

[54] **SILVER, SILVER CHLORIDE ELECTRODES**

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128/417, 252/514

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[58] Field of Search..... 128/2.06 E, 417, 418, 404,
128/405, DIG. 4, 2.1 E; 252/514

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[57] **ABSTRACT**

Silver, silver chloride electrodes comprise a plurality of silver particles and silver chloride particles and an electrically insulating, water impermeable, inert organic matrix therefor. The silver particles and silver chloride particles are interspersed with each other in and throughout the matrix.

25 Claims, 4 Drawing Figures

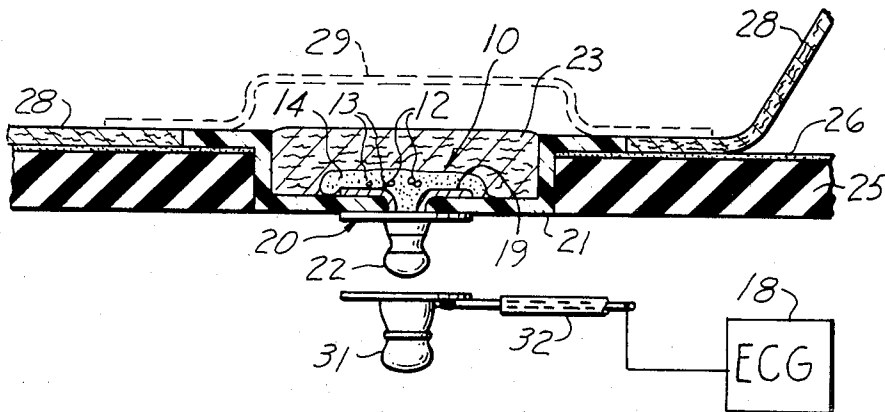


FIG. 1

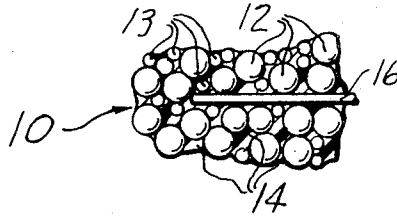


FIG. 2

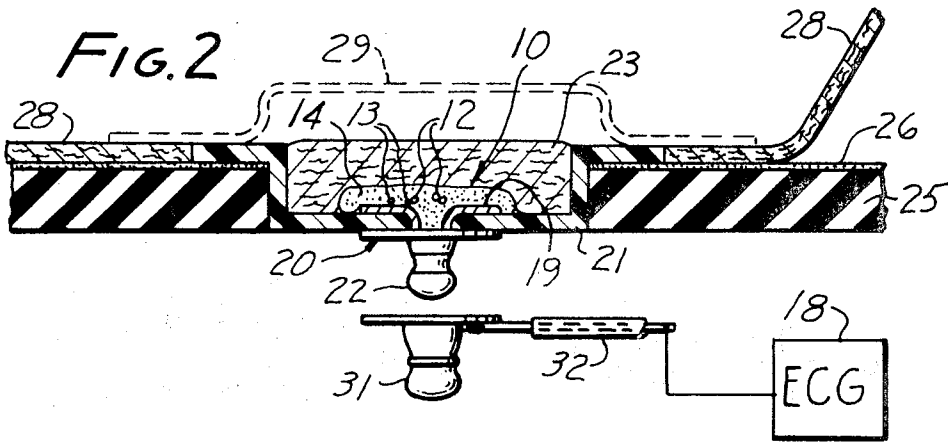


FIG. 3

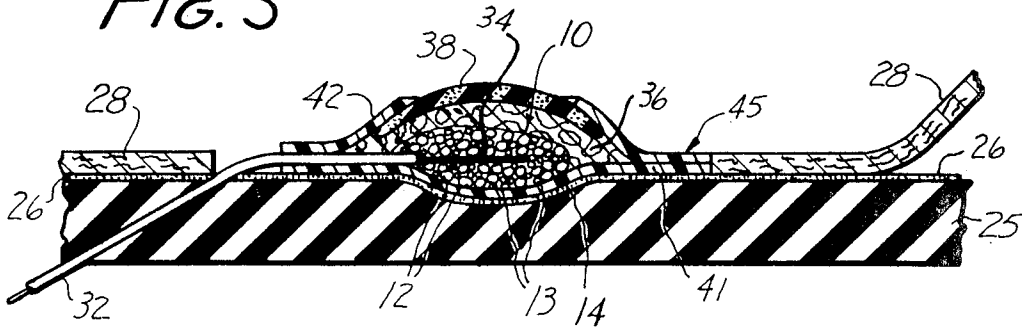
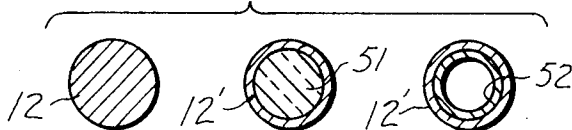


FIG. 4



SILVER, SILVER CHLORIDE ELECTRODES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The subject invention relates to silver, silver chloride electrodes and to methods of making same.

2. Description of the Prior Art

Silver, silver chloride electrodes are useful and well known in the fields of electrochemistry, biochemistry and medicine. For instance, biopotential electrodes are widely used in medical work for making electrical contact with a patient's skin in order to detect and evaluate low-level electrical signals originating within the body. A common use for biopotential electrodes is in the field of cardiology for measurement of the electrocardiogram.

Silver, silver chloride biopotential electrodes are based in their function on the classical silver, silver chloride half-cell of electrochemistry in which the silver chloride stabilizes and controls the electric potential on the surface of the electrode and lowers the work function between the electrode and the electrolytic solution with which it is in contact, thereby making the electrical contact more stable. The performance of silver, silver chloride electrodes is thus greatly superior to the performance of their forerunners which includes silver electrodes and electrodes of a copper-nickel-zinc alloy known as "German silver". The latter electrodes made an extremely variable and easily disturbed electrical contact with the skin which introduced a great deal of electrical noise into the bioelectrical signal, leading to erroneous diagnoses.

However, existing silver, silver chloride electrodes still suffer from serious drawbacks. They are typically expensive to produce and complex to utilize and maintain. Prior-art attempts to remedy these drawbacks have resulted in electrodes that are easily damaged and/or inferior in performance.

Prior-art tendencies and prejudices have seriously impeded the development of a low-cost and preferably disposable silver, silver chloride electrode that would take adequate advantage of the superior features of that electrode type.

For instance, researchers in the field of silver, silver chloride electrodes have found that organic compounds seem to contribute to electrode poisoning. Researchers have also identified the apparent dependence of the standard potential for a mixture of given dielectric constant on the nature of the organic component as an unexpected and particularly important stumbling block. This may, for example, be seen from Janz and Ives, *Silver, Silver Chloride Electrodes*, ANNALS OF THE NEW YORK ACADEMY OF SCIENCES, Volume 148, Art. 1, BIOELECTRODES, Feb. 1, 1968, pp. 210-221, at p. 220, and Feakins and French, *Standard Potentials in Aqueous Organic Media: a General Discussion of the Cell $H_2(Pt)/HCl/AgCl-Ag$* , J. Chem. Soc. (London), 1957, pp. 2581-2589, at pp. 2585 and 86. Findings of this type have discouraged the use of organic compounds in the electrode structure of silver, silver chloride electrodes.

It has also been assumed in the past that the silver chloride component should occur at the surface of silver, silver chloride electrodes and that the silver component should be covered by the silver chloride component except for possible pores. These assumed restric-

tions have impeded the development of low-cost techniques of high efficiency for manufacturing silver, silver chloride electrodes. As Janz and Ives point out in their above mentioned article, which is herewith incorporated by reference herein, the best methods of preparation of silver, silver chloride electrodes to attain maximum stability and reproducibility have been a matter for controversy over the years, and conflicting opinions have remained unresolved (see page 215).

Silver, silver chloride electrodes are also used in other fields of electrochemistry, such as in the production and operation of electric current generating cells and batteries. This may, for instance, be seen in Vinal, *PRIMARY BATTERIES* (John Wiley & Sons, 1950) pp. 17, and 274-281.

As early as 1882, Warren de la Rue built a 15,000 volt battery of 14,400 silver chloride cells. The individual cells consisted of a silver chloride casting around a flattened silver wire and a slender rod of zinc. More modern methods of manufacture of silver, silver chloride electrodes for electric cells have continued to take care that the silver chloride component occurs only on the surface of the electrode and substantially covered the silver component, except for possible pores.

SUMMARY OF THE INVENTION

The subject invention owes its existence to a radical departure from prior-art thinking and prejudice. According to combined main features of the subject invention the silver component and the silver chloride component are located in and at the surface of an electrically insulating, water impermeable, inert organic matrix, and the silver component and silver chloride component are interspersed with each other in and throughout the organic matrix.

From one aspect thereof, the subject invention resides in a silver, silver chloride electrode; and resides more specifically in the improvement comprising, in combination, a plurality of silver particles, a plurality of silver chloride particles, and an electrically insulating, water impermeable, inert organic matrix for the silver particles and silver chloride particles. In accordance with the subject invention, the matrix is not only organic as stated, but the silver particles and silver chloride particles are interspersed with each other in and throughout the matrix, and the interspersed silver particles and silver chloride particles are in electrical contact with each other.

From another aspect thereof, the subject invention resides in a bioelectrode comprising, in combination, a silver, silver chloride electrode, an electrical conductor connected to the silver, silver chloride electrode, means for retaining an electrolyte at the silver, silver chloride electrode, and container means for the silver, silver chloride electrode and for at least part of the conductor and the electrolyte-retaining means. Further according to the invention, the silver, silver chloride electrode in the latter combination comprises a plurality of silver particles, a plurality of silver chloride particles and an electrically insulating, water impermeable, inert organic matrix for the silver particles and silver chloride particles; with the silver particles and silver chloride particles being interspersed with each other in and throughout the matrix, and with the interspersed silver particles and silver chloride particles being in electrical contact with each other.

From yet another aspect thereof, the subject invention resides in a method of making a silver, silver chloride electrode; and resides more specifically in the improvement comprising in combination the steps of providing a plurality of silver particles, providing a plurality of silver chloride particles, providing a curable matrix material for forming an electrically insulating, water impermeable, inert organic matrix for the silver particles and silver chloride particles, intermixing the curable matrix material, silver particles and silver chloride particles intimately with each other, and curing the intermixed material to form a silver, silver chloride electrode having the silver particles and silver chloride particles interspersed with each other, and in electrical contact with each other, in and throughout a cured electrically insulating, water impermeable, inert organic matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention and its objects will become more readily apparent from the following detailed description of preferred embodiments thereof, illustrated by way of example in the following drawings, in which:

FIG. 1 is a section through a silver, silver chloride electrode in accordance with a preferred embodiment of the subject invention;

FIG. 2 is a section through a bioelectrode in accordance with another preferred embodiment of the subject invention;

FIG. 3 is a section through a bioelectrode in accordance with yet another preferred embodiment of the subject invention; and

FIG. 4 is a section, on an enlarged scale, through silver particles useful in the practice of the subject invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

By way of example, electrodes according to the subject invention have utility as reference electrodes, bioelectrodes and electric cell electrodes. By way of further example, and not by way of limitation, the illustrated preferred embodiments will be chiefly described in terms of bioelectrodes that may be applied to the skin of animals and humans for receiving and measuring electrical body signals.

The silver, silver chloride electrode 10 of FIG. 1 consists essentially of a plurality of silver particles 12, a plurality of silver chloride particles 13, and an organic matrix 14 for the silver particles 12 and the silver chloride particles 13. In accordance with the subject invention, the silver particles 12 and the silver chloride particles 13 are interspersed with each other in and throughout the matrix 14. Also, the interspersed silver particles 12 and silver chloride particles 13 are in electrical contact with each other.

In FIG. 1, the silver particles are shown as spheres of a given diameter and the silver chloride particles are shown as spheres of a smaller diameter. This neither implies a limitation to particles of spherical shape, nor is intended as any representation about the relative sizes of the silver and silver chloride particles. Rather, the graphical illustration of FIG. 1 is intended to convey the fact that both the silver particles 12 and the silver chloride particles 13 are interspersed with each other in and throughout the organic matrix 14, and that both silver particles 12 and silver chloride particles 13 are present on the surface of the silver, silver chloride

electrode, as well as throughout the electrode body including the organic matrix 14.

FIG. 1 also shows an electric conductor 16 extending into the matrix 14 and being in electrical contact with the silver particles 12 and silver chloride particles 13. The conductor 16 is not an electrode in the sense in which that term is used for the silver, silver chloride electrode 10 located on the conductor 16. The conductor 16 is also to be distinguished from the silver core of prior-art silver, silver chloride electrodes. In those prior-art electrodes, a silver conductor or silver-coated conductor formed the silver component of the silver, silver chloride electrode and had a thin coating of silver chloride provided thereon. Pursuant to the teachings of the subject invention, there is no electrolytic or ionic contact between the conductor 16 and the electrolyte to which the silver, silver chloride electrode 10 is exposed in practice. Rather, the conductor 16 makes electrical contact with the silver particles 12 and silver chloride particles 13, and any electrical conduction between the electrolyte and the conductor 16 proceeds only by way of the silver particles 12 and silver chloride particles 13.

In the preferred embodiment of FIG. 1, the silver component of the electrode is interspersed in particulate form in the organic matrix 14 with the silver chloride component which is also in particulate form. To be sure, the conductor 16 may be of silver or may have a silver coating. Alternatively, the conductor 16, may, however, be of another conducting metal, such as copper, nickel or stainless steel. Use of silver or of a silver coating for the conductor 16 is preferred to optimize the electrical contact between the conductor 16 and the particles 12 and 13.

The conductor 16 may serve to connect the electrode 10 to an electric circuit or instrument and may, if desired, also serve as a support for the electrode. In the following preferred ranges, the presence and the weight of the conductor 16 are disregarded both with respect to the weight of the electrode and with respect to the weight of any electrode component.

The amounts of silver particles 12, silver chloride particles 13, and organic matrix material 14 in the electrode 10 can vary in wide ranges. In practice, sufficient silver and silver chloride should be present to make sure that the silver and chloride components of the electrode are in electrical contact within the organic matrix 14. This is similar to the provision of electrical contact between silver particles in an electrically conductive varnish, paint or resin of the silver type. Moreover, the silver chloride content should be sufficient relative to the silver content or to the weight of the electrode to provide for the desired contribution of the silver chloride component in the silver, silver chloride electrode. High silver chloride contents, on the other hand, tend to impair the quality and stability of the electrode, including its mechanical quality and stability.

Through various calculations and tests, I have determined preferred broad ranges of weight percentages relative to the weight of the organic matrix 14 and the silver particles 12 and silver chloride particles 13 interspersed in the organic matrix. According to these preferred ranges, the silver particles constitute substantially from 70 to 90 percent by weight, the silver chloride particles constitute substantially from 0.5 to 15 percent by weight, and the organic matrix constitutes

essentially the balance of the weight of the organic matrix with the silver particles and silver chloride particles dispersed therein.

Generally, if the silver particles are shape anisotropic (e.g. needle-shaped silver particles or silver flakes), the content of the silver particles can be lowered relative to the preferred higher content for spherical silver particles.

Preferably, the silver particles and the silver chloride particles are of a purity of about 99.9 percent or higher to avoid generation of spurious potentials from electrode contaminants. Spherical, needle-shaped and flaked silver particles of the desired purity are readily available commercially. Silver chloride particles of the desired purity are also commercially available from such suppliers as J. T. Baker Chemical Company, Phillipsburg, New Jersey, and Mallinckrodt Chemical Works, Saint Louis, Missouri.

Typically, the silver chloride particles are precipitated from an aqueous solution of a soluble silver salt and filtered and washed for providing the desired purity.

According to the subject invention, the matrix is of an electrically insulating material to avoid the occurrence of current-conducting paths within the matrix in parallel to the silver and silver chloride particles. The insulating material of the organic matrix is also water impermeable to prevent electrolyte contacting the electrode from providing ionic conduction within the matrix in parallel to the silver and silver chloride particles. The organic matrix is also of a material which is chemically inert to the electrolyte encountered by the electrode.

A large number of organic materials qualify for the electrode matrix, since there are many organic materials which are electrically insulating, water impermeable and chemically inert to the types of electrolyte encountered by silver, silver chloride electrodes. Those skilled in the art of organic chemistry or in the technology of electrical insulating materials will readily be able to identify a large number of suitable organic materials.

By way of example and not by way of limitation, it is well known that most resins are electrically insulating, water impermeable and chemically inert to the types of electrolyte (e.g. aqueous sodium chloride solutions in the case of bioelectrodes) encountered by silver, silver chloride electrodes. By way of further example, it is well known that most thermoplastic resins, thermosetting resins and elastomers or rubbers are electrically insulating, water impermeable and chemically inert in the above mentioned sense. These properties are also possessed by many high molecular weight waxes.

Typically, the silver particles consist essentially of solid or pure silver as mentioned above and as shown at 12 in FIGS. 1 to 4. However, the silver particles may alternatively be made of, or comprise, silver-coated particles of a material other than silver. In the context of the subject electrodes which function on the basis of surface phenomena, the expression *silver particles* as herein employed is intended to be broad enough to cover powders of silver, including particles of solid silver, and silver-coated particles of an inert material other than silver.

Suitable low-cost, low-density substitutes for powders of solid silver particles include a product sold by Sigmatronics, of Moorestown, New Jersey, under the designation "Siliclad G-100" and consisting of a pow-

der of finely divided ceramic particles essentially each of which has a uniform coating of essentially pure silver. Other substitutes include hollow silica microspheres designated Eccospheres SI (thin-walled bubbles made from silica) and hollow glass microspheres designated Eccospheres/Glass Microballoons, sold by Emerson & Cuming, Inc., of Canton, Massachusetts, and provided with essentially pure silver coatings.

The silver coating shown in FIG. 4 at 12', may be applied to the solid core particles shown in FIG. 4 at 51 or to the hollow core particles shown in FIG. 4 at 52 by such well-known techniques as vacuum deposition, sputtering, precipitation or electroless plating, for instance. Inorganic materials other than ceramics and glass, or organic materials such as plastics resins, may be employed for the core particles on which the silver coating is deposited or plated, since silver coatings have in the past been successfully provided on a large variety of materials.

The above mentioned proportions, expressed in percent by weight, are subject to wide variation if silver substitute powders of silver layers coated on core particles having a density less than the density of silver are employed in lieu of or in combination with solid silver particles. For instance, the manufacturers of the above mentioned silver-coated ceramic particles indicate for their product a density of about one-third the density of silver. The manufacturers of the above mentioned hollow silica microspheres indicate for these microspheres a particle density of 0.26 g/cc and a bulk density of 0.18g/cc.

This makes it impractical to provide constituent ranges in percent by weight which would be generally applicable to solid silver particles and to silver-clad silver particles. Since the function of the silver and silver chloride constituents of the electrode proceeds chiefly on the basis of surface phenomena, it is appropriate under the circumstances to provide generally applicable ranges for silver particles, silver-clad silver particles, and silver chloride particles in terms of percent by volume.

I have in this respect determined through calculation and experiment preferred broad ranges of volume percentages relative to the volume of the organic matrix 14 and the silver particles 12 and silver chloride particles 13 interspersed in the organic matrix. According to these preferred ranges, the silver particles constitute substantially from 15 to 70 percent by volume, the silver chloride particles constitute substantially from 0.2 to 15 percent by volume, and the organic matrix constitutes essentially the balance of the volume of the organic matrix with the silver particles and silver chloride particles dispersed therein.

In similarity to the silver particles, the silver chloride particles could either be made of pure silver chloride or of silver chloride coated on an inert particle core. For economical and practical reasons, it is, however, presently believed that pure silver chloride particles (i.e. silver chloride particles that do not have a core other than silver chloride) are preferable.

The following working examples are supplied by way of illustration, rather than by way of example.

EXAMPLE I

Silver, silver chloride electrodes in accordance with preferred embodiments of the subject invention were manufactured with the aid of an electrically conductive

silver epoxy resin commercially available in liquid form from Emerson & Cuming, Inc., under the trade name "Eccobond Solder 57C". This commercially available product has a resin component which contains about 80 percent by weight of silver powder and about 20 percent by weight of an epoxy resin, relative to the weight of the resin component. This commercial product further has a catalyst component comprising about 80 percent by weight of silver powder and 20 percent by weight of a catalyst, relative to the weight of the catalyst component. The epoxy resin is bis-phenol A. The catalyst is a polyamide. The resin component and the catalyst component were intimately mixed in accordance with the manufacturer's specifications. In accordance with a preferred embodiment, the resin component and the catalyst component were mixed in a ratio of one-to-one, and an amount of 10 milligrams silver chloride particles were added to and intimately intermixed with the mixed resin and catalyst components per each gram of the mixed resin and catalyst components. The silver chloride particles were of a precipitated grade sold by J. T. Baker Company.

If desired, the silver chloride particles may be added to the resin component and/or catalyst component prior to intermixture of the resin and catalyst components.

The silver chloride-doped resin and catalyst mixture was thereafter cured in accordance with manufacturer's specifications by heat exposure. In some runs the silver chloride-doped resin and catalyst mixture was applied to electric conductors, including silver-plated wires and flat metal pieces and blank copper wires, and was thereafter cured on the conductors.

In this manner, low-cost and high-quality silver, silver chloride electrodes were produced.

EXAMPLE II

Example I was repeated with the exception that silver chloride particles were added to the resin component prior to the intermixture of the resin and catalyst components in an amount of 100 milligrams of silver chloride particles per gram of the resin component.

The silver chloride-doped resin component and the catalyst component were intimately intermixed to disperse the silver chloride component throughout the mixture.

This Example yielded low-cost, high-quality silver, silver chloride electrodes upon curing by heat exposure.

EXAMPLE III

Example I was repeated except that silver chloride particles were added to the resin component prior to intermixture of the resin and catalyst component in an amount of 25 milligrams of silver chloride particles per gram of the resin component.

EXAMPLE IV

An electrically conductive resin commercially available in liquid form from Emerson & Cuming, of Canton, Massachusetts, under the trade name "Eccobond Solder 57C" was used to make silver, silver chloride electrodes in accordance with further preferred embodiments of the subject invention. That commercially available product has a resin component containing about 80 percent by weight of silver powder and 20 percent by weight of an epoxy resin, relative to the

weight of the resin component; and a catalyst component consisting of a liquid catalyst having no silver therein. The epoxy resin in this product is bisphenol A. The liquid catalyst in this product is a polyamide. Only a relatively small amount of liquid catalyst is needed for catalyzation.

In accordance with a further preferred embodiment of the subject invention, 6.25 milligrams of silver chloride particles were added to and intimately admixed with the resin component per each gram of the resin component. The silver chloride-doped resin component and the catalyst were thereafter mixed and cured in accordance with manufacturer's specifications to obtain excellent silver, silver chloride electrodes upon curing by heat exposure.

In some runs the silver chloride-doped resin and catalyst mixture was applied to electric conductors, including silver-plated wires and flat metal pieces and blank copper wires, and was thereafter cured on the conductors.

EXAMPLE V

Example IV was repeated except that silver chloride particles were added to the resin component in an amount of 125 milligrams of silver chloride particles per gram of the resin component.

EXAMPLE VI

Further silver, silver chloride electrodes in accordance with preferred embodiments of the subject invention were manufactured with the aid of an electrically conductive, silver-filled styrene-butadiene elastomer commercially available in uncured form from Emerson & Cuming, Inc., of Canton, Massachusetts, under the trade name Eccocoat CC-4, and containing about 70 to 80 percent by weight of silver particles.

In accordance with a preferred embodiment of the subject invention, 50 milligrams of silver chloride particles were added to and intimately admixed with the uncured silver-filled styrene-butadiene elastomer per gram of this elastomer.

The silver chloride-doped elastomer was thereafter cured by air drying for 3 to 4 hours in some runs, and by forced drying for 30 minutes at 80°C in others.

In some runs the silver chloride-doped elastomer was cured after having been applied to electrical conductors, including silver-plated wires and flat metal pieces and blank copper wires.

In this manner, several low-cost and high-quality silver, silver chloride electrodes were produced.

EXAMPLE VII

Example VI was repeated except that silver chloride particles were added to the uncured silver-filled elastomer in an amount of 5 milligrams of silver chloride particles per gram of elastomer.

EXAMPLE VIII

Example VI was repeated except that silver chloride particles were added to the uncured silver-filled elastomer in an amount of 100 milligrams of silver chloride particles per gram of elastomer.

RESULTS

All the electrodes made according to Examples I through VIII performed well in practice and in clinical testing as bioelectrodes. The off-set potentials (i.e. the

potentials observed when two silver, silver chloride electrodes were measured face-to-face) typically were less than 0.5 millivolts. Such a high half-cell stability usually is only found in expensive pressed pellet type electrodes.

The electrode voltage was very stable. Essentially no long term drift of the electrode voltage was observed. This renders the electrodes made according to Examples I through VIII suitable for long term monitoring applications.

Good low-impedance skin contact was established very rapidly after application of these electrodes to human skin. The skin contact was generally less than 1 kilohm assuring the production of sharp and essentially noise-free ECG (electrocardiogram) records, and permitting even the use of older ECG machines.

By way of general comment, silver, silver chloride electrodes according to the subject invention provide performance equivalent to that of the best available research grade electrodes at cost savings of about 80 to 90 percent and more.

In general, the electrodes of the subject invention are, for instance, suitable as electrodes in electric reference or low-current cells, in reference electrodes, and as bioelectrodes.

A disposable bioelectrode in accordance with a preferred embodiment of the subject invention is shown in FIG. 2.

According to FIG. 2, a silver, silver chloride electrode 10 of the above mentioned type is deposited on the inner part 19 of a snap fastener 20. The parts of the snap fastener may be silver plated. The electrode 10 comprises silver particles 12 and silver chloride particles 13 interspersed in an organic matrix 14 as described above. The electrode 10 is located in a plastic cup 21, and a portion of the snap fastener part 19 extends through an aperture in the cup 21. The cup 21 may be of a molded plastics resin, such as polyethylene, polyvinyl chloride, or acrylonitrile-butadiene-styrene.

The inner fastener part 19 is pressed into an outer fastener part 22 to form a swaged unit. A flexible open-cell member or sponge is located on top of the electrode 10 in the cup 21. The function of the sponge 23 is to absorb and retain an electrolyte, such as a saline solution, for the operation of the bioelectrode. The sponge 23 also functions as a shock absorber which isolates the electrode 10 from mechanical disturbances emanating from body parts.

The sponge 23 may be a sponge of cellulose or another hydrophilic material, a rubber sponge, or a flexible polyurethane sponge.

In accordance with a preferred embodiment of the subject invention, a supply of a silver chloride-doped, silver-filled resin and catalyst mixture in accordance with one of the above mentioned examples, or a supply of a silver chloride-doped, silver-filled elastomer in accordance with another example, is deposited in its uncured state on the upper fastener part 19 which has previously been swaged with the outer fastener part 22. The sponge 23 is then inserted into the cup 21 and is pressed against the uncured electrode 10. The electrode 10 may then be cured (such as by heat and pressure) and serve as an adhesive for the sponge 23 at the same time. The sponge or electrolyteretaining means 23 is thus bonded by the matrix 14 to the silver, silver chloride electrode 10, and the silver, silver chloride electrode 10 is bonded by the matrix 14 to the electri-

cal conductor or upper fastener part 19. This greatly simplifies the design of the cup 21 and the manufacture of the bioelectrode device.

To make the bioelectrode easily attachable to parts of the body, a pad 25 of a soft material, such as rubber, closed-cell polyurethane foam, or closed-cell polyethylene foam is provided with an adhesive coating 26. The adhesive 26 may be a commercially available, medical-grade pressure sensitive adhesive of the type marketed, for instance, by Minnesota Mining and Manufacturing Company. The pad 25 has an aperture for receiving the cup 21 and an outer flange of the cup 21 is attached by the adhesive 26 to the pad 25. The adhesive layer 26 is covered with a conventional protective paper layer 28 which is peeled off the adhesive prior to the use of the bioelectrode device. A protective cup 29, shown in dotted outline, may be attached to the bioelectrode device as shown in FIG. 2 to protect the device during storage and shipment. The protective cup 29, if used, is releasably attached to the bioelectrode device by means of an adhesive, and may be manufactured of polyvinyl chloride or polyethylene.

The swaged snap fastener unit 20 may be inserted into a corresponding snap fastener receptacle 31 which is connected to an electrocardiograph (ECG) or other bioelectric instrument 18 by an electrically insulated wire 32. In practice, the protective cup 29, if used, and the protective paper layer 28 are peeled off, a suitable chloride electrolyte, such as a saline solution, is applied to the sponge 23, and the bioelectrode device is applied to the patient's skin and is fastened thereto by the adhesive 26.

Comparing FIGS. 1 and 2, it will be noted that the fastener part 19 performs in the device of FIG. 2 the function of the conductor 16 shown in FIG. 1.

A disposable bioelectrode in accordance with a further preferred embodiment of the invention is shown in FIG. 3. Like reference numerals among FIGS. 2 and 3 designate like or functionally equivalent parts.

According to FIG. 3, the insulated electrical wire 32 has a non-insulated end portion 34 which corresponds to the conductor 16 shown in FIG. 1. The wire may be of silver or at least the end portion 34 may be silver plated. The electrically conductive wire end portion 34 is embedded in a silver, silver chloride electrode 10 according to the subject invention. As mentioned above, the electrode 10 has silver particles 12 and silver chloride particles 13 interspersed in an organic matrix 14. The electrode 10 may be manufactured in accordance with one of the above mentioned examples.

The electrode 10 has an open-cell rigid member 36 located thereon. The member 36 may be of open-cell urethane or other open-cell rigid plastic. Another suitable material for the member 36 is foam glass. The rigid open-cell member retains electrolyte without undue mobility thereof. A flexible sponge 38, which may be of the same material as the sponge 23 in FIG. 2, is located on top of the rigid member 36. In practice, electrolyte is applied to the sponge 38 until the pores of the rigid member 36 have been filled. In this manner, the flexible sponge 38, which serves as a shock absorber isolating the electrode 10 from mechanical disturbances emanating from body parts, and as a retainer of electrolyte, is spaced from the electrode 10, and the open-cell rigid member 36 is located between the flexible sponge 38 and the electrode 10.

The electrode 10, member 36 and sponge 38 are packaged in a laminate which is composed of heat-sealed plastics sheets 41 and 42 of such materials as polyvinyl chloride, polyethylene, ionomer resin, or other material used for blister or vacuum packs. The top sheet 42 has an opening through which the sponge 38 is exposed.

In accordance with a preferred manufacture of the bioelectrode device of FIG. 3, the silver chloride-doped resin and catalyst mixture is applied to the end portion 34 of the wire 32 in an uncured state. The uncured electrode mass with the embedded wire portion 34 is then placed onto the lower sheet 41 of the laminate. The rigid porous member 36 is then placed on top of the uncured electrode mass. The sponge member 38 is placed on top of the rigid porous member 36, and the top sheet 42 is placed on top of the whole assembly so that the central portion of the sponge 38 is exposed. The laminate may then be heat sealed and the electrode mass 10 cured in one operation.

The heat-sealed assembly 45 is then attached to the pad 25 by means of the adhesive layer 26. A peelable protective paper layer 28 is provided as before. A protective cup of the type indicated at 29 in FIG. 2 may also be provided for the bioelectrode device of FIG. 3.

The wire 32 may be attached to the apparatus 18 in any conventional manner. Both the bioelectrode device of FIG. 2 and the bioelectrode device of FIG. 3 may be sealed in a moisture and airtight package of a metal or plastics foil.

I claim:

1. A bioelectrode comprising in combination:
 - a silver, silver chloride electrode comprising a plurality of silver particles, a plurality of silver chloride particles, and an electrically insulating, water impermeable, inert organic matrix for said silver particles and said silver chloride particles, said silver particles and said silver chloride particles being interspersed with each other in and throughout said matrix, and said interspersed silver particles and silver chloride particles being in electrical contact with each other;
 - said silver particles being present in said organic matrix in an amount of from 15% to 70% by volume of said organic matrix with said interspersed silver particles and silver chloride particles;
 - said silver chloride particles being present in said organic matrix in an amount of from 0.2 to 15 percent by volume of said organic matrix with said interspersed silver particles and silver chloride particles;
 - an electrical conductor connected to said silver, silver chloride electrode;
 - means for retaining an electrolyte at said silver, silver chloride electrode; and
 - container means for said silver, silver chloride electrode and for at least part of said conductor and said electrolyte-retaining means.
2. A bioelectrode as claimed in claim 1, wherein:
 - said matrix covers said electrical conductor within said container means and has an exposed surface adjacent said electrolyte-retaining means; and
 - said interspersed silver particles and silver chloride particles are in electrical contact with said conductor and extend throughout said matrix from said

electrical conductor to said exposed surface of said matrix.

3. A bioelectrode as claimed in claim 2, wherein:
 - said electrical conductor comprises a support for said matrix with said interspersed silver particles and silver chloride particles.
4. A bioelectrode as claimed in claim 1, wherein:
 - said silver, silver chloride electrode is bonded by said matrix to said electrical conductor.
5. A bioelectrode as claimed in claim 4, wherein:
 - said electrolyte-retaining means are bonded by said matrix to said silver, silver chloride electrode.
6. A bioelectrode as claimed in claim 1, wherein:
 - said electrolyte-retaining means include a sponge bonded by said matrix to said silver, silver chloride electrode.
7. A bioelectrode as claimed in claim 1, wherein:
 - said electrolyte-retaining means include a flexible sponge spaced from said electrode, and an open-cell rigid member located between said flexible sponge and said electrode.
8. A bioelectrode as claimed in claim 1, including:
 - an adhesive pad connected to said container means to facilitate attachment of the bioelectrode to body parts.
9. A bioelectrode as claimed in claim 1, wherein:
 - said silver particles consist essentially of silver.
10. A bioelectrode as claimed in claim 1, wherein:
 - essentially each of said silver particles comprises a particle core and a coating of silver on said core.
11. A bioelectrode as claimed in claim 1, wherein:
 - essentially each of said silver particles comprises an inorganic core and a coating of silver on said core.
12. A bioelectrode as claimed in claim 1, wherein:
 - said organic matrix is a resin matrix.
13. A bioelectrode as claimed in claim 1, wherein:
 - said organic matrix is an epoxy resin matrix.
14. A bioelectrode as claimed in claim 1, wherein:
 - said organic matrix is elastomeric.
15. A bioelectrode comprising in combination:
 - a silver, silver chloride electrode comprising a plurality of silver particles, a plurality of silver chloride particles, and an electrically insulating, water impermeable, inert organic matrix for said silver particles and said silver chloride particles, said silver particles and said silver chloride particles being interspersed with each other in and throughout said matrix, and said interspersed silver particles and silver chloride particles being in electrical contact with each other;
 - said silver particles being present in said organic matrix in an amount of from 70 to 90 percent by weight of said organic matrix with said interspersed silver particles and silver chloride particles;
 - said silver chloride particles being present in said organic matrix in an amount of from 0.5 to 15 percent by weight of said organic matrix with said interspersed silver particles and silver chloride particles;
 - an electrical conductor connected to said silver, silver chloride electrode;
 - means for retaining an electrolyte at said silver, silver chloride electrode; and

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container means for said silver, silver chloride electrode and for at least part of said conductor and said electrolyte-retaining means.

16. A bioelectrode as claimed in claim 15, wherein:

said matrix covers said electrical conductor within said container means and has an exposed surface adjacent said electrolyte-retaining means; and said interspersed silver particles and silver chloride particles are in electrical contact with said conductor and extend throughout said matrix from said electrical conductor to said exposed surface of said matrix.

17. A bioelectrode as claimed in claim 16, wherein:

said electrical conductor comprises a support for said matrix with said interspersed silver particles and silver chloride particles.

18. A bioelectrode as claimed in claim 15, wherein:

said silver, silver chloride electrode is bonded by said matrix to said electrical conductor.

19. A bioelectrode as claimed in claim 18, wherein:

said electrolyte-retaining means are bonded by said matrix to said silver, silver chloride electrode.

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20. A bioelectrode as claimed in claim 15, wherein:

said electrolyte-retaining means include a sponge bonded by said matrix to said silver, silver chloride electrode.

21. A bioelectrode as claimed in claim 15, wherein:

said electrolyte-retaining means include a flexible sponge spaced from said electrode, and an open-cell rigid member located between said flexible sponge and said electrode.

22. A bioelectrode as claimed in claim 15, including:

an adhesive pad connected to said container means to facilitate attachment of the bioelectrode to body parts.

23. A bioelectrode as claimed in claim 15, wherein:

said silver particles consist essentially of silver.

24. A bioelectrode as claimed in claim 23, wherein:

said organic matrix is an epoxy resin matrix.

25. A bioelectrode as claimed in claim 23, wherein:

said organic matrix is elastomeric.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,834,373

Dated September 10, 1974

Inventor(s) Takuya R. Sato

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

Column 1, line 27, "includes" should be --included--.
Column 7, line 48, "curring" should be --curing--.
Claims 5, 6, 19 and 20 are cancelled.

Signed and sealed this 29th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks