

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 21-2-90

FORM 1

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA **596428**

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

74648/87

Minnesota Mining and Manufacturing Company, incorporated in Delaware, of
3M Centre Saint Paul, Minnesota, 55144, UNITED STATES OF AMERICA,
hereby apply for the grant of a standard patent for an invention entitled:

Electrically-Conductive Pressure-Sensitive Adhesive and
Biomedical Electrodes

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No: Country:

Application Date:

902396

UNITED STATES OF AMERICA

5 September 1986

The address for service is:-

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTY FOURTH day of JUNE 1987

Minnesota Mining and Manufacturing Company

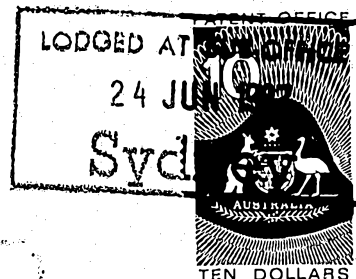
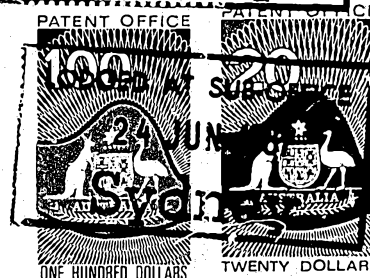
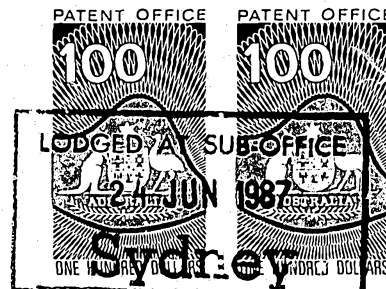
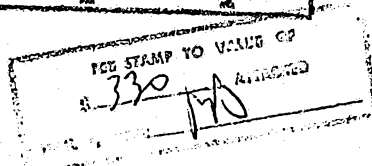
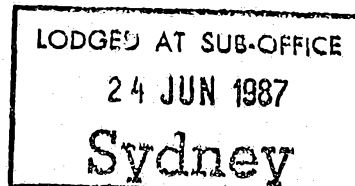
By:

[Signature]

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 29440
S&F CODE: 58400

5845/2



DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENTIn support of the Convention Application made for a
patent for an invention entitled:

Title of Invention

"ELECTRICALLY-CONDUCTIVE PRESSURE-SENSITIVE ADHESIVE
AND BIOMEDICAL ELECTRODES"

Full name(s) and
address(es) of
Declarant(s)

I/We Donald Miller Sell

care of Minnesota Mining and Manufacturing Company
3M Center, St. Paul,
Minnesota, 55144
United States of America
do solemnly and sincerely declare as follows:

Full name(s) of
Applicant(s)1. ~~I am/We are the applicant(s) for the patent~~*(or, in the case of an application by a body corporate)*1. I am/We are authorised by MINNESOTA MINING AND MANUFACTURING
COMPANYthe applicant(s) for the patent to make this declaration on
its/~~their~~ behalf.2. The basic application(s) as defined by Section 141 of the
Act was/~~were~~ made

Basic Country(ies)

in United States of America

Priority Date(s)

on 5 September, 1986

Basic Applicant(s)

by MICHAEL R. ENGEL

Full name(s) and
address(es) of
inventor(s)3. ~~I am/We are the actual inventor(s) of the invention referred
to in the basic application(s)~~*(or where a person other than the inventor is the applicant)*

3. MICHAEL ROY ENGEL

care of Minnesota Mining and Manufacturing Company
3M Center, St. Paul,
Minnesota, 55144 United States of America
~~(respectively)~~

is/~~are~~ the actual inventor(s) of the invention and the facts upon
which the applicant(s) is/~~are~~ entitled to make the application are
as follows:

Set out how Applicant(s)
derive title from actual
inventor(s) e.g. The
Applicant(s) is/~~are~~ the
assignee(s) of the
invention from the
inventor(s)

The said Company is the assignee of the actual inventor.

4. The basic application(s) referred to in paragraph 2 of this
Declaration was/~~were~~ the first application(s) made in a Convention
country in respect of the invention(s) the subject of the application.
Saint Paul,

Declared at Minnesota, this 8th day of June 19 87
U.S.A.

Donald Miller Sell

Signature of Declarant(s)
Donald Miller Sell
Chief Patent Counsel

(12) PATENT ABRIDGMENT **(11) Document No. AU-B-74648/87**
(19) AUSTRALIAN PATENT OFFICE **(10) Acceptance No. 596428**

(54) Title
ELECTRICALLY-CONDUCTIVE PRESSURE-SENSITIVE ADHESIVE AND BIOMEDICAL ELECTRODES

International Patent Classification(s)
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C08L 033/26 C08L 039/06

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(71) Applicant(s)
MINNESOTA MINING AND MANUFACTURING COMPANY

(72) Inventor(s)
MICHAEL ROY ENGEL

(74) Attorney or Agent
SPRUSON & FERGUSON

(56) Prior Art Documents
AU 543967 67840/81 A61N 1/04, A61B 5/04, C09J 3/14,
AU 552528 88022/82 A01N 1/04, C08F 220/06, C09J 3/14

(57) Claim

1. An electrically-conductive, pressure-sensitive adhesive formed by the free radical copolymerization of an adhesive precursor comprising:
at least one water-soluble hydrogen bond donating monomer;
at least one water-soluble hydrogen bond accepting monomer;
a free radical initiator; and
a plasticizing, electrically-conductive solution comprising from 0 to 98% by weight water-soluble, polar organic compound, from 2 to 100% by weight water, and from 0 to 12% by weight soluble salt

wherein the ratio of hydrogen bond accepting sites to hydrogen bond donating sites on the monomers is from about 1:3 to about 6:1, the adhesive precursor contains from about 12% to about 50% by weight total monomers, and the acid sites on the hydrogen bond donating monomer are from about 5% to about 95% neutralized, and the composition is substantially homogeneous and pressure-sensitive adhesive.

2. The composition of claim 1 wherein the adhesive precursor further comprises a multifunctional crosslinker present up to about 2.5% by weight of the total monomers in the adhesive precursor.

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13. A biomedical electrode comprising: an electrical conductor, means integrally associated with the conductor for connecting the electrode to an electromedical instrument, and an electrically-conductive, pressure-sensitive adhesive in electrical contact with the conductor comprising a conformable, cohesive, adhesive copolymer matrix formed by free radical polymerizing an adhesive precursor comprising at least one water-soluble hydrogen bond donating monomer, at least one water-soluble hydrogen bond accepting monomer, and a polymerization initiator wherein the molar ratio of hydrogen bond accepting sites to hydrogen bond donating sites available on the monomers is from about 1:3 to about 6:1, and a plasticizing, electrically-conductive solution comprised of from 0 to 98% by-weight water-soluble, polar organic compound, 2 to 100% by weight water, and 0 to 12% by weight water-soluble salt, wherein the electrically-conductive, pressure-sensitive adhesive contains from about 12% to about 50% by weight non-volatile copolymer matrix, the hydrogen bond donating sites on the copolymer are from about 5% to about 95% neutralized and the composition is substantially homogeneous and pressure-sensitive adhesive.

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S & F Ref: 29440

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

This document contains the amendments made under Section 49 and is correct for printing.

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the amendments allowed under Section 83 (2) by the Supervising Examiner on

and is correct for printing

Name and Address
of Applicant:

Minnesota Mining and Manufacturing Company
3M Centre Saint Paul
Minnesota 55144
UNITED STATES OF AMERICA

Address for Service:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Electrically-Conductive Pressure-Sensitive Adhesive and
Biomedical Electrodes

The following statement is a full description of this invention, including the best method of performing it known to me/us

**Electrically-Conductive, Pressure-Sensitive
Adhesive and Biomedical Electrodes**

5

Field of the Invention

This invention relates to electrically-
conductive, pressure-sensitive adhesive compositions having
10 a polymeric matrix comprised of copolymers of hydrogen bond
donating monomers and hydrogen bond accepting monomers. In
another aspect, the invention relates to a biomedical
electrode having a pressure-sensitive adhesive as the
electrically-conductive, skin interfacing material.

15

Background of the Invention

An adhesive composition which serves to adhere a
biomedical electrode to skin and to establish an electrical
connection between skin and an electrical medical apparatus
20 desirably has multiple characteristics which are difficult
to achieve in one composition. The composition should have
the characteristics of a good medical adhesive and those of
a good electrical conductor.

A good medical pressure-sensitive adhesive needs
25 to be dermally non-irritating, sufficiently plastic and
tacky to wet skin and adhere, and sufficiently cohesive
both to resist shear and peel forces and to pull away from
skin without leaving a residue. Compositions which make
good medical adhesives are well known. Exemplary classes
30 are polyvinyl ethers and copolymers of acrylic acid and
isooctylacrylate. Copolymers used on many commercially
available medical tapes include adhesives made from
isooctylacrylate and up to ten percent by weight acrylic
acid or N-vinylpyrrolidone. An exemplary formulation is a
35 copolymer of 96% isooctylacrylate and 4% acrylic acid;
another adhesive is based on 91% isooctylacrylate and 9%
N-vinylpyrrolidone. While these formulations make

excellent medical adhesives, they are not suitable for electrically-conductive adhesives. Conductive adhesives require a substantial amount of plasticizing electrically-conductive liquid. The plasticizing electrically-conductive liquid is polar and usually has ionic species in solution. The isooctylacrylate and acrylic acid or N-vinylpyrrolidone copolymers are not crosslinked and are not soluble in water and other polar liquids. If they are mixed with polar liquids and ionic solutions, phase separation results.

The electrical properties desired of a conductive, pressure-sensitive adhesive relate to its ability to transmit ionic electric current to or from the body and, in co-operation with a conductor, to convert ionic current to electric current or electric current to ionic current. The ability of the composition to accurately transmit the ionic electric current generated by biomedical events is very important. To optimize electrical performance, a low impedance at the interface of the composition and the skin is desirable. Also important is the ability of the biomedical electrode to translate ionic current to electrical current and electrical current to ionic current. In many instances this translation is effected by means of an electrochemical reaction. For example, in a classic silver/silver chloride system the conductor is a layer of metallic silver having a thin layer of silver chloride on its surface, and the electrolyte medium (conductive gel or conductive adhesive) contains chloride ions. The electrical performance of this system depends in part on the concentration and mobility of ionic species in the composition. The hydrogen ion concentration is also relevant. In other systems, the translation may be effected by capacitive coupling. In that circumstance, the charge density of the electrode is important to the ability of the electrode to translate the signals encountered. Here again, the concentration of ionic species is important to good performance. For example, in a patient grounding plate large alternating currents (typically 0.5-1A at about 500 KHz) are encountered. In these conditions, capacitive coupling is possible and the presence of ionic species facilitates transfer.

Conductive pressure-sensitive adhesives are shown in many patents. U.S. Patent No. 4,274,420 to Hymes, U.S. Patent No. 4,352,359 to Larimore, and U.S. Patent Nos. 4,524,087, 4,539,996, and 4,554,924 to Engel are exemplary.

5 Two of the Engel Patents (U.S. Patent Nos. 4,524,087 and 4,539,996) disclose an electrically-conductive adhesive formed by an essentially solventless free radical polymerization of an adhesive precursor having a polyhydric alcohol, at least one ionic monomer, a crosslinker, and an
10 initiator. Non-ionic comonomers may be included. Ionic monomers listed are salts of α,β -unsaturated carboxylic acids such as potassium and sodium acrylate and sodium methacrylate. Non-ionic comonomers listed are acrylic acid, methacrylic acid, and hydroxyethyl methacrylate.

15 The third Engel patent (U.S. Patent No. 4,554,924) discloses a conductive adhesive formed by an essentially solventless free radical polymerization of an adhesive precursor having a polyhydric alcohol, at least one non-ionic monomer, an initiator, a crosslinker, and an
20 ionizable salt present in an amount sufficient to render the composition conductive. Non-ionic monomers shown are acrylic acid, methacrylic acid, hydroxyethyl methacrylate, and N-vinylpyrrolidone. The specification states that the non-ionic polymerizable material may comprise one non-ionic
25 monomer or a mixture of non-ionic monomers. Also, it says ionic monomers may be included.

Conductive adhesives made according to the Engel patents are used in patient grounding plates, transcutaneous electrical nerve stimulation (TENS)
30 electrodes, and diagnostic electrocardiogram (EKG/ECG) electrodes. While these adhesives provide excellent adhesive and electrical properties for some applications, optimizing the electrical properties without adversely affecting adhesion properties has not proved possible.
35 Experience has shown that increasing the water content of the Engel adhesive compositions to about 25% improves the electrical performance of electrodes coated with the

adhesives. The reason for this empirical observation is not known; one possible explanation is that increased water facilitates wetting of skin, thereby reducing skin impedance. Unfortunately, increasing water content to
5 optimum levels for electrical performance is found to decrease the initial tack and cohesive strength of the polymer, resulting in poor skin adhesion and residue left on the skin when the electrode is removed. While tackifiers may be used, they have not been found
10 particularly helpful in optimizing the electrical and adhesive properties.

Another conductive adhesive is disclosed in U.K. Patent Appln. 2,115,431 (published September 7, 1983). That publication describes adhesives formed by dissolving
15 or dispersing polymers in a plasticizing liquid and subjecting the mixture to radiation energies at least equivalent to 100,000 electron volts (X-ray, gamma and beta ray, and electron beam irradiation). The conductive adhesive described is prepared from polyvinylpyrrolidone,
20 polyethylene glycol, magnesium acetate, methyl paraben, propyl paraben, FD&C Blue #2 and water.

A commercially electrically-conductive adhesive sold under the trademark PolyhesiveTM (Valleylab, Inc., Boulder, CO) is believed to be made according to the
25 disclosure of U.K. Appn. 2,115,437. That adhesive exhibits good electrical properties but performs poorly as a biomedical adhesive. The initial adhesion to skin is not strong enough for many applications and the adhesive tends to lose moisture with time resulting in loss of adhesion at
30 the edges of an electrode.

The conductive adhesives described above are crosslinked swellable polymeric matrices. When a polymeric matrix has sufficient crosslinking it can be fully swelled without dissolving. When these crosslinked materials are
35 swelled with water they are called hydrogels. A non-adhesive hydrogel used for contact lenses is disclosed in U.K. Patent Appl. 2,130,743 (published June 6, 1984) and

- may be made as a terpolymer of a monomer mixture comprising N-vinylpyrrolidone, a short chain alkyl acrylate or methacrylate, and a short chain unsaturated carboxylic acid. That application requires the N-vinylpyrrolidone and the ester to make up the majority of the monomer mixture. It recommends the acid monomer not exceed 10% of the monomer mixture. The examples all have acid monomers comprising less than 4% (by weight) of the total monomers and less than 5% (by weight) of the N-vinylpyrrolidone.
- 10 U.S. Patent No. 4,451,630 shows another terpolymer used for contact lenses having N-vinylpyrrolidone and a short chain unsaturated acrylic acid. The monomer mixture for that terpolymer is N-vinylpyrrolidone (25 to 50% by weight) methacrylic or acrylic acid (up to 5% by weight), a
- 15 triazine crosslinker (0.1 to 1% by weight), and hydroxy alkyl acrylate or methacrylate (balance). The examples have acid monomer comprising less than 2% by weight of the total monomer mixture and less than 5% by weight of the N-vinylpyrrolidone.
- 20 A class of adhesives that can be dispersed or dissolved in polar solutions including water is the class of repulpable adhesives. They are generally not crosslinked. One such repulpable adhesive is made with a comonomer of butyl acrylate and methyl diethanol ammonium
- 25 acrylate. While ionic species may be somewhat soluble in these adhesives sufficient ionic concentration and mobility for optimal electrical performance has not been possible when the total water content is low enough to avoid dispersion of the polymers.
- 30 Another repulpable adhesive is soluble in both acid and basic solutions. Japanese Appl. No. 80-18772 (published May 17, 1980) describes a non-conductive adhesive that has a copolymer made from a polymerizable vinyl carboxyl containing monomer and a vinylpyrrolidone,
- 35 vinylpyridine or other basic monomer. The copolymer contains acid functional groups and alkaline functional groups in a prescribed ratio of 60-99.5% acid monomer to

40-0.5% basic monomer. The adhesive contains a water soluble plasticizer such as a polyhydric alcohol.

Mixtures of polymers rich in hydrogen bond donating groups with polymers rich in hydrogen bond accepting sites are known to be insoluble in water. For example, polyacrylic acid, a polymer rich in hydrogen bond donating sites, and polyvinylpyrrolidone, a polymer rich in hydrogen bond accepting sites, are each soluble in water. When solutions containing the two polymers are mixed, a partially swelled matrix rapidly precipitates out of solution.

Summary of the Invention

The present invention overcomes the problem of adversely affecting adhesion when optimizing electrical properties. The composition of the present invention displays adhesion properties far better than the prior art Engel and PolyhesiveTM conductive adhesives together with electrical properties equivalent to or better than those of the prior art Engel and PolyhesiveTM adhesives.

The electrically-conductive, pressure-sensitive adhesive compositions of the present invention are a homogeneous mixture of a copolymer matrix and a plasticizing, electrically-conductive solution.

The copolymer matrix is formed from a free radical polymerizable adhesive precursor having at least one water-soluble hydrogen bond donating monomer, at least one water-soluble hydrogen bond accepting monomer, and a free radical initiator of either the photo or thermal class. The ratio of hydrogen bond donating sites to hydrogen bond accepting sites in the monomer mixture is from about 1:3 to about 6:1.

The plasticizing, electrically-conductive solution contains from 0 to 98% by weight water-soluble polar organic compound, 2 to 100% by weight water, and 0 to 12% by weight water-soluble salt.

The adhesive composition contains from 12% to 50% by weight non-volatile copolymer matrix. The acidic hydrogen bond donating sites on the copolymer are from 5% to 95% neutralized. The composition is substantially homogeneous, i.e., it has essentially no phase separation, and provides a pressure-sensitive adhesive. While small areas of phase separation, observable in a web of adhesive composition as opaque patches, may be acceptable for certain applications, complete homogeneity is far preferred.

The composition does not need to be covalently crosslinked, but a crosslinker may be used. A multifunctional crosslinker may be added to the adhesive precursor up to about 0.5% by weight.

The composition may be made by preparing an adhesive precursor and polymerizing the monomers with a free radical reaction. The adhesive precursor comprises at least one water-soluble hydrogen bond donating monomer, at least one water-soluble hydrogen bond accepting monomer, a free radical initiator of either the photo or thermal class and a plasticizing, electrically-conductive solution. The plasticizing, electrically-conductive solution has from 0 to 98% by weight water-soluble polar organic compound, from 2 to 100% water, and from 0 to 12% soluble salt. The precursor is comprised of from 12% to 50% by weight monomers. Preferably the precursor is comprised of about 20% by weight monomers and the hydrogen bond accepting monomer and the hydrogen bond donating monomer are present in equal amounts. Acidic hydrogen bond donating sites are from 5 to 95% neutralized. Where covalent crosslinking is desired the adhesive precursor may further comprise up to about 0.5% by weight multifunctional crosslinking monomer.

The monomers suitable for this invention when copolymerized display sufficient interaction in the presence of water and polar plasticizers to produce improved physical properties (adhesion, cohesion) without phase separation.



The hydrogen bond donating monomers useful in the present invention include any polymerizable monomer having at least one hydrogen bond donating group such as unsaturated organic acids. Polymerizable ethylenically unsaturated organic acids such as carboxylic acids, phosphonic and phosphinic acids, and sulfonic acids may be used. The monomer should be soluble in the plasticizing electrically conducting solution. Short chain α,β -ethylenically unsaturated carboxylic acids having from 3 to 8 carbon atoms are preferred. Especially preferred are acrylic acid and methacrylic acid.

The hydrogen bond accepting monomers useful in the present invention include any polymerizable monomer having at least one hydrogen bond accepting group. N-vinyl amides, N-vinyl lactams and α,β -unsaturated amides such as acrylamide or substituted acrylamides may be used. The monomer should be soluble in the plasticizing electrically conducting solution. N-vinylpyrrolidone is preferred.

The nature of the interaction among the chains in the copolymer matrix are not understood. Without intending to be limited to any mechanistic theory, the interaction is believed to involve hydrogen bonding between chains in the copolymer matrix. Hydrogen bonds are formed, in general, between a donor molecule containing a hydrogen attached to an oxygen, nitrogen, or fluorine atom and an acceptor molecule containing oxygen, nitrogen, or fluorine atom. These bonds are weaker than covalent bonds and tend to rapidly break and form in solution.

The strength of a particular hydrogen bond is related in general to the acidity of the hydrogen on the donor group, and the basicity of the acceptor group plus any steric considerations effecting the geometry of the bond.

The net effect of such hydrogen bonding on physical properties of polymeric donors and acceptors is difficult to quantitatively predict due to the complex steric consideration in systems. Where the hydrogen bond

accepting and donating materials are dissolved in highly polar solvents which also readily form hydrogen bonds (water, glycerol) the effect of hydrogen bonding among the various components is particularly difficult to predict.

- 5 In such systems, an equilibrium exists between all the possible interactions.

The plasticizing electrically-conductive solution is "electrically-conductive" if it contains polar or ionic species effective to provide sufficient electrical
10 conductivity in the final composition for the intended application. The solution may contain from 0% to 98% by weight water-soluble, polar organic compound. The polar organic compound may be a polyhydric alcohol monomer or polymer. Low molecular weight polyoxyethylene glycols are
15 suitable (average M.W. 200 to 600 e.g., CarbowaxTM 200 and 600 available from Union Carbide). Glycerol is preferred. The plasticizing electrically-conductive solution may also contain from 2% to 100% water. Additionally the solution may contain up to 12% by weight of soluble salt such as a
20 halide. The chloride, iodide, and bromide salts of sodium and potassium may conveniently be used. Particularly preferred is potassium chloride.

The ratio of soluble polar organic compound to water and the concentration of salt may be varied depending
25 on the rheological and electrical properties desired. Suitable ratios of organic compound to water are 4:1, 2:1, and 1:1. Preferably water comprises at least 20%, and most preferably 25%, by weight, of the total composition. Preferably the salt may comprise from 0% to 6% by weight of
30 the plasticizing, electrically-conductive solution. Those skilled in the art of biomedical electrodes appreciate that when the polymer matrix is about 30% neutralized a small amount of water and no soluble salt in the plasticizing solution will result in a final adhesive that is
35 sufficiently electrically-conductive for use on grounding plate electrodes. In contrast, the preferred salt, potassium chloride, in a concentration of 1.25% by weight

of the plasticizing, electrically-conductive solution is preferred where the intended use is on monitoring electrodes having the ability to recover from potential overloads applied during defibrillation.

- 5 The preferred composition has light covalent crosslinking. In that case the adhesive precursor includes a multifunctional monomer. Suitable crosslinkers include triethylene-glycol-bis-methacrylate (TEGBM), ethylene-glycol-bis-methacrylate, methylene bis-acrylamide, 10 triethylene-glycol-bis-acrylate, and 3,3'-ethylidene-bis (N-vinyl-2-pyrrolidone). Additional crosslinkers are listed in U.S. Patent No. 4,536,554. The amount of crosslinker may be varied depending on the choice of monomers and crosslinkers and the polymerization 15 conditions. When the monomers are acrylic acid and N-vinyl-pyrrolidone, the crosslinker is preferably TEGBM, 3,3-ethylidene-bis-(N-vinyl-2-pyrrolidone) or methylene bisacrylamide. Crosslinker levels from 0.25% to 0.625% by weight of total monomers may be conveniently used. The 20 most preferred crosslinker is TEGBM present at a level of 0.625% by weight of total monomers.

- The polymerization may be started with an initiator of either the photo or thermal class. Photo initiators are preferred. Examples of useful photo 25 initiators are disclosed in the article "Photo Initiators - An Overview" by Berner et al., in the Journal of Radiation Curing (April 1979), pp. 2 through 9. The preferred photo initiator is benzildimethylketal. Examples of useful thermal initiators are benzoyl peroxide, 30 azo-bis-iso-butyronitrile, di-t-butyl peroxide and bromyl peroxide. The actual selection of initiator is dependent on the monomers and other components of the adhesive precursor.

- The preferred electrically-conductive adhesive 35 displays excellent rheological and electrical properties. A biomedical electrode having a suitable conductor, e.g. silver silver/chloride, and incorporating the preferred

composition meets the defibrillation recovery potential standards set forth in the AAMI voluntary standard "American National Standard for Pregelled ECG Disposable Electrodes" published by the Association for Advancement of
5 Medical Instrumentation. Electrodes incorporating the preferred composition as the only adhesive may be used as diagnostic electrodes. Electrodes incorporating the preferred composition and a medical tape can be used for extended monitoring without excessive drying. In both
10 cases the electrical properties are improved with observation of reduced skin impedance and adhesive properties are substantially improved with better tack and no residue upon removal.

The biomedical electrode of the present invention
15 comprises an conductor and a layer of the electrically-conductive, pressure-sensitive adhesive composition in electrical contact with the conductor. The conductor is configured to be attachable to an electromedical instrument. Those skilled in the art are familiar with
20 numerous stud and eyelet constructions, and with metallic foils and polymeric substrates coated with a thin layer of conductive metal or a conductive metal and metal salt, e.g., aluminum, tin, silver/silver chloride. The conductor may also be an electrically active form of carbon, e.g.,
25 graphite.

The electrically-conductive, pressure-sensitive adhesive has two surfaces; one contacts the conductor, and the second functions in use to contact and adhere to a patient's skin. When the biomedical electrode is to be
30 used as a patient grounding plate or a long term (e.g., at least 3 days) monitoring electrode, a medical tape comprised of a backing coated with a biocompatible pressure-sensitive adhesive may be added to the surface of the conductor opposing the electrically-conductive,
35 pressure-sensitive adhesive with an apron of medical tape extending beyond the periphery of the conductor. The medical tape assists in holding the electrode to the skin

and in the case of grounding plate electrodes serves to insulate the conductor surface from direct electrical contact with the patient and to prevent current flow along short circuits (e.g. blood or water).

- 5 When the biomedical electrode is a diagnostic electrode the conductor is preferably a polymeric substrate (e.g., polyester) coated with, or laminated to tin. The conductive adhesive is made by the photoinitiated polymerization of an adhesive precursor. The preferred
10 adhesive precursor comprises by weight about 10% hydrogen bond donating monomer (preferably acrylic acid); 10% hydrogen bond accepting monomer (preferably N-vinyl-pyrrolidone); 0.125% crosslinker (preferably TEGBM); 0.07% photoinitiator (preferably benzildimethylketal available as
15 IrgacureTM 651, Ciba Giegy), 1% soluble salt (preferably potassium chloride); 25.5% water and 53.3% glycerol. The acrylic acid is 50% neutralized preferably with sodium hydroxide. The layer of pressure-sensitive adhesive is preferably coated on the tin over a surface area of about
20 1 in² (6.5 cm²) to a thickness of about 35 mils.

- When the biomedical electrode is a monitoring electrode, the conductor is preferably a polymeric substrate coated with metallic silver and a thin layer of silver chloride. The electrically-conductive adhesive is
25 preferably the same as recited above for a diagnostic electrode. The electrode preferably meets the AAMI voluntary standards for polarization recovery referenced above and described below in the Examples.

- When the biomedical electrode is a patient
30 grounding plate the conductor is preferably an aluminum foil or a polymeric film coated with or laminated to aluminum. The electrically-conductive adhesive is formed by the photoinitiated polymerization of an adhesive precursor. The adhesive precursor comprises by weight
35 about 10% hydrogen bond donating monomer (preferably acrylic acid); about 10% hydrogen bond accepting monomer (preferably N-vinyl-pyrrolidone), 0.125% crosslinker

(preferably TEGBM), 0.07% photoinitiator (preferably benzildimethylketal available as IrgacureTM 651, Ciba Giegy), 25.5% water and 54.3% glycerol. The hydrogen bond donating monomer is preferably 20%-50% neutralized with sodium hydroxide.

Brief Description of the Drawings

Fig. 1 is a perspective view of a diagnostic biomedical electrode of the present invention;

10 Fig. 2 is an exploded sectional view of the diagnostic biomedical electrode of the present invention through line 2-2 of Fig. 1;

Fig. 3 is an exploded perspective view of a monitoring biomedical electrode of the present invention;

15 Fig. 4 is a perspective view of a grounding plate biomedical electrode of the present invention;

Fig. 5 is a sectional view of the grounding plate biomedical electrode of the present invention through line 5-5 of Fig. 4; and

20 Fig. 6 is a circuit diagram for use in a defibrillation overload recovery test.

Detailed Description of the Preferred Embodiments

The composition of the present invention is preferably made with a photoinitiated polymerization of monomers dissolved in the plasticizing, electrically-conductive solution. In this process essentially all the materials present in the precursor are present in the same or modified form in the final composition. The plasticizing, electrically-conductive solution serves as a solvent for the monomers in the polymerization step and is present as the plasticizing, electrically-conductive liquid in the final composition. The monomers are converted in the polymerization to a copolymer matrix which may be, but need not be, covalently crosslinked. Preferably, a bifunctional crosslinking monomer is included and polymerization is carried to greater than 99% completion

leaving less than 1% monomer in the final composition. The process may be carried out in situ with the adhesive precursor coated on an electrode conductor or backing substrate. Alternatively, the adhesive precursor can be
5 coated on a transfer sheet to make a web of adhesive which subsequently may be incorporated into a composite such as a biomedical electrode. In either case, the adhesive precursor is preferably coated and cured on a thin scrim, e.g., 4 mils CerexTM (Monsanto), to facilitate mechanical
10 handling in manufacturing processes.

The composition is preferably incorporated into a biomedical electrode. Figs. 1 and 2 show a diagnostic biomedical electrode 10 according to the present invention. The preferred electrode 10 comprises a polymeric substrate
15 12, e.g. polyester, coated on one side with tin 14. A layer 18 of electrically-conductive adhesive composition coats a first portion 16 of the tin surface while a second portion 17 of the tin surface is a strip along one edge of the surface and free for attachment to a leadwire of an
20 electromedical sensing device. Optional release liner 19 protects the electrically-conductive, pressure-sensitive adhesive 18 prior to use. The preferred electrode when tested in pairs face-to-face as described below, exhibits an impedance in ohms at 10 Hz not exceeding 2,000 ohms.
25 The impedance preferably should not exceed 1,000 ohms. These performance levels are met with a diagnostic electrode having a conductive adhesive surface area of 1 in² (6.5 cm²) and a conductive adhesive thickness of 35 mils.

The preferred electrically-conductive adhesive
30 for a diagnostic electrode is made from an adhesive precursor having by weight 10% acrylic acid (50% neutralized with sodium hydroxide), 10% N-vinylpyrrolidone, 0.125% TEGBM, 0.07% benzildimethylketal (IrgacureTM 651, Ciba Giegy), 1% potassium chloride 25.5%
35 water and 53.5% glycerol.

The relative proportions and total amount of monomer, the total amount of crosslinker, the degree of

neutralization of the hydrogen bond donating monomer, the amount of soluble salt and the ratio of water to polar organic liquid may all be varied with acceptable results. As the amount of crosslinker is reduced or eliminated the
5 amount of hydrogen bond donating and accepting sites should be increased. Accordingly, when no crosslinker is used the total amount of solids is increased, for example to 30%, and the degree of neutralization of the hydrogen bond donating monomer is decreased for example to about 5% of
10 the available sites.

A preferred monitoring biomedical electrode 20 of the present invention is shown in Fig. 3. That electrode construction is described and claimed in commonly assigned Application Ser. No. 865,521 filed May 21, 1986. The
15 monitoring electrode 20 has a backing 21 coated with biocompatible pressure-sensitive adhesive (PSA) 22. The backing 21 and biocompatible PSA 22 are formed with two cutouts along one edge so that the edge has three tabs. A bonding sheet 23 adheres to a portion of the biocompatible
20 PSA 22. The bonding sheet 23 is aligned transverse to the cutout along one edge of the backing 21 and biocompatible PSA 22.

An electrical conductor 24 is comprised of a conformable film (e.g. polyester) that has been coated
25 with a primer comprised of a binder and powder particles and thereafter coated with metallic silver. The metallic silver is then treated to convert a portion of the surface layer to silver chloride. The preferred electrical conductor is described and claimed in ^{US Patent No. 4,848,348} ~~commonly assigned~~
30 ~~Application Ser. No. 865,522 filed May 21, 1986.~~ The electrical conductor 24 is aligned transverse to the length of the bonding sheet 23 and preferably along the center of the three edge tabs on the backing and biocompatible PSA.

The conductor is shown in Fig. 3 with the
35 conformable polymeric film face adjacent the bonding sheet 23 and a portion of the biocompatible PSA 22. For purposes of clarity the film face of conductor 24 is divided into



two portions. Portion 25 spans the bonding sheet while portion 26 adheres to a portion of the biocompatible PSA 22. The silver/silver chloride surface 27 opposing portion 26 is free for attachment to a leadwire.

5 A web of electrically-conductive pressure-sensitive adhesive 28 is aligned with the bonding sheet. It adheres to and has electrical contact with that portion of the conductor 24 underlying the bonding sheet 23. The remainder of the web of conductive adhesive adheres to the
10 bonding sheet 23. An optional release liner 29 protects the exposed surfaces of biocompatible PSA 22 and the web of electrically-conductive adhesive 28.

The preferred monitoring electrode will adhere to skin for at least three days without excessive drying of
15 the adhesive (and concomitant loss of electrical performance). It can be removed without leaving an adhesive residue, and it meets the voluntary AAMI Standards for overload polarization recovery. The preferred monitoring electrode meets these performance requirements
20 when the silver metal surface has a layer of silver chloride equivalent to at least about 30 mC, the electrically-conductive adhesive contains about 0.5% chloride ion, and the adhesive is made with the same precursor described above for the preferred diagnostic
25 electrode.

A preferred patient grounding plate biomedical electrode is shown in Figs. 4 and 5. The preferred grounding plate biomedical electrode 30 comprises an insulating backing 31 coated on one surface with a
30 biocompatible PSA 32. The backing 31 may be a closed cell vinyl foam. An electrode plate 33 adheres to a portion of the biocompatible PSA 32. The electrode plate may be an aluminum foil or a conformable polymeric backing 34, e.g., polyester, having aluminum deposited on one surface. The
35 electrode plate 33 has an integrally associated connector tab 35 suited to electrically connect the grounding plate biomedical electrode to a leadwire which in use is

connected to an electrosurgery generator. A web of electrically-conductive adhesive 36 coats the entire electrically-conductive surface of electrode plate 33 except the connector tab 35. An insulating strip 37 covers
5 that portion of the surface of the connecting tab 35 which underlies the backing 31 and biocompatible PSA 32. The backing 31 and biocompatible PSA 32 have an apron 38 extending beyond the periphery of the electrode plate 33 and electrically-conductive adhesive 36. Those skilled in
10 the art will appreciate that the apron 38 together with insulating strip 37 serves to insulate the electrode plate from direct contact with a patient's skin thereby avoiding thermal burns and from contact with other conductors (e.g. blood or water) which may result in an electrical short
15 circuit. An optional release liner 39 may be used to protect adhesive surfaces prior to use.

The preferred grounding plate biomedical electrode has excellent adhesion and low impedance electrical contact with a patient's skin (to avoid hot
20 spots or loss of contact due to motion). These performance criteria are met when the surface area of the electrically-conductive adhesive 36 and electrode plate 33 are 20 in² (130 cm²), the electrically-conductive adhesive 36 is coated 20 mils thick, and the electrically-conductive
25 adhesive is made from a precursor having by weight 10% acrylic acid (20-50% neutralized with sodium hydroxide), 10% N-vinylpyrrolidone, 0.125% TEGBM, 0.07 benzildimethyketal Irgacure No. 651, Ciba Giegy), 25.5% water and 54.4% glycerol.

30 A further understanding of the benefits and versatility of the electrically-conductive adhesive of the present invention and biomedical electrodes incorporating that adhesive will be appreciated from the following non-limiting examples.

35 In the examples, the following procedures are used.

Procedure A - Adhesive Preparation

The soluble salt (if any) is added to water in a glass container and dissolved. Neutralizing base is added
5 and dissolved. Thereafter the water-soluble polar organic compound is added and dissolved.

In a separate container the hydrogen bond donating monomer is mixed with the polymerization initiator and crosslinker (if any).

10 The salt, water, polar organic compound solution is mixed with the hydrogen bond donating monomer mixture. Just prior to coating on a substrate, the hydrogen bond accepting monomer is dissolved in the mixture and polymerization is initiated.

15 The adhesive precursor is coated on a substrate and exposed to U.V. radiation in a nitrogen atmosphere for time sufficient to complete polymerization. Immediately following polymerization the composition is visually inspected for opacity which is noted as phase separation.

20

Procedure B - Initial Tack

Immediately following polymerization the composition is evaluated for initial tack. In this test
25 firm pressure is applied to the sample with a thumb and the thumb is removed. The samples are rated as follows:

- 0 very soft, poor tack, residue on thumb upon removal
- 1 soft, poor tack, small amount of residue on thumb
- 2 moderately soft, acceptable tack, no residue
- 3 moderately soft, good tack, no residue
- 4 moderately firm, acceptable tack, no residue
- 5 very firm, little or no tack

30

35

Procedure C - Impedance

Impedance in ohms of an electrode is measured using a Model 4800A Vector Impedance Meter manufactured by
5 Hewlett Packard, Palo Alto, California. Measurements are conducted in the conventional manner on electrode pairs connected face-to-face (adhesive-to-adhesive) using a low level signal suitable for measurements on ECG electrodes. The impedance of the electrode at 10 Hz is recorded.

10

Procedure D - Polarization Potential

The polarization potential of an electrode is determined using the procedure and circuit described in the
15 AAMI Test Standard "American National Standard for Pregelled ECG Disposable Electrodes" published by the Association for Advancement of Medical Instrumentation. The circuit is shown in Fig. 6.

1. Two electrodes 40 and 42 are connected
20 adhesive-to-adhesive and connected to the test circuit (Fig. 6) with switch 44 closed and switches 46 and 48 open.

2. At least 10 seconds are allowed for the capacitor 50 to fully charge to 200 V; switch 44 is then opened.

25 3. The capacitor 50 is discharged through the electrode pair by holding switch 46 closed long enough to discharge the capacitor 50 to less than 2 V. This time is no longer than 2 seconds.

30 4. Switch 48 is closed immediately, and the electrode pair is connected to the offset potential measurement system (switch 46 open).

5. The electrode offset potential is recorded to the nearest 1 mV, 5 seconds after the closure of switch 48 and every 10 seconds thereafter for the next 30 seconds.
35 The overload and measurement is repeated three times.

In the test circuit (Fig. 6), resistor 52 has a resistance of 10 kilohms, and resistor 54 is a 5 watt, 100 ohm resistor. Capacitor 50 has a capacitance of 10 μ F. All capacitors and resistors are within 90 to 110 percent of the specified values. The offset recorder input amplifier 56 has a resistance of 10 megaohms and has an input impedance from 0 to 10 Hz of 10 M Ω , $\pm$ 10 percent, and a bias current of less than 200 nA. The error of the voltage-recording equipment is no greater than $\pm$ 5 percent of full scale of 100 mV. A 10 mV change is measurable with an error no greater than $\pm$ 1 mV. For this purpose, the full scale range and resolution of the recording instrument may be adjusted as needed. The test sequence (steps 1-5) is repeated for 3 electrode pairs. The polarization potential noted for an electrode of a particular construction is the numerical average of the potentials measured 15 seconds after the fourth pulse for each of the three sample pairs.

Example 1

20

The preferred homogeneous pressure-sensitive electrically-conductive adhesive of the present invention was made following Procedure A. The reaction mixture was coated to a thickness of 35 mils on a silicone coated release paper (HP Smith). A scrim (CerexTM, Monsanto) was impregnated into the reaction mixture prior to polymerization. Polymerization was accomplished by exposing the precursor to UV irradiation (360 nm lamp available from General Electric) for four minutes under a nitrogen atmosphere. No opacity was observed. Following Procedure B, the initial tack of the adhesive composition was rated 3. The constituents of the precursor and their relative amounts are shown in Table I.

35

TABLE I

	<u>Constituents</u>	<u>Amount By Weight</u>
	Acrylic Acid	10%
	N-vinylpyrrolidone	10%
5	Glycerol	50.6%
	Water	25.5%
	benzildimethylketal	0.07%
	TEGBM	0.125%
	KCl	1.0%
10	NaOH	2.77%

Example 2

The adhesive composition made in Example 1 was used to make a diagnostic electrode. The electrical conductor was a polyester film having a continuous layer of tin laminated to one surface. The conductor had a surface area slightly larger than 1 in² (6.5 cm²). A web of adhesive having a surface area of 1 in² (6.5 cm²) together with the silicone coated transfer sheet on which it was formed was laminated to the tin surface of the conductor. A steel roller was passed back and forth over the composite once to assure good wetting of the tin by the adhesive.

The electrodes were tested for impedance using Procedure C. The face to face impedance is 900 Ω.

Example 3

The adhesive composition made in Example 1 is used in the construction of a monitoring electrode as described above and shown in Fig. 3. The backing is a polyethylene foam having closed cells (Voltek, Inc., Lawrence NH) and has a surface area of 3.5 in². The biocompatible pressure-sensitive adhesive is based on a copolymer of isoctyacrylate (90%) and N-vinylpyrrolidone (9% by weight) and is coated 11.5 grains/in² (48 g/m²). The bonding sheet is a spun bonded nylon (Monsanto, St.

Louis, MO), the electrical conductor is made with conformable polyester backing coated with a primer comprised of binder and particles (commercially available as ImperialTM Lapping Film, 3M St. Paul, MN). Silver is vapor deposited on the film and a portion of the silver is converted to silver chloride. The conductor measures 1.25" by 0.5". The electrically-conductive adhesive web measures 2" by 0.75" and is 35 mils thick.

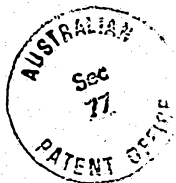
Impedance and polarization potentials were tested using procedures B and C on these monitoring electrodes. Table II summarizes the results.

Table II

15	Offset, mV	0.6
	10 Hz impedance, ohms	150
	100K Hz impedance, ohms	50
	Polarization potential, mV	
	5 sec, 1st discharge	20.8
20	5 sec, 2nd discharge	16.6
	5 sec, 3rd discharge	14.9
	5 sec, 4th discharge	13.8
	Trace quality	very good
25	<u>Example 4</u>	

A wide range of samples are made following procedure A. The total weight of the two monomers studied varies from 12% to 50%. The ratio of the two monomers is varied within each total weight of monomer studied. Each 100g precursor contains 1.0g KCl, 25.5g H₂O, NaOH (in an amount sufficient to neutralize 50% of the acid groups), 0.07g benzildimethylketal, 0.125g TEGBM, acrylic acid (AA), N-vinylpyrrolidone (NVP), and glycerol (balance).

35. Procedure B is used to describe initial tack. The results are summarized in Table III. An asterisk (*) indicates observation of patches of opacity.



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TABLE III

Percent Monomer	<u>100% AA</u>	<u>1/.11</u>	<u>1/.25</u>	<u>1/.42</u>	<u>1/.66</u>	<u>1/1</u>	<u>1/1.5</u>	<u>1/2.3</u>	<u>1/4</u>	<u>1/9</u>	<u>100% NVP</u>
12	0										
18	2	1.5									
20	5*	4*	4*	3	3	3	2	1	1*	0	0
30	5*		4		3.5		3		2		1
40									3.5		1
50									5*		1

Example 5

Eight samples, ranging from 0% to 100% neutralization are made according to Procedure A. In each 100g sample the reaction mixture contains 10g acrylic acid, 10g N-vinylpyrrolidone, 1.0 KCl, 0.07 benzildimethylketal, 0.125g TEGBM, 25.5g H₂O, NaOH (in an amount sufficient to result in the degree of neutralization), and glycerol (balance). Using procedure B to describe tack, the results are summarized in Table IV. An asterisk (*) indicates phase separation observed as patches of opacity.

TABLE IV

Sample #	Percent Neutralization	Tack
1	0	5*
2	5	3.5
3	20	3
4	40	3
5	60	2
6	80	2
7	95	1.5
8	100	0*

Example 6

Nine samples are made following procedure A. Each 100g reaction mixture contains 10g acrylic acid, 10g N-vinylpyrrolidone, 2.77g NaOH, 1.0g KCl, 0.07g benzildimethylketal, 0.125g TEGBM, water and glycerol. The ratio of water to glycerol is varied over a wide range while keeping all other components at a constant level. The samples are evaluated for initial tack using Procedure B and the results are summarized in Table V. An asterisk (*) indicates patches of opacity.

TABLE V

	<u>Sample #</u>	<u>Glycerol (g)</u>	<u>Water (g)</u>	<u>Tack</u>
	1	76.1	0	3
5	2	66.1	10	2
	3	56.1	20	3
	4	46.1	30	3
	5	36.1	40	4
	6	26.1	50	4
10	7	16.1	60	4*
	8	6.1	70	4*
	9	0	76.1	4

Example 7

15

Five samples, with different amounts of salt incorporated, are made according to Procedure A. Each 100g reaction mixture contains 10g acrylic acid, 10g N-vinylpyrrolidone, 2.77g NaOH, KCl, 0.07g benzildimethylketal, 0.125g TEGM, 25.5g H₂O and glycerol (balance). Using procedure B to describe tack, results are summarized in Table VI. An asterisk (*) indicates opacity.

TABLE VI

25

	<u>Sample #</u>	<u>g KCl</u>	<u>Tack</u>
	1	3	3
	2	6	2
	3	9	5*
30	4	0	3
	5	1	3

Example 8

35

Samples are made following Procedure A using different crosslinkers and levels of crosslinkers ranging from 0.0125% to 0.5%. The crosslinkers include

triethylene-glycol-bismethacrylate (TEGBM),
3,3-ethylidene-bis-(n-vinyl pyrrolidone) (EBVP), and
methylenebisacrylamide (MBA). Each 100g reaction mixture
contains 10g acrylic acid, 10g N-vinylpyrrolidone, 1g KCl,
5 0.07 benzildimethylketal, crosslinker, 25.5g water, and
glycerol (balance). Using procedure B to evaluate initial
tack, the results are summarized in Table VII.

TABLE VII

10

Sample #	Crosslinker (g)	Tack
1	TEGBM 0.05	1
2	TEGBM 0.1	3
3	TEGBM 0.3	4
15 4	TEGBM 0.5	5
5	EBVP 0.0125	1
6	EBVP 0.025	3
7	EBVP 0.075	4
8	EBVP 0.125	3
20 9	MBA 0.0125	1
10	MBA 0.025	3
11	MBA 0.075	4
12	MBA 0.125	5

25

Example 9

A variety of samples are made following Procedure
A in which different hydrogen bond donating and hydrogen
30 bond accepting monomers are used. Each 100g reaction
mixture contains monomers, 1g KCl, 0.07g
benzildimethylketal, 0.125g TEGBM, 25.5g water and glycerol
(balance). The hydrogen bond donating monomers used are
acrylic acid (AA), itaconic acid (ITA), and maleic acid
35 (MA) with sufficient sodium hydroxide to neutralize 50% of
the acid groups. The hydrogen bond accepting monomers used
are N-vinylpyrrolidone (NVP) and dimethyl acrylamide

(diMeA). Using Procedure B to describe tack, the results are summarized in TABLE VIII.

TABLE VIII

5

	<u>Monomers</u>	<u>Tack</u>
	AA (10g)/diMeA (10g)	3
	AA (14g)/diMeA (6g)	3
	AA (6g)/diMeA (14g)	3
10	AA (15g)/diMeA (15g)	4
	AA (20g)/diMeA (20g)	4
	AA (8g), ITA (2g)/NVP (10g)	2
	AA (9g), MA (1g)/NVP (10g)	2

15

Example 10

Four samples are made following Procedure A. Each 100g reaction mixture contains 10g acrylic acid, 10g N-vinylpyrrolidone, 2.77g NaOH, 1g KCl, 0.07g benzildimethylketal, 0.125g TEGBM, and 50.6g polar organic compound. Using procedure B to describe tack, the results are summarized in Table IX.

25

TABLE IX

	<u>Sample #</u>	<u>Glycerol(g)</u>	<u>Sorbitol(g)</u>	<u>Carbowax 200(g)</u>	<u>Tack</u>
	1	25.3	25.3	-	4
	2	37.9	12.6	-	3
30	3	25.3	-	25.3	3
	4	37.9	-	12.6	2

Example 11

35

The following describes the method for the thermal polymerization of the adhesive precursor material.

The procedure for making the sample is identical to that described in Procedure A except that potassium persulfate (the thermal initiator) is dissolved in the water. Table X shows the relative amounts of each component. The adhesive precursor is coated on a substrate and exposed to 50°C for approximately 8 hours in a nitrogen atmosphere. Following Procedure B the initial tack of this thermally polymerized adhesive is rated 1.

10

TABLE X

		<u>Amount by Weight</u>
		<u>(Percent)</u>
	<u>Constituent</u>	
	Acrylic acid	10
	n-vinylpyrrolidone	10
15	Glycerol	50.2
	Water	25.5
	Potassium persulfate	0.4
	TEGBM	0.125
	KCl	1.0
20	NaOH	2.77

Example 12

Adhesion of the preferred diagnostic electrode to skin is compared to that of commercially available electrodes. One electrode tested is the Littmann 2322 diagnostic electrode (3M, St. Paul, MN). That electrode has a tin laminated to polyester conductor and a conductive adhesive like those described in U.S. Patent 4,544,824. Another electrode compared is the Sentry Silver Circuit #10009 (Sentry Medical Products, Santa Ana, CA). The package indicates that the Sentry Silver circuit electrode has a silver/silver chloride conductor and a polyhesive conductive adhesive. The polyhesive conductive adhesive (Valleylab Inc., Boulder, CO) is believed to be made according to the disclosure of U.K. Appln. 2,115,431.

Samples of the electrodes to be tested are placed on the subject's back in horizontal rows. The electrodes

are then pressed onto the skin using a rubber roller to ensure even contact. Immediately after application of the array of electrodes, they are removed one at a time beginning with the first electrode applied. To remove an electrode, a clip and a cord are used to attach one edge of the electrode to an instrument capable of pulling on the cord and measuring the force required versus time. The electrode is pulled at an angle of 180° back across itself at a speed of 6 in./min. The force to peel the electrode from the skin is recorded. The maximum value corrected for the width of the electrode is reported as the skin adhesion. Because skin varies greatly from individual to individual and from place to place on a single individual, the test is conducted many times. The values reported in Table XI are numerical averages of the number of replicates shown in parentheses. The absolute values are not considered particularly significant. The rank of values within a panel is considered significant. In the panels performed, the rank from low to high is consistently Silver CircuitTM electrodes followed by Littmann 2322 electrodes followed by electrodes with the adhesive of the present invention.

TABLE XI

Average Skin Adhesion g/in (Replicates)				
Panel	Silver Circuit	Littmann	New Adhesive	
1	19.5 (36)	37.8 (36)	74.1 (36)	
2	48.3 (24)	69.6 (28)	--	
3	36.6 (32)	72.4 (32)	--	
4	--	44.7 (18)	103 (24)	
5	--	63.8 (35)	96.3 (36)	

The foregoing description has been directed to preferred embodiments for the purposes of illustration and explanation. Those skilled in the art will appreciate that many modifications and changes will be possible without departing from the scope and spirit of the invention. The following claims are intended to embrace all such modifications and variations.

The claims defining the invention are as follows:

1. An electrically-conductive, pressure-sensitive adhesive formed by the free radical copolymerization of an adhesive precursor comprising:
at least one water-soluble hydrogen bond donating monomer;
at least one water-soluble hydrogen bond accepting monomer;
a free radical initiator; and
a plasticizing, electrically-conductive solution comprising from 0 to 98% by weight water-soluble, polar organic compound, from 2 to 100% by weight water, and from 0 to 12% by weight soluble salt

wherein the ratio of hydrogen bond accepting sites to hydrogen bond donating sites on the monomers is from about 1:3 to about 6:1, the adhesive precursor contains from about 12% to about 50% by weight total monomers, and the acid sites on the hydrogen bond donating monomer are from about 5% to about 95% neutralized, and the composition is substantially homogeneous and pressure-sensitive adhesive.

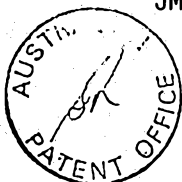
2. The composition of claim 1 wherein the adhesive precursor further comprises a multifunctional crosslinker present up to about 2.5% by weight of the total monomers in the adhesive precursor.

3. The composition of claim 1 wherein the hydrogen bond donating monomer is selected from the group consisting of α , β -ethylenically unsaturated carboxylic acids having up to eight carbon atoms and organic phosphonic, phosphinic and sulfonic acids having a polymerizable vinyl group, and the hydrogen bond accepting monomer is selected from the group consisting of N-vinyl amides, N-vinyl lactams and α , β -unsaturated amides.

4. The composition of claim 1 wherein the hydrogen bond donating monomer is selected from the group consisting of α , β -ethylenically unsaturated carboxylic acids having up to eight carbon atoms and organic phosphonic and sulfonic acids having a polymerizable vinyl group, and the hydrogen bond accepting monomer is selected from the group consisting of N-vinyl amides, N-vinyl lactams, and α , β -unsaturated amides.

5. The composition of claim 1 wherein the hydrogen bond donating monomer is acrylic acid, the hydrogen bond accepting monomer is N-vinylpyrrolidone, the weight ratio of acrylic acid to N-vinyl pyrrolidone is from about 1:2 to about 3:1, and the final composition comprises from about 15% to about 25% by weight copolymer matrix.

JMR/1041h



6. The composition of claim 1 wherein the water-soluble, polar organic compound is selected from a group consisting of monomeric and polymeric polyhydric alcohols.

7. The composition of claim 1 wherein the water-soluble polar organic compound is glycerol.

8. The composition of claim 1 wherein the soluble salt is a chloride, bromide, or iodide salt of sodium or potassium and comprises from 0 to 6% by weight of the plasticizing, electrically-conductive solution.

9. The composition of claim 1 wherein the soluble salt is potassium chloride and it comprises about 1.25% by weight of the plasticizing, electrically-conductive solution.

10. The composition of claim 1 wherein the adhesive precursor comprises by weight

from about 5% to 43.5% acrylic acid

from about 7% to 45% N-vinylpyrrolidone

from about 0.05% to 0.3% triethylene-glycol-bis-methacrylate

from about 0.02% to 0.1% benzildimethylketal

from about 5% to 60% water

from about 0.5% to 12% potassium chloride

from about 30% to 70% glycerol, and

the acrylic acid is from about 5% to 95% neutralized with sodium hydroxide.

11. The composition of claim 1 wherein the adhesive precursor comprises by weight

from about 8% to 12% acrylic acid

from about 8% to 12% N-vinylpyrrolidone

from about 0.10% to 0.15% triethylene-glycol-bis-methacrylate

from about 0.5% to 0.7% benzildimethylketal

from about 23% to 27% water

from about 0.75% to 1.25% potassium chloride

from about 48% to 52% glycerol, and

the acrylic acid is from about 45% to 55% neutralized with sodium hydroxide.

12. A process for making an electrically-conductive, pressure-sensitive adhesive comprising:

a) providing an adhesive precursor comprising at least one hydrogen bond donating monomer, at least one hydrogen bond accepting monomer, a free radical initiator; and

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a plasticizing, electrically-conductive solution comprised from 0 to 98% by weight water-soluble organic compound, from 2 to 100% by weight water, and from 0 to 12% by weight soluble salt.

wherein the ratio of hydrogen bond accepting sites to hydrogen bond donating sites on the monomers is from about 1:3 to about 6:1, the adhesive precursor contains from about 12% to about 50% by weight of total monomers, the hydrogen bond donating sites on the hydrogen bond donating monomer are from about 5% to about 95% neutralized, and the composition is substantially homogeneous and pressure-sensitive adhesive;

b) coating the adhesive precursor on a substrate; and

c) initiating polymerization of the monomers in the adhesive precursor.

13. A biomedical electrode comprising: an electrical conductor, means integrally associated with the conductor for connecting the electrode to an electromedical instrument, and an electrically-conductive, pressure-sensitive adhesive in electrical contact with the conductor comprising a conformable, cohesive, adhesive copolymer matrix formed by free radical polymerizing an adhesive precursor comprising at least one water-soluble hydrogen bond donating monomer, at least one water-soluble hydrogen bond accepting monomer, and a polymerization initiator wherein the molar ratio of hydrogen bond accepting sites to hydrogen bond donating sites available on the monomers is from about 1:3 to about 6:1, and a plasticizing, electrically-conductive solution comprised of from 0 to 98% by-weight water-soluble, polar organic compound, 2 to 100% by weight water, and 0 to 12% by weight water-soluble salt, wherein the electrically-conductive, pressure-sensitive adhesive contains from about 12% to about 50% by weight non-volatile copolymer matrix, the hydrogen bond donating sites on the copolymer are from about 5% to about 95% neutralized and the composition is substantially homogeneous and pressure-sensitive adhesive.

14. The biomedical electrode of claim 13 further characterized by a medical tape comprised of a backing and a biocompatible pressure-sensitive adhesive coated on one surface of the backing wherein the conductor adheres to a portion of the medical tape and the remainder of the medical tape extends beyond the perimeter of the conductor.



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15. A method of making the biomedical electrode comprising:

a) providing a web of conductor,

b) covering the conductor with an electrically-conductive, pressure-sensitive adhesive comprised of a conformable, cohesive, adhesive copolymer formed by free radical polymerizing an adhesive precursor comprising at least one water-soluble hydrogen bond donating monomer, at least one water-soluble hydrogen bond accepting monomer, and a polymerization initiator wherein the molar ratio of hydrogen bond accepting sites to hydrogen bond donating sites available on the monomers is from about 1:3 to about 6:1, and a plasticizing, electrically-conductive solution comprised of from 0 to 98% by weight water-soluble, polar organic compound, 2 to 100% by weight water, and 0 to 12% by weight water-soluble salt; wherein the electrically-conductive, pressure-sensitive adhesive contains from about 12% to about 50% by weight non-volatile copolymer matrix, the hydrogen bond donating sites on the copolymer are from about 5% to about 95% neutralized and the composition is substantially homogeneous and pressure-sensitive adhesive; and

c) cutting the laminate of steps a and b to form electrodes.

16. The method of claim 15 further comprising laminating onto the surface of the conductor opposing the electrically-conductive, pressure-sensitive adhesive a medical tape comprised of a backing and a biocompatible pressure-sensitive adhesive coated on one surface of the backing and cutting the medical tape to a shape and size that provides an apron of medical tape extending beyond the perimeter of the conductor.

17. An electrically-conductive, pressure-sensitive adhesive substantially as described herein with reference to and as illustrated by any one of the Examples other than comparative Examples.

18. A biomedical electrode substantially as described herein with reference to and as illustrated by Figs. 1 and 2 or Fig. 3 or Figs. 4 and 5 of the accompanying drawings.



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19. A process for making an electrically-conductive, pressure-sensitive adhesive substantially as described herein with reference to any one of the Examples other than comparative Examples.

DATED this TWENTY-FIFTH day of JANUARY 1990
Minnesota Mining and Manufacturing Company

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



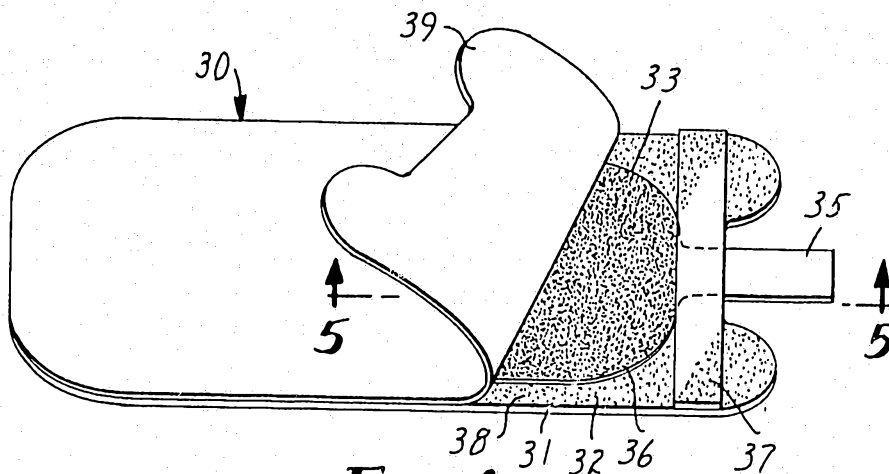


FIG. 4

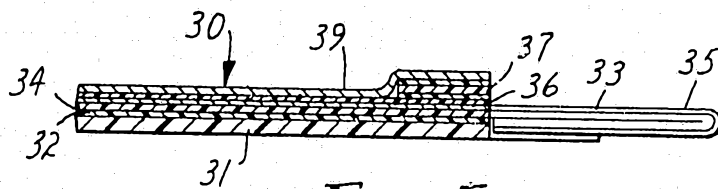


FIG. 5

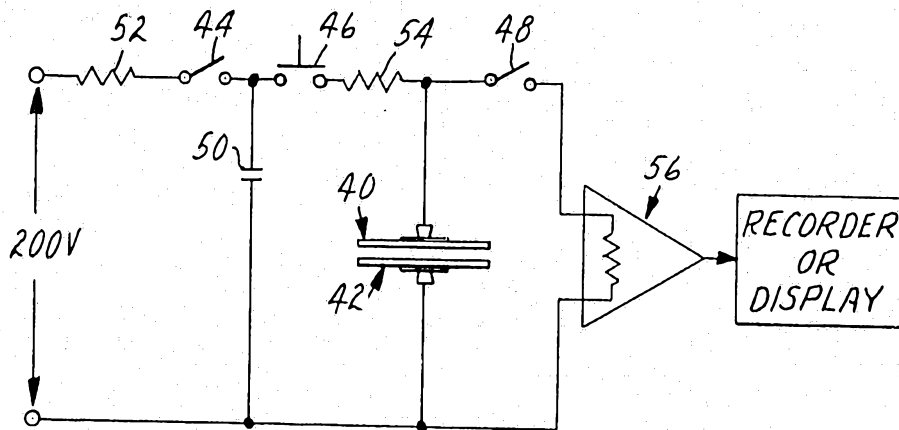


FIG. 6