and has substantially aligned di-

pole molecules having a positive heterocharge wherein said negative homocharge is not less than approximately 0.3 volt greater than said positive heterocharge.

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DALTON L. TRULUCK, Primary Examiner

U.S. Cl. X.R.

128—334

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,609,768 Dated October 5, 1971

Inventor(s) Waldemar A. Ayres (408-1585)

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE CLAIMS:

Claim 2, lines 3 and 4, after "material" delete "adapted to have" and insert ... "having" ...

Claim 3, lines 3 and 4, after "material" delete "adapted to have" and insert ... "having" ...

Signed and sealed this 21st day of March 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents