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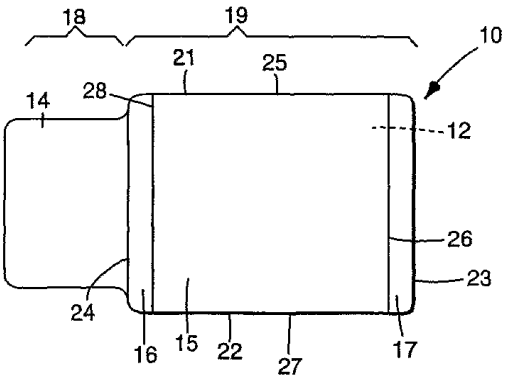
(54)【発明の名称】生体用電極における腐食防止

(57)【要約】
好ましくはメルカプタンおよびアゾールからなる群より選択される有機腐食抑制剤によって、その貯蔵寿命中に腐食から保護される非分極性銀／塩化銀生体用電極。導体は、その１面に部分的に塩化された銀の層が施されたフィルムの形態でポリマー材料を含む。



【特許請求の範囲】
【請求項１】
導電性媒体に接触する導体を含む生体用電極であって、前記導体が、少なくとも部分的に塩化された銀の導電的に活性の供給源を含み、電極が少なくとも１つの有機腐食抑制剤をさらに含む、生体用電極。
【請求項２】
前記導体が、その１面に部分的に塩化された銀の層が施されたフィルムの形態でポリマー材料を含む、請求項１に記載の生体用電極。
【請求項３】
導電性媒体に接触する導体を含む生体用電極であって、前記導体が、その上に少なくとも部分的に塩化された銀を有する基材を含み、銀が有機腐食抑制剤で処理されている、生体用電極。
【請求項４】
部分的に塩化された銀および少なくとも１つの有機腐食抑制剤を含む導電性層を有する導体を調製するステップと、
導電性媒体層を前記導電性層に塗布するステップと、
を含む、生体用電極を調製する方法。
【請求項５】
有機腐食抑制剤がメルカプタンおよびアゾールからなる群より選択される、請求項１～４のいずれか１項に記載の生体用電極または方法。
【請求項６】
薬剤が、２－メルカプトベンゾオキサゾールおよびオクタデカンチオールからなる群より選択される、請求項１～４のいずれか１項に記載の生体用電極または方法。
【請求項７】
薬剤が、導体中の元素銀の少なくとも０．０１重量％の量で存在する、請求項１～６のいずれか１項に記載の生体用電極または方法。
【請求項８】
導体が、その上に銀／塩化銀含有インクを有するバッキングを含む、請求項１～７のいずれか１項に記載の生体用電極または方法。
【発明の詳細な説明】
【技術分野】
【０００１】
本発明は、生体用電極の製造と使用に関する。
【背景技術】
【０００２】
現代医学は、電気的信号または電流が患者の身体から受信され、あるいは患者の身体に伝達される、多くの医学的手技を用いる。これらの手技で使用される医療機器と患者の皮膚間のインタフェースは、通常、生体用電極を含む。このような電極は典型的に、機器に電気的に接続する導体と、患者の皮膚に付着または別のやり方で接触する導電性媒体とを含む。
【０００３】
生体用電極を活用する治療的手技および装置としては、疼痛管理のための経皮的電気刺激（ＴＥＮＳ）装置、側弯症などの症状を治療するための神経筋刺激（ＮＭＳ）技術、胸腔に電気エネルギーを与えして心臓を除細動するための除細動電極、および電気外科で作られる切開内に与えられる電気エネルギーを受け入れる分散電極が挙げられる。
【０００４】
生体用電極を利用する診断的手技としては、心臓の活動をモニターし、心臓異常を診断するための心電図（ＥＣＧ）が挙げられる。
【０００５】
診断的目的のために使用されている、あるいは有用であると記載されている生体用電極の

代表例としては、その内容全体を参照して本願明細書に援用する、米国特許第４，３５２，３５９号（ラリモア（Ｌａｒｉｍｏｒｅ））、第４，５２４，０８７号（エンゲル（Ｅｎｇｅｌ））、第４，５３９，９９６号（エンゲル（Ｅｎｇｅｌ））、第４，５５４，９２４号（エンゲル（Ｅｎｇｅｌ））、第４，８４８，３４８号（カリム（Ｃａｒｉｍ））、第４，８４８，３５３号（エンゲル（Ｅｎｇｅｌ））、第５，０１２，８１０号（ストランド（Ｓｔｒａｎｄ）ら）、第５，１３３，３５６号（ブライアン（Ｂｒｙａｎ）ら）、第５，２１５，０８７号（アンダーソン（Ａｎｄｅｒｓｏｎ）ら）、および第５，２９６，０７９号（デュアン（Ｄｕａｎ）ら）が挙げられる。

【０００６】

診断用途では、高度に電気的に安定であることから、非分極性電極、特に銀／塩化銀電極が一般的に好まれる集電装置になっている。低コストバージョンでは、これらの電極は、銀／塩化銀粒子およびポリマーバインダーを含有する導電性インクから、絶縁バッキング上に狭いセクションで被覆される。銀／塩化銀電極は、腐食性攻撃に対してまずまず抵抗性であり、概して長い貯蔵寿命を有するが、高含水量と高塩素イオン濃度とが組み合わさった低ｐＨなどの特定のゲル条件下では、それらは加速された腐食を被り早発性の電気的故障を示すことができる。

【０００７】

生体用電極内の腐食を制御するために、犠牲陽極が電極アセンブリー内に織り合わされて集電装置に電気的に接続される。機能的ではあるが、このような保護は、設計制約と追加的な材料費のためにコスト的に効果的でないかもしれない。

【０００８】

生体用電極のための銀／塩化銀材料の代替案も提案されており、その例は水素化チタンおよび特定の炭素含有材料である。しかしこのような仕組みは概して過度に複雑かつ高価で、材料は集約的である。

【発明の開示】

【発明が解決しようとする課題】

【０００９】

したがってなおも簡単に組み立てられて比較的コスト的に効果的である、腐食抵抗性の生体用電極に対する必要性がある。

【課題を解決するための手段】

【００１０】

一態様では、本発明は、有機腐食抑制剤によって腐食から保護される、非分極性生体用電極を提供する。生体用電極は導電性媒体に接触する導体を含み、導体は少なくとも部分的に塩化された銀の導電的に活性の供給源を含み、電極は少なくとも１つの有機腐食抑制剤を含む。

【００１１】

別の態様では、本発明は、導体が、その上に少なくとも部分的に塩化された銀を有する基材を含み、銀が有機腐食抑制剤で処理されている、導電性媒体に接触する導体を含有する生体用電極を提供する。

【００１２】

さらに別の態様では、本発明は、

部分的に塩化された銀および少なくとも１つの有機腐食抑制剤を含む導電性層を有する導体を調製するステップと、

導電性媒体層を導電性層に塗布するステップと、を概して含む、

生体用電極を調製する方法を提供する。

【発明を実施するための最良の形態】

【００１３】

一態様では、本発明は、導電性媒体に接触する導体を有する生体用電極を提供する。導体は、その上に部分的に塩化された銀を有する導電性基材を含み、少なくとも１つの有機腐食抑制剤の存在によって腐食から保護される。導電性基材は、その上に銀含有層がある薄

いフィルムの形態でポリマー材料を含んでも良く、あるいは導体は、その上に銀含有層があるスタッドの形態で、グラファイト添加ポリマーまたはその他の導電性材料を含んでも良い。銀含有層は、銀添加インク、蒸着銀またはその他の活性銀供給源を含有できる。このような層内の銀は、塩化銀を塗布層に内在性にすることで、あるいは銀被覆表面を別個に部分的に塩化することで、部分的に塩化されても良い。

【００１４】

導電性ゲルおよびその他の電解質も有用であると見なされるが、導電性媒体は、導電性接着剤によって電極に最も都合良く提供される。米国特許第５，９５２，３９８号明細書で記載されたものをはじめとする、重合したマイクロエマルジョンからできた導電性接着剤も有用と見なされる。腐食抑制剤は、導体の部分的に塩化された銀層を腐食抑制剤で処理することで、あるいは銀添加インク配合物中に薬剤を含めることで、電極構造体中に組み込んでも良い。後者は、被覆インク層が塗布された後に、薬剤をそれに塗布することで達成されても良い。腐食抑制剤はまた、導電性媒体に直接含まれても良い。

【００１５】

有用な腐食抑制剤としては、腐食を適切に遅延させ、導電性材料と適合性である、すなわち導体と導電性媒体間のインタフェースの電気的性質を劣化させない、あらゆる薬剤が挙げられる。好ましい腐食抑制剤はまた、腐食保護損失を引き起こして皮膚接触可能性を増大させる導電性媒体中への浸出に抵抗し、ヒトの皮膚に対して低毒性を示す。製造実施においては、銀添加インクの手段によって導体上に銀をのせることが都合がよいので、薬剤は好ましくはこのようなインクのための既知の溶剤キャリア中で高度に可溶性でもあり、比較的低い蒸気圧を有して、インクコーティングを乾燥させるのに必要な熱処理に耐える。最も好ましい腐食抑制剤は、メルカプタンおよびアゾールからなる群より選択される。具体的な代表的化合物としては、２－メルカプトベンゾオキサゾールおよびオクタデカンチオールが挙げられる。

【００１６】

図１および図２は、本発明の診断用電極１０の一実施態様のそれぞれ底および側面の平面図である。哺乳類の皮膚から最も遠い表面から、電極１０は、導電性接着剤の領域１５に接触する電気的導電性表面１４をその少なくとも一部の上に有する側面１３を有する、非導電性可撓性のバッキング１２を含む。生体適合性感圧皮膚接着剤の２つの別個の対向する領域１６および１７は、側面１３、そして好ましくは導電性の表面１４に接触する。電極１０の非使用時に、接着剤の領域１５、１６、および１７に接触する剥離ライナーは図示されていない。

【００１７】

可撓性のバッキング１２は、タブ部分１８およびパッド部分１９を含む。タブ部分１８およびパッド部分１９のどちらも導電性の表面１４を有するが、導電性接着剤の領域１５はパッド部分１９のみに接触する。タブ部分１８は、ＥＣＧ信号を電気器具に伝達する電気的接続部への脱着性付着に適する。

【００１８】

パッド部分１９は、端２１、２２、２３、および２４によって画定される外周を有する。比較として導電性接着剤の領域１５は、端２５、２６、２７、および２８によって画定される外周を有する。端２５～２８内の導電性接着剤の領域１５の表面区域は、パッド部分１９の端２１～２４内のパッド部分１９の表面区域に接触する。

【００１９】

生体適合性皮膚接着剤の領域１６および１７は領域１５のようにイオン導電性でないが、側面１３上の別個の位置で、そして好ましくは導電性表面１４の別個の位置で、パッド部分１９に好ましくは接触して、電極１０の哺乳類患者の皮膚への接着剤接触の保持を助ける。タブ部分１８に近位および遠位の、パッド部分１９上の別個の対向する位置は、使用中に電極１０にかかる応力のために、タブ部分１８とパッド部分１９の双方を二等分する線に沿って、電極１０の端のめくれによって、電極１０が、最も影響を受けやすい２つの位置で追加的接着性を有するので、哺乳類皮膚への比較的高レベルの接着を提供する。

【００２０】
図２に見られるように、好ましくは生体適合性感圧皮膚接着剤領域１６および１７は、パッド部分１９の側面１３、そして好ましくは導電性表面１４に直接接触する。また好ましくは、約０．２５ｍｍ～約０．７５ｍｍの厚さの範囲、そして好ましくは約０．５０ｍｍの厚さである、領域１６および１７の最終厚（加工後）は、イオン導電性接着剤の領域１５の最終厚の４０％、そして好ましくは２０％内である。理想的には、領域１５および領域１６および１７の最終厚は等しく、あるいは差が１０％未満である。
【００２１】
電極１０を構築するための材料選択は、生体用電極構造体の当業者には既知である。全てその内容を参照して本願明細書に援用する、米国特許第４，３５２，３５９号（ラリモア（Ｌａｒｉｍｏｒｅ））、第４，５２４，０８７号（エンゲル（Ｅｎｇｅｌ））、第４，５３９，９９６号（エンゲル（Ｅｎｇｅｌ））、第４，５５４，９２４号（エンゲル（Ｅｎｇｅｌ））、第４，８４８，３４８号（カリム（Ｃａｒｉｍ））、第４，８４８，３５３号（エンゲル（Ｅｎｇｅｌ））、第５，０１２，８１０号（ストランド（Ｓｔｒａｎｄ））ら）、第５，１３３，３５６号（ブライアン（Ｂｒｙａｎ）ら）、第５，２１５，０８７号（アンダーソン（Ａｎｄｅｒｓｏｎ）ら）、第５，２９６，０７９号（デュアン（Ｄｕａｎ）ら）、米国特許第５，３８５，６７９号（ウイ（Ｕｙ）ら）、米国特許第５，７０２，７５３号（ヤシス（Ｙａｓｉｓ）ら）、および米国特許第５，７７９，６３２号（ディーツ（Ｄｉｅｔｚ）ら）明細書は、全てＥＣＧ手技に有用な生体用電極の構造体のための適切な材料について記載している。
【００２２】
当業者に既知の多数の非導電性材料の中で、現在バッキング１２のために好ましいのはバージニア州ホープウェルのＩＣＩアメリカス（ＩＣＩ Ａｍｅｒｉｃａｓ（Ｈｏｐｅｗｅｌｌ，ＶＡ））から「メリネックス（Ｍｅｌｉｎｅｘ）」商標のフィルム（例えば３２９および３３９）として市販される約０．１ｍｍ厚さのポリエステルフィルムである。好ましくはフィルムをコロナ処理で処理して、バッキングに対する導電性表面の接着を改善できる。
【００２３】
当業者に既知の多数の導電性材料の中で、グラファイトまたは金属などの導電性粒子を含有するインクが有用であり、金属含有インクが好ましい。導電性表面１４のために現在好ましいのは、全てマサチューセッツ州ウォルサムのエルコン（Ｅｒｃｏｎ，Ｉｎｃ．（Ｗａｌｔｈａｍ，Ｍａｓｓ））から市販される「Ｎ－３０」インクなどの銀含有インク、「Ｒ－３００」インクなどの銀／塩化銀含有インク、またはＲ－３０１ＭＰＫ（＋２４０）（登録商標）インクである。このような銀／塩化銀インクは、グラビアコーティングによってバッキングに都合良く塗布されても良い。インクジェット印刷、シルクスクリーン印刷、およびナイフコーティングをはじめとする多くのその他の方法が、適切と見なされる。
【００２４】
導電性接着剤の領域１５は、当業者に既知の多数の導電性接着剤の中で、全てその内容を参照して本願明細書に援用する、米国特許第５，０１２，８１０号（ストランド（Ｓｔｒａｎｄ））１６欄の表で記載され、米国特許第４，５２４，０８７号、第４，５３９，９９６号、第４，８４８，３５３号、および第４，５５４，９２４号明細書（全てエンゲル（Ｅｎｇｅｌ））、第５，２９６０７９号（デュアン（Ｄｕａｎ））ら）、第５，３８５，６７９号（ウイ（Ｕｙ）ら）、および第５，３３８，４９０号（ディーツ（Ｄｉｅｔｚ））ら）で記載されて開示されている導電性接着剤であることができる。現在好ましい導電性接着剤の領域１５は、その内容を参照して本願明細書に援用するディーツ（Ｄｉｅｔｚ）らに付与された米国特許第５，７７９，６３２号明細書で記載されているような、親水性および疎水性組成物の相互貫入領域を有する共連続生体適合性導電性接着剤である。コーティングを容易にするために、参照した米国特許第５，７７９，６３２号明細書の導電性接着剤の粘度を増大させることが都合が良い場合もある。重合に先だって、概して２０

０，０００～８００，０００の分子量を有するポリアクリル酸のかなりの量を添加して、これを達成できる。このような工程に関する追加的詳細は、その内容を参照して本願明細書に援用する同時係属米国特許出願第０９／８４４，０３１号にある。

【００２５】

当業者に既知の多数の生体適合性皮膚接着剤の中で、接着剤の領域１６および１７のために現在好ましいのは、アクリレート感圧接着剤、および粘着性付与ポリスチレン－ポリイソプレンブロック共重合体感圧接着剤である。このようなアクリレートエステル共重合体接着剤については、全てその内容を参照して本願明細書に援用する、米国特許第第２，９７３，２８６号、第Ｒｅ２４，９０６号、第Ｒｅ３３，３５３号、第３，３８９，８２７号、第４，１１２，２１３号、第４，３１０，５０９号、第４，３２３，５５７号、第４，７３２，８０８号、第４，９１７，９２８号、第４，９１７，９２号明細書、および欧州特許公開第００５１９３５号で概して記載されている。粘着性付与ブロック共重合体接着剤については、その内容を本願明細書に援用した、サタス（Ｓａｔａｓ）編「感圧接着剤技術ハンドブック（Ｈａｎｄｂｏｏｋ ｏｆ Ｐｒｅｓｓｕｒｅ Ｓｅｎｓｉｔｉｖｅ Ａｄｈｅｓｉｖｅ Ｔｅｃｈｎｏｌｏｇｙ）」第二版、ヴァン・ノストランド・ラインホルド（Ｖａｎ Ｎｏｓｔｒａｎｄ Ｒｅｉｎｈｏｌｄ）出版（１９８９年）の第１３章である、ユーインズ（Ｅｗｉｎｓ）著「熱可塑性ゴム：Ａ－Ｂ－Ａブロック共重合体（Ｔｈｅｒｍｏｐｌａｓｔｉｃ Ｒｕｂｂｅｒｓ：Ａ－Ｂ－Ａ Ｂｌｏｃｋ Ｃｏｐｏｌｙｍｅｒｓ）」で概して記載されている。生体用電極における生体適合性皮膚接着剤としての粘着性付与ブロック共重合体接着剤の使用については、米国特許第４，２０４，３１２号で記載されている。

【００２６】

その内容を参照して本願明細書に援用する、サタス（Ｓａｔａｓ）編、感圧接着剤技術ハンドブック（Ｈａｎｄｂｏｏｋ ｏｆ Ｐｒｅｓｓｕｒｅ Ｓｅｎｓｉｔｉｖｅ Ａｄｈｅｓｉｖｅ Ｔｅｃｈｎｏｌｏｇｙ）第二版、ヴァン・ノストランド・ラインホルド（Ｖａｎ Ｎｏｓｔｒａｎｄ Ｒｅｉｎｈｏｌｄ）出版（１９８９年）の第３４章である、サタス（Ｓａｔａｓ）著「コーティング機器（Ｃｏａｔｉｎｇ Ｅｑｕｉｐｍｅｎｔ）」で記載されるように、押出しコーティング、ナイフコーティング、およびカーテンコーティングをはじめとする様々なコーティング方法が、導電性接着剤と生体適合性皮膚接着剤の双方について利用できる。ハンドナイフコーティングを用いることができる。押出しダイと、ナイフダイと、カーテンコーティングダイと、その内容を参照して本願明細書に援用するサタス（Ｓａｔａｓ）編、コーティング技術ハンドブック（Ｃｏａｔｉｎｇｓ Ｔｅｃｈｎｏｌｏｇｙ Ｈａｎｄｂｏｏｋ，）マルセル・デッカー（Ｍａｒｃｅｌ Ｄｅｋｋｅｒ，Ｉｎｃ．）出版（１９９１年）の第１１章であるリッペルト（Ｌｉｐｐｅｒｔ）著「低粘度流体のためのスロットダイコーティング（Ｓｌｏｔ Ｄｉｅ Ｃｏａｔｉｎｇ ｆｏｒ Ｌｏｗ Ｖｉｓｃｏｓｉｔｙ Ｆｌｕｉｄｓ）」で概して記載される、高剪断フラットしごきリップ、中程度剪断フラットしごきリップ、中程度剪断ロッドしごきリップ、またはシャープナイフしごきリップを有するその他のタイプのスロットダイとをはじめとするスロットダイが、好ましくは使用される。コーティング方法の選択およびスロットダイの使用は、それが高粘度１００％固形分ホットメルトであるか、ウェブ上で重合する中程度粘度１００％固形分材料であるか、あるいは中程度から低い粘度の溶剤または水によって伝達される材料であるかなどの接着剤前駆体の性質に左右される。当業者は、後者の場合、コーティングステップが乾燥工程を伴うこと、そして溶剤または水の損失のために、この乾燥工程がコーティングヘッドでの厚さよりも薄い接着剤の最終厚に帰結することを理解するであろう。双方のタイプの接着剤が患者皮膚との接触を有するために、導電性接着剤の最終厚は生体適合性感圧接着剤の最終厚の４０％以内であるべきである。

【実施例】

【００２７】

実施例１

マサチューセッツ州ウォルサムのエルコン（Ｅｒｃｏｎ Ｉｎｃ．（Ｗａｌｔｈａｍ，Ｍ

Ａ．））から「Ｒ３００」として市販される銀／塩化銀導電性インク溶液を得た。このインクは固形分５８％を有し、その内元素銀は７０％を構成する。インクのためのキャリア溶剤は、メチルプロピルケトン（ＭＰＫ）であった。処理剤として、純度９５％の２－メルカプトベンゾオキサゾール（ＭＢＯ）をウィスコンシン州ミルウォーキーのアルドリッチ・ケミカルズ（Ａｌｄｒｉｃｈ　Ｃｈｅｍｉｃａｌｓ（Ｍｉｌｗａｕｋｅｅ，ＷＩ））から得た。３個の１００ｇのインクサンプルを秤り取った。これらのそれぞれに、ＭＰＫにあらかじめ溶解したＭＢＯ溶液を添加して、インク中の元素銀を基準にして０．１、０．５、および１．０重量％の最終ＭＢＯ濃度を得た。これらのインクサンプルをワイヤコーティング手技を使用して、バージニア州ホープウェルのＩＣＩフィルム（ＩＣＩ　Ｆｉｌｍｓ（Ｈｏｐｅｗｅｌｌ，ＶＡ，））からメリネックス（Ｍｅｌｉｎｅｘ）™５０５として市販される、０．１ｍｍポリエステルフィルムから製造したポリマーバッキング上に薄く塗布した。次に被覆されたフィルムを室温で５分間乾燥し、続いて２００°Ｆ（９３℃）で５分間乾燥した。対照インクサンプル（ＭＢＯを含有しない）を全く同じやり方で塗布した。

【００２８】

これらの全サンプルで、ディーツ（Ｄｉｅｔｚ）らに付与された米国特許第５，７７９，６３２号の開示に従って配合したｐＨ２．８を有する共連続接着剤を銀コーティングに付着させた。次にサンプルを電気的接触のための銀インク露出タブを有する長方形の電極片に切断した。

【００２９】

実施例２

製造直後に、対照群および各ＭＢＯレベルからの電極を類似組成物の別の電極と対にした。これらの対を互いに付着して、それらの共連続接着剤層が向い合って接触するように配置した。この配置は医療器具開発協会（ＡＡＭＩ）が公表する、ＥＣＧ使い捨て電極に使用される生体用電極の適切な性能を判定するための規格、具体的にはその内容を参照して本願明細書に援用する、Ｄ．Ｃ．オフセット（１００ｍＶ）、Ａ．Ｃ．インピーダンス（２ｋΩ）、および除細動過負荷回復（４回のコンデンサー放電の５秒後に１００ｍＶ未満、および残留分極電位増減率１ｍＶ／秒以下）特性最低基準の試験方法および条件のための「ゲル付きＥＣＧ使い捨て電極に関する米国標準規格（Ａｍｅｒｉｃａｎ　Ｎａｔｉｏｎａｌ　Ｓｔａｎｄａｒｄ　ｆｏｒ　Ｐｒｅｇｅｌｌｅｄ　ＥＣＧ　Ｄｉｓｐｏｓａｂｌｅ　Ｅｌｅｃｔｒｏｄｅｓ）」医療器具開発協会（１９８４）で規定されている。

【００３０】

いくつかの電極対で製造直後に、これらの標準ＡＡＭＩ試験を実施し、別の電極群は２０３°Ｆ（９５℃）で４８時間老化させて、これらにもＡＡＭＩ試験を実施した。結果を下記の第１表に示す。

【００３１】

【表１】

第１表

組成物		60秒でのDCオフセット（mV）	Z_{10}（Ω）	4パルス後のSDR	SDR勾配（mV／秒）	Z_{10}（Ω）
	許容値	(10)	(2000)	(100)	(1未満)	(2000)
対照	未老化	0.2	307	11.5	−0.3	171
	老化	−8.1	4022	25.9	−2.3	3741
0.1% MBO	未老化	−0.1	147	8.7	−0.3	140
	老化	0.5	4013	9.4	−0.2	553
0.5% MBO	未老化	−3.0	416	13.4	−0.4	263
	老化	0.1	257	18.0	−0.7	214
1.0% MBO	未老化	1.2	636	18.9	−0.8	475
	老化	1.8	915	33.1	−2.0	851

【００３２】
この実験の対照サンプルから、老化が最終的にこの電極にインピーダンス増大を生じさせ、最終的にそれを使用に耐えなくすることが分かる。外見から判断して、銀／塩化銀インタフェースの腐食がこの増大の理由と考えられる。十分な量のＭＢＯが、この影響から電極を保護するようであり、処理済みサンプルの視覚的にクリーンな外見がこの結論を支持する。しかしある時点で、大量のＭＢＯの添加は電極の分極からの回復に影響し始めるので、元素銀の約０．５重量％レベルのＭＢＯが最適の結果を与えるようである。
【００３３】
実施例３
大規模実験を実施して、商業規模および商業的パッケージング条件下での本発明の実施可能性を立証した。実施例１で記載した、片面に表示があるタイプのポリエステルフィルム

を実施例１からの６つのＭＢＯ濃度レベルの銀／塩化銀インクで被覆した。ここでもＭＥＫ中の溶液としてＭＢＯを銀インクに添加した。ＭＢＯ溶液の添加によってインクを約５％に希釈した。６個の被覆されたロールのＭＢＯ含量は、０％、０．１％、０．３％、０．５％、０．７％、および０．９％ｗ／ｗ（コーティング中の元素銀重量を基準にして）であった。これらの６種のインクを溶剤コーターによって、ポリエステルフィルムに２回の通過で塗布した。１回目のコーティング通過はおよそ０．７ｍｇ／ｃｍ^{2}ポリエステルバッキングの銀含量を付着させ、２回目の通過はレベルをおよそ１．５ｍｇ／ｃｍ^{2}に増大させた。

【００３４】

概して米国特許第５，７０２，７５３号の開示に従って、カード当たり１０個の電極がある電極カードを作って、これらの被覆されたバッキングを全て電極に転換した。次にパウチあたり２枚のカードで、ポリライナーパウチに電極カードをパックした。処理剤のレベルを変動させたこと以外は、得られた電極は、ミネソタ州セントポールの３Ｍ社（３ＭＣｏ．（Ｓｔ．Ｐａｕｌ，Ｍｉｎｎｅｓｏｔａ））から市販されるモデル２３６０静止電極に類似した。各処理剤レベルの無作為サンプルをＡＡＭＩ規格に従って即座に試験する一方、その他は老化させてから規格に従って試験した。これらのパウチを２０３°Ｆ（９５℃）で８日間老化させ、次に試験前に室温に１時間平衡化させた。結果を下記の表に示す。

【００３５】

【表２】

第２表

組成物		60秒でのDCオフセット（mV）	Z_{10}（Ω）	4パルス後のSDR	SDR勾配（mV／秒）	Z_{10}（Ω）
	許容値	(10)	(2000)	(100)	(1未満)	(2000)
対照	未老化	0.1	108	11.1	-0.3	71
	老化	-13.6	4005	10.7	-0.7	782
0.1% MBO	未老化	-0.2	860	11.3	-0.4	330
	老化	1.5	4036	388	-15.6	4055
0.3% MBO	未老化	-0.1	1005	11.5	-0.3	442
	老化	-0.5	610	18.9	-1.2	535
0.5% MBO	未老化	-0.4	851	13.4	-0.4	388
	老化	-0.6	154	13.4	-0.4	142
0.7% MBO	未老化	0.4	953	14.3	-0.4	452
	老化	-0.7	238	17.0	-1.0	204
0.9% MBO	未老化	-0.7	1205	18.6	-0.6	555
	老化	-1.4	4052	270	-13.8	4051

【００３６】

ファント・ホッフの法則に従って、９５℃での８日間は、室温で３年あまりの老化にほぼ相当する。結果は、ＭＢＯ添加が電極の腐食抵抗性に有益な効果を有すること、この電極構造体の最適ＭＢＯ包含量が元素銀含量を基準にして０．３％～０．５％の間にあることを明らかに示す。しかし腐食に対して有用なレベルの保護を提供する最小レベル薬剤は、スクエア当たりに存在する銀の量の絶対値に左右されると考えられる。より多くの銀含量

を有するいくつかの代案の構造体では、元素銀含量のわずか０．０１重量％程度のＭＢＯが、本発明による可働電極を提供するとさらに考えられる。

【００３７】

実施例４

電極サンプルは、処理剤がインクの元素銀含量の０．１重量％の量で添加されたオクタデカンチオール（ＯＴ）であったこと以外は、概して実施例１に従って製造した。次にサンプルを１５０°Ｆ（６５℃）で４９日間老化させた。次にサンプルＡＡＭＩ規格に従って試験した。結果を下記の表に示す。

【００３８】

【表３】

第３表

組成物		60秒でのDCオフセット（mV）	Z_{10}（Ω）	4パルス後のSDR	SDR勾配（mV／秒）	Z_{10}（Ω）
	許容値	（10）	（2000）	（100）	（1未満）	（2000）
対照	老化	−3．1	4034	9．5	−0．4	4023
0.1% OT	老化	−1．6	387	12	−0．2	166

【００３９】

この実施例は、本発明との関連で使用しても良い処理剤が、いくらかの疎水性を有しても作動することを実証する。しかし使用しても良いこのような疎水性薬剤の量は限られる。大量のこのような薬剤が導電性層の表面エネルギーを変化させ、導電性接着剤による銀／塩化銀表面の濡れに影響することが観察された。

【図面の簡単な説明】

【００４０】

【図１】本発明による診断用電極の平面図である。

【図２】図１の診断用電極の側面図である。

【図３】製造中の診断用電極のアレイの模式図である。

【国際公開パンフレット】

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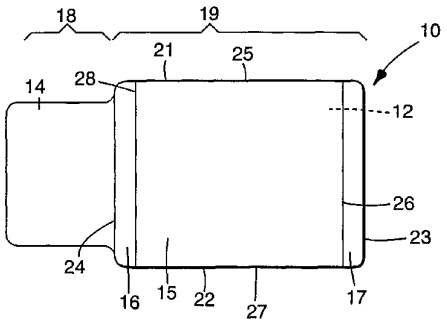
(54) **Title:** CORROSION PREVENTION IN BIOMEDICAL ELECTRODES



(57) **Abstract:** A non-polarizable, silver/silver chloride biomedical electrode that is protected against corrosion during its shelf life by an organic corrosion retarding agent, preferably selected from the group consisting of mercaptans and azoles. The conductor comprises a polymeric material in the form of a film upon one side of which is disposed a layer of partially chlorided silver.

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CORROSION PREVENTION IN BIOMEDICAL ELECTRODES

TECHNICAL FIELD

This invention relates to the making and using of biomedical electrodes.

BACKGROUND OF THE INVENTION

Modern medicine employs many medical procedures where electrical signals or currents are received from or delivered to a patient's body. The interface between medical equipment used in these procedures and the skin of the patient usually includes a biomedical electrode. Such an electrode typically includes a conductor connected electrically to the equipment and a conductive medium adhered to or otherwise in contact with the patient's skin.

Therapeutic procedures and devices that make use of biomedical electrodes include transcutaneous electronic nerve stimulation (TENS) devices for pain management; neuromuscular stimulation (NMS) techniques for treating conditions such as scoliosis; defibrillation electrodes for dispensing electrical energy to a chest cavity to defibrillate the heart; and dispersive electrodes to receive electrical energy dispensed into an incision made during electrosurgery.

Diagnostic procedures that make use of biomedical electrodes include electrocardiograms (ECGs) for monitoring heart activity and diagnosing heart abnormalities.

Representative examples of biomedical electrodes that have been used for, or described as useful for, diagnostic purposes include U.S. Pat. Nos. 4,352,359 (Larimore); 4,524,087 (Engel); 4,539,996 (Engel); 4,554,924 (Engel); 4,848,348 (Carim); 4,848,353 (Engel); 5,012,810 (Strand et al.); 5,133,356 (Bryan et al.); 5,215,087 (Anderson et al.); and 5,296,079 (Duan et al.), the entire contents of which are hereby incorporated by reference.

For diagnostic applications, non-polarizable electrodes, and in particular silver/silver chloride electrodes, have become the current collectors of choice because of their high electrical stability. In low-cost versions, these electrodes are coated in thin sections from a conductive ink containing silver/silver chloride particles and a polymeric binder onto an insulating backing. While silver/silver chloride electrodes are reasonably resistant to corrosive attack and generally have a long shelf-life, under certain gel conditions such as a low pH in conjunction with a high water content and high chloride concentration, they can undergo accelerated corrosion and exhibit premature electrical failure.

To control corrosion in biomedical electrodes, sacrificial anodes have been interwoven in an electrode assembly and electrically connected to a current collector. While functional, such protection may not be cost-effective due to design constraints and added material costs.

Alternative for silver/silver chloride materials have also been proposed for biomedical electrodes, among them titanium hydride and certain carbon-containing materials. Such arrangements, however, are generally unduly complex, expensive and material-intensive.

There remains a need, therefore, for corrosion-resistant biomedical electrodes that are simply constructed and relatively cost-effective.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a non-polarizable biomedical electrode that is protected against corrosion by an organic corrosion retarding agent. The biomedical electrode comprises a conductor in contact with a conductive medium, wherein the conductor comprises a conductively active source of at least partially chlorided silver and wherein the electrode includes at least one organic corrosion retarding agent.

In another aspect, the invention provides a biomedical electrode comprising a conductor in contact with a conductive medium, wherein the conductor comprises a substrate having at least partially chlorided silver thereon and wherein the silver has been treated with an organic corrosion retarding agent.

In still another aspect, the invention provides methods of preparing biomedical electrodes, the methods generally comprising the steps of:

preparing a conductor having a conductive layer comprising partially chlorided silver and at least one organic corrosion retarding agent; and

applying a layer of conductive medium to the conductive layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a bottom plan view of a diagnostic electrode according to the present invention.

FIG. 2 is a side plan view of the diagnostic electrode of FIG. 1.

FIG. 3 is an array of diagnostic electrodes during manufacture.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In one aspect the invention provides a biomedical electrode having a conductor in contact with a conductive medium. The conductor includes a conductive substrate having partially chlorided silver thereon and is protected from corrosion by the presence of at least one organic corrosion retarding agent. The conductive substrate may comprise a polymeric material in the form of a thin film upon which there is a silver-containing layer, or the conductor may comprise a graphite loaded polymer or other conductive material in the form of a stud upon which is a silver-containing layer. The silver-containing layer can contain a silver-loaded ink, a vapor deposit of silver or some other source of active silver. The silver in such a layer may be partially chlorided, either by having silver chloride intrinsic to the applied layer or by separately partially chloriding a silvered surface.

A conductive medium is most conveniently provided for the electrode by a conductive adhesive, although conductive gels and other electrolytes also are considered useful. Conductive adhesives made from polymerized microemulsions, including those described in U.S. Patent No. 5,952,398, are also considered useful. The corrosion retarding agent may be incorporated into the electrode construction either by treating the partially chlorided silver layer of the conductor with the corrosion retarding agent or by including the agent in the formulation of a silver-loaded ink. The latter may be

accomplished by applying the agent to the coated ink layer after it has been applied. The corrosion retarding agent may also be included directly in the conductive medium.

Useful corrosion retarding agents include any agent that adequately retards corrosion and that is compatible with the conductive materials, *i.e.*, does not degrade the electrical properties of the interface between the conductor and the conductive medium. Preferred corrosion retarding agents will also resist leaching into the conductive medium, which could cause a loss of corrosion protection and raise the possibility of dermal contact, and will exhibit low toxicity towards human skin. Since in manufacturing practice it is convenient to place the silver onto the conductor by means of a silver-loaded ink, the agents will also preferably be highly soluble in known solvent carriers for such inks and will have relatively low vapor pressures to withstand the thermal treatment required to dry ink coatings. The most preferred corrosion retarding agents are selected from the group consisting of mercaptans and azoles. Specific, representative compounds include 2-mercaptobenzoxazole and octadecanethiol.

FIGS. 1 and 2 are bottom and side plan views, respectively, of one embodiment of a diagnostic electrode 10 of the present invention. From the surface farthest away from mammalian skin, electrode 10 comprises a non-conductive flexible backing 12 having a side 13 having on at least a portion thereof an electrically conductive surface 14 contacting a field 15 of conductive adhesive. Two separate opposing fields 16 and 17 of biocompatible pressure sensitive skin adhesive contact side 13 and preferably electrically conductive surface 14. Not shown is a release liner that contacts fields 15, 16, and 17 of adhesive when electrode 10 is not in use.

Flexible backing 12 comprises a tab portion 18 and a pad portion 19. Both tab portion 18 and pad portion 19 have electrically conductive surface 14, but field 15 of conductive adhesive contacts only pad portion 19. Tab portion 18 is suitable for releasable attachment to an electrical connector that delivers the ECG signals to the electrical instrumentation.

Pad portion 19 has a perimeter defined by edges 21, 22, 23, and 24. By comparison, field 15 of conductive adhesive has a perimeter defined by edges 25, 26, 27, and 28. The surface area of field 15 of conductive adhesive within edges 25-28 contacts the surface area of pad portion 19 within edges 21-24 of pad portion 19.

Fields 16 and 17 of biocompatible skin adhesive are not ionically conductive as is field 15 but are preferably contacting pad portion 19 in separate locations on side 13 and preferably in separate locations on electrically conductive surface 14 to assist in the maintenance of adhesive contact of electrode 10 to skin of a mammalian patient. The separate opposing locations on pad portion 19 proximal and distal to tab portion 18 provide a relatively high level of adhesion to mammalian skin because the electrode 10 has added adhesiveness in the two locations most likely to be affected by edge lifting of the electrode 10 due to stress applied to the electrode 10 during use: along a line bisecting both the tab portion 18 and the pad portion 19.

As seen in FIG. 2, preferably the biocompatible pressure sensitive skin adhesive fields 16 and 17 is in direct contact with side 13, and preferably electrically conductive surface 14, of pad portion 19. Also preferably, the final thickness (after processing) of fields 16 and 17, ranging from about 0.25 mm to about 0.75 mm thick, and preferably about 0.50 mm thick, is within 40 percent, and preferably within 20 percent, of the final thickness of the field 15 of ionically conductive adhesive. Ideally, the final thickness of field 15 and fields 16 and 17 are equal or within a difference of less than 10 percent.

Selection of materials to construct electrode 10 are known to those skilled in the art of biomedical electrode construction. U.S. Pat. Nos. 4,352,359 (Larimore); 4,524,087 (Engel); 4,539,996 (Engel); 4,554,924 (Engel); 4,848,348 (Carim); 4,848,353 (Engel); 5,012,810 (Strand et al.); 5,133,356 (Bryan et al.); 5,215,087 (Anderson et al.); 5,296,079 (Duan et al.); U.S. Pat. No. 5,385,679 (Uy et al.); U.S. Pat. No. 5,702,753 (Yasis et al.); and U.S. Pat. No. 5,779,632 (Dietz et al) all describe suitable materials for the construction of biomedical electrodes useful for ECG procedures, and all are incorporated by reference as if fully rewritten herein.

Of the numerous electrically nonconductive materials known to those skilled in the art, presently preferred for backing material 12 are polyester films of about 0.1 mm thickness commercially available as "Melinex" branded films (*e.g.*, 329 and 339) from ICI Americas of Hopewell, VA. Preferably, the film can be treated with a corona treatment to improve the adhesion of the electrically conductive surface to the backing material.

Of the numerous electrically conductive materials known to those skilled in the art, inks containing electrical conductive particles such as graphite or metals are useful with

metal-containing inks being preferred. Presently preferred for electrically conductive surface 14 is a silver containing ink such as "N-30" ink, a silver/silver chloride containing ink such as "R-300" ink, or R-301MPK (+240)® ink, all commercially available from Ercon, Inc. of Waltham, Mass. Such a silver/silver chloride ink may be conveniently be applied to a backing by gravure coating. Many other methods are considered suitable, including ink jet printing, silkscreen printing, and knife coating.

Of the numerous conductive adhesives known to those skilled in the art, field 15 of conductive adhesive can be those conductive adhesives as described in the table at column 16 of U.S. Pat. No. 5,012,810 (Strand et al.) and as disclosed in U.S. Pat. Nos. 4,524,087; 4,539,996; 4,848,353; and 4,554,924 (all Engel); 5,296 079 (Duan et al.); U.S. Pat. No. 5,385,679 (Uy et al.); and U.S. Pat. No. 5,338,490 (Dietz et al.) all of which are incorporated by reference herein. Presently preferred for field 15 of conductive adhesive is a bicontinuous biocompatible conductive adhesive having interpenetrating domains of hydrophilic and hydrophobic composition as described in U.S. Pat. No. 5,779,632 to Dietz et al, which is incorporated by reference herein. It is sometimes convenient to increase the viscosity of the conductive adhesive of the 5,779,632 reference for ease in coating. Adding a quantity of polyacrylic acid having a molecular weight generally between 200,000 and 800,000 prior to polymerization can be done to accomplish this. Additional details regarding such a process can be found in co-pending U.S. patent application serial number 09/844,031, which is incorporated herein by reference.

Of the numerous biocompatible skin adhesives known to those skilled in the art, presently preferred for fields 16 and 17 of adhesive are acrylate pressure sensitive adhesives and tackified polystyrene-polyisoprene block copolymers pressure sensitive adhesives. Such acrylate ester copolymer adhesives are generally described in U.S. Pat. Nos. 2,973,286; Re 24,906; Re 33,353; 3,389,827; 4,112,213; 4,310,509; 4,323,557; 4,732,808; 4,917,928; 4,917,929; and European Patent Publication 0 051 935, all incorporated herein by reference. Tackified block copolymer adhesives are generally described in Ewins, "Thermoplastic Rubbers: A-B-A Block Copolymers" which is Chapter 13 of Satas, Ed., Handbook of Pressure Sensitive Adhesive Technology, Second Edition, Van Nostrand Reinhold, 1989, which is incorporated herein by reference. Use of tackified

block copolymer adhesives as biocompatible skin adhesives in biomedical electrodes is described in U.S. Pat. No. 4,204,312.

A variety of coating methods is available for both the conductive adhesive and the biocompatible skin adhesive including extrusion coating, knife coating, and curtain coating as described in Satas, "Coating Equipment" which is Chapter 34 of Satas, Ed., Handbook of Pressure Sensitive Adhesive Technology, Second Edition, Van Nostrand Reinhold, 1989, which is incorporated herein by reference. Hand knife coating can be employed. A slot die is preferably used, which can include an extrusion die, a knife die, a curtain coating die and other types of slot dies with a high shear flat wiping lip, a medium shear flat wiping lip, a medium shear rod wiping lip, or a sharp knife wiping lip, which are generally described in Lippert, "Slot Die Coating for Low Viscosity Fluids", which is Chapter 11 of Satas, Ed., Coatings Technology Handbook, Marcel Dekker, Inc., 1991, which is incorporated by reference herein. The choice of the coating method and use of slot dies depend on the nature of the adhesive precursor, whether it is a high viscosity 100% solids hot-melt, a moderate viscosity 100% solids material to be polymerized on-web, or a moderate to low viscosity solvent or water delivered material. One skilled in the art will recognize that in the latter case, the coating step includes a drying process and this drying process results in a final thickness of adhesive that is thinner than the thickness at the coating head due to loss of solvent or water. The final thickness of conductive adhesive should be within 40% of the final thickness of the biocompatible pressure sensitive adhesive in order for both types of adhesive to have contact with the skin of a patient.

EXAMPLES

Example 1

A silver/silver chloride conductive ink solution commercially available as "R300" was obtained from Ercon Inc. of Waltham, MA. This ink has a solids content of 58%, of which the elemental silver comprises 70%. The carrier solvent for the ink was methyl propyl ketone (MPK). A quantity of 2-mercaptobenzoxazole (MBO) with a purity of 95% was obtained from Aldrich Chemicals of Milwaukee, WI to be the treating agent. Three 100 gram samples of the ink were weighed out. To each of these was added a solution of

MBO predissolved in MPK so as to obtain final concentrations of 0.1%, 0.5%, and 1.0% MBO on a weight basis based on elemental silver in the ink. These ink samples were thinly coated onto a polymeric backing made from 0.1 mm polyester mm polyester film commercially available as Melinex™ 505 from ICI Films, Hopewell, VA, using a wire-coating procedure. The coated film was then dried at room temperature for 5 minutes followed by drying at 200 °F (93 °C) for 5 minutes. A control ink sample (containing no MBO) was coated in exactly the same way.

A bicontinuous adhesive compounded according to the disclosure of U.S. Pat. No. 5,779,632 to Dietz et al, and having a pH of 2.8, was attached to the silver coating for all these samples. The samples were then cut into rectangular electrode pieces that had an exposed tab of silver ink for electrical contact.

Example 2

Immediately after fabrication, electrodes from the control group and from each of the levels of MBO were paired together with other electrodes of similar composition. These pairs were adhered to each other, their layers of bicontinuous adhesive being placed in contact face-to-face. This arrangement is specified in a standard published by the Association for the Advancement of Medical Instrumentation (AAMI) for determining the proper performance for a biomedical electrode used for ECG Disposable Electrodes, specifically the "American National Standard for Pregelled ECG Disposable Electrodes" Association for the Advancement of Medical Instrumentation (1984), the disclosure of which is incorporated by reference, for testing methods and conditions for minimum standards for the properties of D.C. Offset (100 mV), A.C. Impedance (2 kOhms), and Defibrillation Overload Recovery (less than 100 mV 5 seconds after 4 capacitor discharges and a rate of change of residual polarization potential no greater than 1 mV/sec.)

These standard AAMI tests were run on some of the electrode pairs immediately after fabrication. Another group of electrodes were aged at 203°F (95°C) for 48 hours and also subjected to the AAMI testing. The results are shown in Table 1 below.

Table 1

Composition		DC offset (mV) at 60 s (10)	Z_{10} (ohms) (2000)	SDR after 4 pulses (100)	SDR slope (mV/s) (Less than 1)	Z_{10} (ohms) (2000)
	Acceptable values ►					
Control	unaged	0.2	307	11.5	-0.3	171
	aged	-8.1	4022	25.9	-2.3	3741
0.1% MBO	unaged	-0.1	147	8.7	-0.3	140
	aged	0.5	4013	9.4	-0.2	553
0.5% MBO	unaged	-3.0	416	13.4	-0.4	263
	aged	0.1	257	18.0	-0.7	214
1.0% MBO	unaged	1.2	636	18.9	-0.8	475
	aged	1.8	915	33.1	-2.0	851

It can be seen from the control sample in this experiment that aging eventually causes this electrode to develop increased impedance, eventually causing it to become unacceptable for use. Judging by the visual appearance, it is believed that corrosion of the silver/silver chloride interface is the reason for this increase. It is to be noted that a sufficient quantity of MBO appears to protect the electrode from this effect, with the clean visual appearance of the treated samples lending support to this conclusion. However, at a certain point the addition of larger quantities of MBO begins to affect the recovery of the electrode from depolarization, so that a level of about 0.5 percent MBO by weight of elemental silver appears to give optimum results.

Example 3

A larger scale experiment was performed to verify the operability of the invention on a commercial scale and under the conditions of commercial packaging. Polyester film of the type described in Example 1, and bearing indicia on one side, was coated with the silver/silver chloride ink from Example 1 at six levels of concentration of MBO. Once again, the MBO was added to the silver ink as a solution in MEK. The ink was diluted

about 5% by the addition of the MBO solution. The MBO content in the 6 coated rolls was 0%, 0.1%, 0.3%, 0.5%, 0.7%, and 0.9% w/w (based on the weight of elemental silver in the coating). These six inks were applied by solvent coater to the polyester film in two passes. It was noted that the first coating pass deposited silver content of approximately 0.7 mg/cm^2 of the polyester backing, and that the second pass increased the level to approximately 1.5 mg/cm^2.

All of these coated backings were converted to electrodes generally according to the disclosure of U.S. patent 5,702,753, creating electrode cards with 10 electrodes per card. The electrode cards were then packed in polyliner pouches, with two cards per pouch. Except for the varying levels of treating agent, the resulting electrodes were similar to the model 2360 resting electrode commercially available from 3M Co. of St. Paul, Minnesota. Random samples of each level of treating agent were tested immediately according to the AAMI standard, while others were aged and then tested according to the standard. Those pouches were aged at 203 °F (95 °C) for eight days and then allowed to equilibrate to room temperature for one hour before testing. The results are shown in the table below.

Table 2

Composition		DC offset (mV) at 60 s (10)	Z_{10} (ohms) (2000)	SDR after 4 pulses (100)	SDR slope (mV/s) (Less than 1)	Z_{10} (ohms) (2000)
	Acceptable values ►					
Control	unaged	0.1	108	11.1	-0.3	71
	aged	-13.6	4005	10.7	-0.7	782
0.1% MBO	unaged	-0.2	860	11.3	-0.4	330
	aged	1.5	4036	388	-15.6	4055
0.3% MBO	unaged	-0.1	1005	11.5	-0.3	442
	aged	-0.5	610	18.9	-1.2	535
0.5% MBO	unaged	-0.4	851	13.4	-0.4	388
	aged	-0.6	154	13.4	-0.4	142
0.7% MBO	unaged	0.4	953	14.3	-0.4	452
	aged	-0.7	238	17.0	-1.0	204
0.9% MBO	unaged	-0.7	1205	18.6	-0.6	555
	aged	-1.4	4052	270	-13.8	4051

According to the Van't Hoff rule, 8 days at 95 °C is roughly equivalent to a little over 3 years of aging at room temperature. The results clearly show that MBO addition has a beneficial effect on the corrosion resistance of the electrode and that the optimal MBO inclusion amount for this electrode construction lies between 0.3% and 0.5% based on elemental silver content. However, it is believed that the minimum level of agent that provides a useful level of protection against corrosion is dependent on the absolute value of the amount of silver present per square area. It is further believed that as little as 0.01% of MBO by weight of elemental silver content would provide a workable electrode according to the present invention in some alternate constructions having more silver content.

Example 4

Electrode samples were made generally according to Example 1, except that the treating agent was octadecanethiol (OT), added in the amount of 0.1 percent by weight of the elemental silver content of the ink. The samples were then aged at 150 °F (65 °C) for 49 days. The samples were then tested according to the AAMI standard. The results are described the table below.

Table 3

Composition	Acceptable values ►	DC offset (mV) at 60 s (10)	Z_{10} (ohms) (2000)	SDR after 4 pulses (100)	SDR slope (mV/s) (Less than 1)	Z_{10} (ohms) (2000)
Control	aged	-3.1	4034	9.5	-0.4	4023
0.1% OT	aged	-1.6	387	12	-0.2	166

The example demonstrates that treating agents that may be used in connection with the present invention may have some hydrophobic character and still be functional. However, the amount of such hydrophobic agents that may be used is limited. It was observed that larger amounts of such agents modified the surface energy of the conductive layer, which affected the wetting of the silver/silver chloride surface by the conductive adhesive.

We claim:

1. A biomedical electrode comprising a conductor in contact with a conductive medium, wherein the conductor comprises a conductively active source of at least partially chlorided silver and wherein the electrode further comprises at least one organic corrosion retarding agent.

2. The biomedical electrode of claim 1 wherein the conductor comprises a polymeric material in the form of a film upon one side of which is disposed a layer of partially chlorided silver.

3. A biomedical electrode, comprising a conductor in contact with a conductive medium, wherein the conductor comprises a substrate having at least partially chlorided silver thereon, wherein the silver has been treated with an organic corrosion retarding agent.

4. A method of preparing a biomedical electrode, comprising the steps of:
preparing a conductor having a conductive layer comprising partially chlorided silver and at least one organic corrosion retarding agent; and
applying a layer of conductive medium to the conductive layer.

5. The biomedical electrode or method according to any one of claims 1-4 wherein the organic corrosion retarding agent is selected from the group consisting of mercaptans and azoles.

6. The biomedical electrode or method according to any one of claims 1-4 wherein the agent is selected the group consisting of 2-mercaptobenzoxazole and octadecanethiol.

7. The biomedical electrode or method according to any of the preceding claims wherein the agent is present in an amount of at least 0.01 percent by weight of elemental silver in the conductor.

8. The biomedical electrode or method according to any of the preceding claims wherein the conductor comprises a backing having silver/silver chloride containing ink thereon.

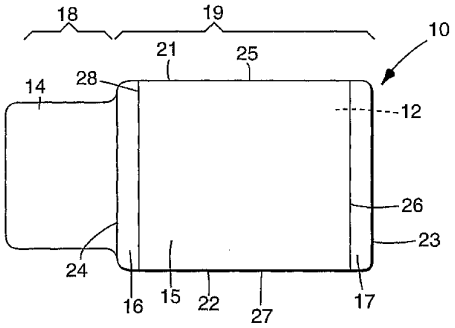
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Fig.1

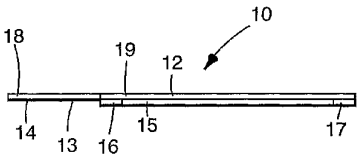
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Fig.2

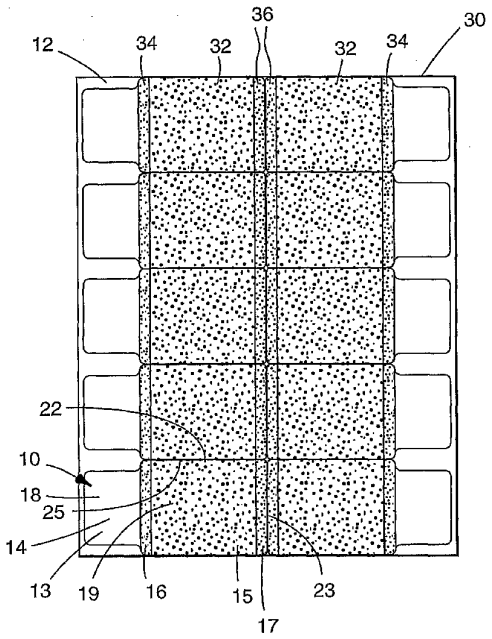

Fig.3

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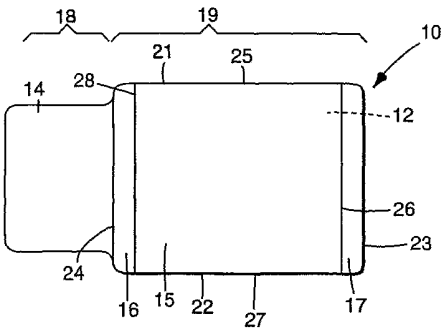
(54) Title: CORROSION PREVENTION IN BIOMEDICAL ELECTRODES



(57) Abstract: A non-polarizable, silver/silver chloride biomedical electrode that is protected against corrosion during its shelf life by an organic corrosion retarding agent, preferably selected from the group consisting of mercaptans and azoles. The conductor comprises a polymeric material in the form of a film upon one side of which is disposed a layer of partially chlorided silver.

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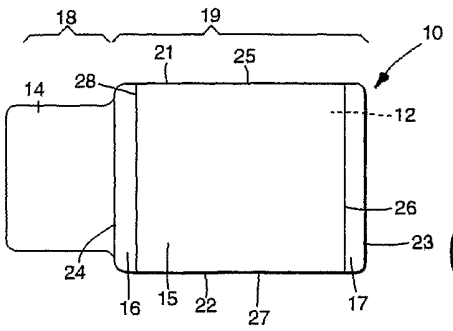

(57) Abstract: A non-polarizable, silver/silver chloride biomedical electrode that is protected against corrosion during its shelf life by an organic corrosion retarding agent, preferably selected from the group consisting of mercaptans and azoles. The conductor comprises a polymeric material in the form of a film upon one side of which is disposed a layer of partially chlorided silver.

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CORROSION PREVENTION IN BIOMEDICAL ELECTRODES

TECHNICAL FIELD

This invention relates to the making and using of biomedical electrodes.

BACKGROUND OF THE INVENTION

Modern medicine employs many medical procedures where electrical signals or currents are received from or delivered to a patient's body. The interface between medical equipment used in these procedures and the skin of the patient usually includes a biomedical electrode. Such an electrode typically includes a conductor connected electrically to the equipment and a conductive medium adhered to or otherwise in contact with the patient's skin.

Therapeutic procedures and devices that make use of biomedical electrodes include transcutaneous electronic nerve stimulation (TENS) devices for pain management; neuromuscular stimulation (NMS) techniques for treating conditions such as scoliosis; defibrillation electrodes for dispensing electrical energy to a chest cavity to defibrillate the heart; and dispersive electrodes to receive electrical energy dispensed into an incision made during electrosurgery.

Diagnostic procedures that make use of biomedical electrodes include electrocardiograms (ECGs) for monitoring heart activity and diagnosing heart abnormalities.

Representative examples of biomedical electrodes that have been used for, or described as useful for, diagnostic purposes include U.S. Pat. Nos. 4,352,359 (Larimore); 4,524,087 (Engel); 4,539,996 (Engel); 4,554,924 (Engel); 4,848,348 (Carim); 4,848,353 (Engel); 5,012,810 (Strand et al.); 5,133,356 (Bryan et al.); 5,215,087 (Anderson et al.); and 5,296,079 (Duan et al.), the entire contents of which are hereby incorporated by reference.

For diagnostic applications, non-polarizable electrodes, and in particular silver/silver chloride electrodes, have become the current collectors of choice because of their high electrical stability. In low-cost versions, these electrodes are coated in thin sections from a conductive ink containing silver/silver chloride particles and a polymeric binder onto an insulating backing. While silver/silver chloride electrodes are reasonably resistant to corrosive attack and generally have a long shelf-life, under certain gel conditions such as a low pH in conjunction with a high water content and high chloride concentration, they can undergo accelerated corrosion and exhibit premature electrical failure.

To control corrosion in biomedical electrodes, sacrificial anodes have been interwoven in an electrode assembly and electrically connected to a current collector. While functional, such protection may not be cost-effective due to design constraints and added material costs.

Alternative for silver/silver chloride materials have also been proposed for biomedical electrodes, among them titanium hydride and certain carbon-containing materials. Such arrangements, however, are generally unduly complex, expensive and material-intensive.

There remains a need, therefore, for corrosion-resistant biomedical electrodes that are simply constructed and relatively cost-effective.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a non-polarizable biomedical electrode that is protected against corrosion by an organic corrosion retarding agent. The biomedical electrode comprises a conductor in contact with a conductive medium, wherein the conductor comprises a conductively active source of at least partially chlorided silver and wherein the electrode includes at least one organic corrosion retarding agent.

In another aspect, the invention provides a biomedical electrode comprising a conductor in contact with a conductive medium, wherein the conductor comprises a substrate having at least partially chlorided silver thereon and wherein the silver has been treated with an organic corrosion retarding agent.

In still another aspect, the invention provides methods of preparing biomedical electrodes, the methods generally comprising the steps of:

preparing a conductor having a conductive layer comprising partially chlorided silver and at least one organic corrosion retarding agent; and

applying a layer of conductive medium to the conductive layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a bottom plan view of a diagnostic electrode according to the present invention.

FIG. 2 is a side plan view of the diagnostic electrode of FIG. 1.

FIG. 3 is an array of diagnostic electrodes during manufacture.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In one aspect the invention provides a biomedical electrode having a conductor in contact with a conductive medium. The conductor includes a conductive substrate having partially chlorided silver thereon and is protected from corrosion by the presence of at least one organic corrosion retarding agent. The conductive substrate may comprise a polymeric material in the form of a thin film upon which there is a silver-containing layer, or the conductor may comprise a graphite loaded polymer or other conductive material in the form of a stud upon which is a silver-containing layer. The silver-containing layer can contain a silver-loaded ink, a vapor deposit of silver or some other source of active silver. The silver in such a layer may be partially chlorided, either by having silver chloride intrinsic to the applied layer or by separately partially chloriding a silvered surface.

A conductive medium is most conveniently provided for the electrode by a conductive adhesive, although conductive gels and other electrolytes also are considered useful. Conductive adhesives made from polymerized microemulsions, including those described in U.S. Patent No. 5,952,398, are also considered useful. The corrosion retarding agent may be incorporated into the electrode construction either by treating the partially chlorided silver layer of the conductor with the corrosion retarding agent or by including the agent in the formulation of a silver-loaded ink. The latter may be

accomplished by applying the agent to the coated ink layer after it has been applied. The corrosion retarding agent may also be included directly in the conductive medium.

Useful corrosion retarding agents include any agent that adequately retards corrosion and that is compatible with the conductive materials, *i.e.*, does not degrade the electrical properties of the interface between the conductor and the conductive medium. Preferred corrosion retarding agents will also resist leaching into the conductive medium, which could cause a loss of corrosion protection and raise the possibility of dermal contact, and will exhibit low toxicity towards human skin. Since in manufacturing practice it is convenient to place the silver onto the conductor by means of a silver-loaded ink, the agents will also preferably be highly soluble in known solvent carriers for such inks and will have relatively low vapor pressures to withstand the thermal treatment required to dry ink coatings. The most preferred corrosion retarding agents are selected from the group consisting of mercaptans and azoles. Specific, representative compounds include 2-mercaptobenzoxazole and octadecanethiol.

FIGS. 1 and 2 are bottom and side plan views, respectively, of one embodiment of a diagnostic electrode 10 of the present invention. From the surface farthest away from mammalian skin, electrode 10 comprises a non-conductive flexible backing 12 having a side 13 having on at least a portion thereof an electrically conductive surface 14 contacting a field 15 of conductive adhesive. Two separate opposing fields 16 and 17 of biocompatible pressure sensitive skin adhesive contact side 13 and preferably electrically conductive surface 14. Not shown is a release liner that contacts fields 15, 16, and 17 of adhesive when electrode 10 is not in use.

Flexible backing 12 comprises a tab portion 18 and a pad portion 19. Both tab portion 18 and pad portion 19 have electrically conductive surface 14, but field 15 of conductive adhesive contacts only pad portion 19. Tab portion 18 is suitable for releasable attachment to an electrical connector that delivers the ECG signals to the electrical instrumentation.

Pad portion 19 has a perimeter defined by edges 21, 22, 23, and 24. By comparison, field 15 of conductive adhesive has a perimeter defined by edges 25, 26, 27, and 28. The surface area of field 15 of conductive adhesive within edges 25-28 contacts the surface area of pad portion 19 within edges 21-24 of pad portion 19.

Fields 16 and 17 of biocompatible skin adhesive are not ionically conductive as is field 15 but are preferably contacting pad portion 19 in separate locations on side 13 and preferably in separate locations on electrically conductive surface 14 to assist in the maintenance of adhesive contact of electrode 10 to skin of a mammalian patient. The separate opposing locations on pad portion 19 proximal and distal to tab portion 18 provide a relatively high level of adhesion to mammalian skin because the electrode 10 has added adhesiveness in the two locations most likely to be affected by edge lifting of the electrode 10 due to stress applied to the electrode 10 during use: along a line bisecting both the tab portion 18 and the pad portion 19.

As seen in FIG. 2, preferably the biocompatible pressure sensitive skin adhesive fields 16 and 17 is in direct contact with side 13, and preferably electrically conductive surface 14, of pad portion 19. Also preferably, the final thickness (after processing) of fields 16 and 17, ranging from about 0.25 mm to about 0.75 mm thick, and preferably about 0.50 mm thick, is within 40 percent, and preferably within 20 percent, of the final thickness of the field 15 of ionically conductive adhesive. Ideally, the final thickness of field 15 and fields 16 and 17 are equal or within a difference of less than 10 percent.

Selection of materials to construct electrode 10 are known to those skilled in the art of biomedical electrode construction. U.S. Pat. Nos. 4,352,359 (Larimore); 4,524,087 (Engel); 4,539,996 (Engel); 4,554,924 (Engel); 4,848,348 (Carim); 4,848,353 (Engel); 5,012,810 (Strand et al.); 5,133,356 (Bryan et al.); 5,215,087 (Anderson et al.); 5,296,079 (Duan et al.); U.S. Pat. No. 5,385,679 (Uy et al.); U.S. Pat. No. 5,702,753 (Yasis et al.); and U.S. Pat. No. 5,779,632 (Dietz et al) all describe suitable materials for the construction of biomedical electrodes useful for ECG procedures, and all are incorporated by reference as if fully rewritten herein.

Of the numerous electrically nonconductive materials known to those skilled in the art, presently preferred for backing material 12 are polyester films of about 0.1 mm thickness commercially available as "Melinex" branded films (e.g., 329 and 339) from ICI Americas of Hopewell, VA. Preferably, the film can be treated with a corona treatment to improve the adhesion of the electrically conductive surface to the backing material.

Of the numerous electrically conductive materials known to those skilled in the art, inks containing electrical conductive particles such as graphite or metals are useful with

metal-containing inks being preferred. Presently preferred for electrically conductive surface 14 is a silver containing ink such as "N-30" ink, a silver/silver chloride containing ink such as "R-300" ink, or R-301MPK (+240)® ink, all commercially available from Ercon, Inc. of Waltham, Mass. Such a silver/silver chloride ink may be conveniently be applied to a backing by gravure coating. Many other methods are considered suitable, including ink jet printing, silkscreen printing, and knife coating.

Of the numerous conductive adhesives known to those skilled in the art, field 15 of conductive adhesive can be those conductive adhesives as described in the table at column 16 of U.S. Pat. No. 5,012,810 (Strand et al.) and as disclosed in U.S. Pat. Nos. 4,524,087; 4,539,996; 4,848,353; and 4,554,924 (all Engel); 5,296 079 (Duan et al.); U.S. Pat. No. 5,385,679 (Uy et al.); and U.S. Pat. No. 5,338,490 (Dietz et al.) all of which are incorporated by reference herein. Presently preferred for field 15 of conductive adhesive is a bicontinuous biocompatible conductive adhesive having interpenetrating domains of hydrophilic and hydrophobic composition as described in U.S. Pat. No. 5,779,632 to Dietz et al, which is incorporated by reference herein. It is sometimes convenient to increase the viscosity of the conductive adhesive of the 5,779,632 reference for ease in coating. Adding a quantity of polyacrylic acid having a molecular weight generally between 200,000 and 800,000 prior to polymerization can be done to accomplish this. Additional details regarding such a process can be found in co-pending U.S. patent application serial number 09/844,031, which is incorporated herein by reference.

Of the numerous biocompatible skin adhesives known to those skilled in the art, presently preferred for fields 16 and 17 of adhesive are acrylate pressure sensitive adhesives and tackified polystyrene-polyisoprene block copolymers pressure sensitive adhesives. Such acrylate ester copolymer adhesives are generally described in U.S. Pat. Nos. 2,973,286; Re 24,906; Re 33,353; 3,389,827; 4,112,213; 4,310,509; 4,323,557; 4,732,808; 4,917,928; 4,917,929; and European Patent Publication 0 051 935, all incorporated herein by reference. Tackified block copolymer adhesives are generally described in Ewins, "Thermoplastic Rubbers: A-B-A Block Copolymers" which is Chapter 13 of Satas, Ed., Handbook of Pressure Sensitive Adhesive Technology, Second Edition, Van Nostrand Reinhold, 1989, which is incorporated herein by reference. Use of tackified

block copolymer adhesives as biocompatible skin adhesives in biomedical electrodes is described in U.S. Pat. No. 4,204,312.

A variety of coating methods is available for both the conductive adhesive and the biocompatible skin adhesive including extrusion coating, knife coating, and curtain coating as described in Satas, "Coating Equipment" which is Chapter 34 of Satas, Ed., Handbook of Pressure Sensitive Adhesive Technology, Second Edition, Van Nostrand Reinhold, 1989, which is incorporated herein by reference. Hand knife coating can be employed. A slot die is preferably used, which can include an extrusion die, a knife die, a curtain coating die and other types of slot dies with a high shear flat wiping lip, a medium shear flat wiping lip, a medium shear rod wiping lip, or a sharp knife wiping lip, which are generally described in Lippert, "Slot Die Coating for Low Viscosity Fluids", which is Chapter 11 of Satas, Ed., Coatings Technology Handbook, Marcel Dekker, Inc., 1991, which is incorporated by reference herein. The choice of the coating method and use of slot dies depend on the nature of the adhesive precursor, whether it is a high viscosity 100% solids hot-melt, a moderate viscosity 100% solids material to be polymerized on-web, or a moderate to low viscosity solvent or water delivered material. One skilled in the art will recognize that in the latter case, the coating step includes a drying process and this drying process results in a final thickness of adhesive that is thinner than the thickness at the coating head due to loss of solvent or water. The final thickness of conductive adhesive should be within 40% of the final thickness of the biocompatible pressure sensitive adhesive in order for both types of adhesive to have contact with the skin of a patient.

EXAMPLES

Example 1

A silver/silver chloride conductive ink solution commercially available as "R300" was obtained from Ercon Inc. of Waltham, MA. This ink has a solids content of 58%, of which the elemental silver comprises 70%. The carrier solvent for the ink was methyl propyl ketone (MPK). A quantity of 2-mercaptobenzoxazole (MBO) with a purity of 95% was obtained from Aldrich Chemicals of Milwaukee, WI to be the treating agent. Three 100 gram samples of the ink were weighed out. To each of these was added a solution of

MBO predissolved in MPK so as to obtain final concentrations of 0.1%, 0.5%, and 1.0% MBO on a weight basis based on elemental silver in the ink. These ink samples were thinly coated onto a polymeric backing made from 0.1 mm polyester mm polyester film commercially available as Melinex™ 505 from ICI Films, Hopewell, VA, using a wire-coating procedure. The coated film was then dried at room temperature for 5 minutes followed by drying at 200 °F (93 °C) for 5 minutes. A control ink sample (containing no MBO) was coated in exactly the same way.

A bicontinuous adhesive compounded according to the disclosure of U.S. Pat. No. 5,779,632 to Dietz et al, and having a pH of 2.8, was attached to the silver coating for all these samples. The samples were then cut into rectangular electrode pieces that had an exposed tab of silver ink for electrical contact.

Example 2

Immediately after fabrication, electrodes from the control group and from each of the levels of MBO were paired together with other electrodes of similar composition. These pairs were adhered to each other, their layers of bicontinuous adhesive being placed in contact face-to-face. This arrangement is specified in a standard published by the Association for the Advancement of Medical Instrumentation (AAMI) for determining the proper performance for a biomedical electrode used for ECG Disposable Electrodes, specifically the "American National Standard for Pregelled ECG Disposable Electrodes" Association for the Advancement of Medical Instrumentation (1984), the disclosure of which is incorporated by reference, for testing methods and conditions for minimum standards for the properties of D.C. Offset (100 mV), A.C. Impedance (2 kOhms), and Defibrillation Overload Recovery (less than 100 mV 5 seconds after 4 capacitor discharges and a rate of change of residual polarization potential no greater than 1 mV/sec.)

These standard AAMI tests were run on some of the electrode pairs immediately after fabrication. Another group of electrodes were aged at 203°F (95°C) for 48 hours and also subjected to the AAMI testing. The results are shown in Table 1 below.

//

Table I

Composition	Acceptable values ▶	DC offset (mV) at 60 s (10)	Z_{10} (ohms) (2000)	SDR after 4 pulses (100)	SDR slope (mV/s) (Less than 1)	Z_{10} (ohms) (2000)
Control	unaged	0.2	307	11.5	-0.3	171
	aged	-8.1	4022	25.9	-2.3	3741
0.1% MBO	unaged	-0.1	147	8.7	-0.3	140
	aged	0.5	4013	9.4	-0.2	553
0.5% MBO	unaged	-3.0	416	13.4	-0.4	263
	aged	0.1	257	18.0	-0.7	214
1.0% MBO	unaged	1.2	636	18.9	-0.8	475
	aged	1.8	915	33.1	-2.0	851

It can be seen from the control sample in this experiment that aging eventually causes this electrode to develop increased impedance, eventually causing it to become unacceptable for use. Judging by the visual appearance, it is believed that corrosion of the silver/silver chloride interface is the reason for this increase. It is to be noted that a sufficient quantity of MBO appears to protect the electrode from this effect, with the clean visual appearance of the treated samples lending support to this conclusion. However, at a certain point the addition of larger quantities of MBO begins to affect the recovery of the electrode from depolarization, so that a level of about 0.5 percent MBO by weight of elemental silver appears to give optimum results.

Example 3

A larger scale experiment was performed to verify the operability of the invention on a commercial scale and under the conditions of commercial packaging. Polyester film of the type described in Example 1, and bearing indicia on one side, was coated with the silver/silver chloride ink from Example 1 at six levels of concentration of MBO. Once again, the MBO was added to the silver ink as a solution in MEK. The ink was diluted

about 5% by the addition of the MBO solution. The MBO content in the 6 coated rolls was 0%, 0.1%, 0.3%, 0.5%, 0.7%, and 0.9% w/w (based on the weight of elemental silver in the coating). These six inks were applied by solvent coater to the polyester film in two passes. It was noted that the first coating pass deposited silver content of approximately 0.7 mg/cm^2 of the polyester backing, and that the second pass increased the level to approximately 1.5 mg/cm^2.

All of these coated backings were converted to electrodes generally according to the disclosure of U.S. patent 5,702,753, creating electrode cards with 10 electrodes per card. The electrode cards were then packed in polyliner pouches, with two cards per pouch. Except for the varying levels of treating agent, the resulting electrodes were similar to the model 2360 resting electrode commercially available from 3M Co. of St. Paul, Minnesota. Random samples of each level of treating agent were tested immediately according to the AAMI standard, while others were aged and then tested according to the standard. Those pouches were aged at 203 °F (95 °C) for eight days and then allowed to equilibrate to room temperature for one hour before testing. The results are shown in the table below.

Table 2

Composition		DC offset (mV) at 60 s (10)	Z_{10} (ohms) (2000)	SDR after 4 pulses (100)	SDR slope (mV/s) (Less than 1)	Z_{10} (ohms) (2000)
	Acceptable values ▶					
Control	unaged	0.1	108	11.1	-0.3	71
	aged	-13.6	4005	10.7	-0.7	782
0.1% MBO	unaged	-0.2	860	11.3	-0.4	330
	aged	1.5	4036	388	-15.6	4055
0.3% MBO	unaged	-0.1	1005	11.5	-0.3	442
	aged	-0.5	610	18.9	-1.2	535
0.5% MBO	unaged	-0.4	851	13.4	-0.4	388
	aged	-0.6	154	13.4	-0.4	142
0.7% MBO	unaged	0.4	953	14.3	-0.4	452
	aged	-0.7	238	17.0	-1.0	204
0.9% MBO	unaged	-0.7	1205	18.6	-0.6	555
	aged	-1.4	4052	270	-13.8	4051

According to the Van't Hoff rule, 8 days at 95 °C is roughly equivalent to a little over 3 years of aging at room temperature. The results clearly show that MBO addition has a beneficial effect on the corrosion resistance of the electrode and that the optimal MBO inclusion amount for this electrode construction lies between 0.3% and 0.5% based on elemental silver content. However, it is believed that the minimum level of agent that provides a useful level of protection against corrosion is dependent on the absolute value of the amount of silver present per square area. It is further believed that as little as 0.01% of MBO by weight of elemental silver content would provide a workable electrode according to the present invention in some alternate constructions having more silver content.

Example 4

Electrode samples were made generally according to Example 1, except that the treating agent was octadecanethiol (OT), added in the amount of 0.1 percent by weight of the elemental silver content of the ink. The samples were then aged at 150 °F (65 °C) for 49 days. The samples were then tested according to the AAMI standard. The results are described the table below.

Table 3

Composition	Acceptable values ▶	DC offset (mV) at 60 s (10)	Z_{10} (ohms) (2000)	SDR after 4 pulses (100)	SDR slope (mV/s) (Less than 1)	Z_{10} (ohms) (2000)
Control	aged	-3.1	4034	9.5	-0.4	4023
0.1% OT	aged	-1.6	387	12	-0.2	166

The example demonstrates that treating agents that may be used in connection with the present invention may have some hydrophobic character and still be functional. However, the amount of such hydrophobic agents that may be used is limited. It was observed that larger amounts of such agents modified the surface energy of the conductive layer, which affected the wetting of the silver/silver chloride surface by the conductive adhesive.

We claim:

1. A biomedical electrode comprising a conductor in contact with a conductive medium, wherein the conductor comprises a conductively active source of at least partially chlorided silver and wherein the electrode further comprises at least one organic corrosion retarding agent.

2. The biomedical electrode of claim 1 wherein the conductor comprises a polymeric material in the form of a film upon one side of which is disposed a layer of partially chlorided silver.

3. A biomedical electrode, comprising a conductor in contact with a conductive medium, wherein the conductor comprises a substrate having at least partially chlorided silver thereon, wherein the silver has been treated with an organic corrosion retarding agent.

4. A method of preparing a biomedical electrode, comprising the steps of:

preparing a conductor having a conductive layer comprising partially chlorided silver and at least one organic corrosion retarding agent; and

applying a layer of conductive medium to the conductive layer.

5. The biomedical electrode or method according to any one of claims 1-4 wherein the organic corrosion retarding agent is selected from the group consisting of mercaptans and azoles.

6. The biomedical electrode or method according to any one of claims 1-4 wherein the agent is selected the group consisting of 2-mercaptobenzoxazole and octadecanethiol.

7. The biomedical electrode or method according to any of the preceding claims wherein the agent is present in an amount of at least 0.01 percent by weight of elemental silver in the conductor.

8. The biomedical electrode or method according to any of the preceding claims wherein the conductor comprises a backing having silver/silver chloride containing ink thereon.

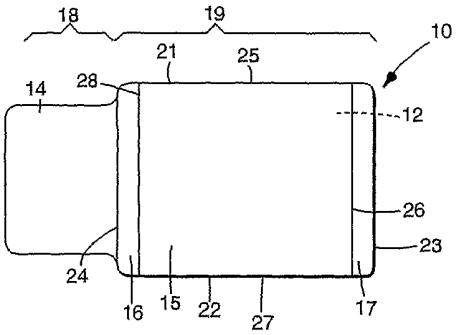
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Fig.1

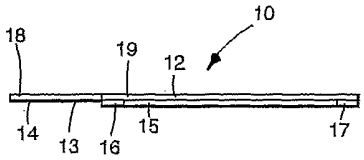
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Fig.2

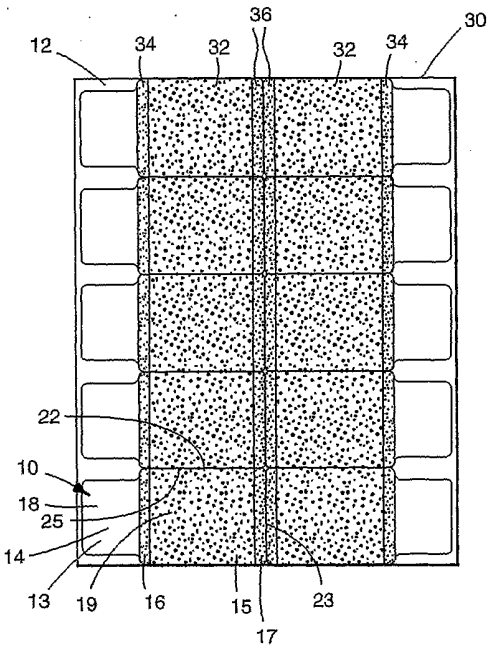

Fig.3

【国際調査報告】

INTERNATIONAL SEARCH REPORT

Intern plication No
PCT/US 02/10885

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61N1/04 A61B5/0408

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61N A61B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 729 575 A (ELF AQUITAINE) 26 July 1996 (1996-07-26) page 3, line 3 -page 6, line 31; figures	1-4
A	US 5 746 207 A (MCADAMS ERIC THOMAS ET AL) 5 May 1998 (1998-05-05) column 2, line 40 -column 4, line 67; figures	1-4
A	US 5 133 356 A (GALATOWITSCH JOSEPH L ET AL) 28 July 1992 (1992-07-28) cited in the application column 2, line 32 -column 6, line 66; figures	1,4

-/--

[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

° Special categories of cited documents :

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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& document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 August 2002	19/08/2002

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Intern application No
PCT/US 02/10885

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 012 810 A (STRAND JEROME E ET AL) 7 May 1991 (1991-05-07) cited in the application column 4, line 37 -column 8, line 26; figures	1,4

INTERNATIONAL SEARCH REPORT

Internat pplication No
PCT/US 02/10885

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
FR 2729575	A	26-07-1996	FR	2729575 A1	26-07-1996
			AU	4626296 A	14-08-1996
			WO	9622809 A1	01-08-1996
US 5746207	A	05-05-1998	DE	4410017 A1	29-09-1994
			FR	2704417 A1	04-11-1994
			GB	2276326 A ,B	28-09-1994
			JP	6296594 A	25-10-1994
US 5133356	A	28-07-1992	AU	650727 B2	30-06-1994
			AU	1301492 A	22-10-1992
			CA	2062857 A1	17-10-1992
			DE	69219946 D1	03-07-1997
			DE	69219946 T2	20-11-1997
			DK	509704 T3	22-12-1997
			EP	0509704 A2	21-10-1992
			US	5226225 A	13-07-1993
US 5012810	A	07-05-1991	AU	613513 B2	01-08-1991
			AU	4012389 A	29-03-1990
			AU	636786 B2	06-05-1993
			AU	8176391 A	24-10-1991
			CA	1335303 A1	18-04-1995
			DE	68919964 D1	26-01-1995
			DE	68919964 T2	08-06-1995
			EP	0360496 A1	28-03-1990
			US	5078138 A	07-01-1992
			US	5078139 A	07-01-1992
			US	5215087 A	01-06-1993
			US	5133355 A	28-07-1992

フロントページの続き

(81)指定国 AP(GH,GM,KE,LS,MW,MZ,SD,SL,SZ,TZ,UG,ZM,ZW),EA(AM,AZ,BY,KG,KZ,MD,RU,TJ,TM),EP(AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE,TR),OA(BF,BJ,CF,CG,CI,CM,GA,GN,GQ,GW,ML,MR,NE,SN,TD,TG),AE,AG,AL,AM,AT,AU,AZ,BA,BB,BG,BR,BY,BZ,CA,CH,CN,CO,CR,CU,CZ,DE,DK,DM,DZ,EC,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KP,KR,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,MZ,NO,NZ,OM,PH,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TN,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZM,ZW

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Ｆターム(参考) 4C053 BB02 BB24 BB35 BB36