

Date of Deposit: October 4, 1999

Case No. **9793/21**

JC710 U.S. PTO

PATENT APPLICATION TRANSMITTAL LETTER

10/04/99

To the Assistant Commissioner for Patents:

Transmitted herewith for filing is the patent application of: Raghbir Singh Bhullar for: LASER DEFINED FEATURES FOR PATTERNED LAMINATES AND ELECTRODES: Enclosed are:

- ☒ 9 sheet(s) of drawings, 16 pages of application (including title page), and the following Appendices:
: _____.
- ☐ Declaration.
- ☐ Power of Attorney.
- ☐ Verified statement to establish small entity status under 37 CFR §§ 1.9 and 1.27.
- ☐ Assignment transmittal letter and Assignment of the invention to : _____.
- ☒ PTO 1449; Information Disclosure Statement.

JC542 U.S. PTO
09/411940
10/04/99

Claims as Filed	Col. 1	Col. 2
For	No. Filed	No. Extra
Basic Fee		
Total Claims	38 -20	13
Indep. Claims	5 -3	2
Multiple Dependent Claims Present		

Small Entity	
Rate	Fee
	\$ 380
x\$9=	\$
x\$39=	\$
+\$130=	\$
Total	\$

Other Than Small Entity	
Rate	Fee
	\$ 760
18 x\$18=	\$324
2 x\$78=	\$156
+\$260=	\$
Total	\$1,240

*If the difference in col. 1 is less than zero, enter "0" in col. 2.

- ☒ Please charge my Deposit Account No. 23-1925 in the amount of \$: 1,240. A duplicate copy of this sheet is enclosed.
- ☐ A check in the amount of \$: _____ to cover the filing fee is enclosed.
- ☒ The Assistant Commissioner is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. 23-1925. A duplicate copy of this sheet is enclosed.
- ☒ Any additional filing fees required under 37 CFR § 1.16.
- ☒ Any patent application processing fees under 37 CFR §1.17.
- ☐ The Assistant Commissioner is hereby authorized to charge payment of the following fees during the pendency of this application or credit any overpayment to Deposit Account No. 23-1925. A duplicate copy of this sheet is enclosed.
- ☐ Any filing fees under 37 CFR § 1.16 for presentation of extra claims.
- ☐ Any patent application processing fees under 37 CFR § 1.17.
- ☐ The issue fee set in 37 CFR § 1.18 at or before mailing of the Notice of Allowance, pursuant to 37 CFR § 1.311(b).

October 4, 1999
Date


Paul E. Rauch, Ph.D.
Registration No. 38,591
BRINKS HOFER GILSON & LIONE

"Express Mail" mailing label number EL 272 342 291 US

Date of Deposit: October 4, 1999

Our Case No. 9793/21

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FOR UNITED STATES LETTERS PATENT

INVENTOR: Raghbir Singh Bhullar

TITLE: LASER DEFINED FEATURES FOR
PATTERNED LAMINATES AND
ELECTRODE

ATTORNEY: Paul E. Rauch, Ph.D.
Registration No. 38,591
Jeffery M. Duncan
Registration No. 31,609
BRINKS HOFER GILSON & LIONE
P.O. BOX 10395
CHICAGO, ILLINOIS 60610
(312) 321-4200

LASER DEFINED FEATURES FOR PATTERNED LAMINATES AND ELECTRODES

BACKGROUND OF THE INVENTION

5 The present invention relates to laser ablation to pattern a metallic layer, as well as an electrode for an electrochemical biosensor.

 Electrochemical biosensors are well known. They have been used to determine the concentration of various analytes from biological samples, particularly from blood. Electrochemical biosensors are described in U.S. Patent Nos. 5,413,690; 5,762,770 and 5,798,031; as well as in International Publication No. WO99/13101, each of which are hereby incorporated by reference.

10 An electrochemical biosensor typically includes a sensor strip. The sensor strip includes a space that holds the sample to be analyzed, may include reagents to be released into the sample, and includes an electrode set. The electrode set normally includes an insulating substrate, electrodes that contact the sample, which have contact pads for electrically connecting the electrodes to the electronics of electrochemical biosensor.

15 It is desirable for electrochemical biosensors to be able to analyze electrolytes using as small a sample as possible, and therefore it is necessary to miniaturize the sensor strip, as well as its parts, including the electrodes, as much as possible. Usually screen printing techniques have been used to form miniaturized electrodes.

20 Electrodes formed by screen printing techniques can only be formed from composition that are both electrically conductive and which are screen printable. Furthermore, screen printing techniques only allow for the reliable formation of structures and patterns having a feature size of approximately 75 μm or greater. In addition, screen printing is a wet chemical process. It would be desirable to have a new method of forming electrodes which allows for the use of different composition, and which can form features smaller than 75 μm .

Laser ablation is a technique using a laser to cut or mold a material. This technique usually uses a high power excimer laser, such as a krypton-fluoride excimer laser with an illumination wavelength of 248 nm, to blast away surface material. This technique has been used to ablate metals, polymers and even biological material, such as the cornea of the human eye. Such systems are well known to those of ordinary skill in the art, and are described in U.S. Patent Nos. 5,576,073 and 5,593,739, each of which is hereby incorporated by reference.

SUMMARY OF THE INVENTION

In one aspect, the invention is a method of making a patterned laminate comprising ablating through a portion of a metallic layer with a laser. The metallic layer comprises at least one member of gold, platinum, palladium and iridium. Furthermore, the metallic layer is on, and in contact with, an insulating substrate, for example, a polymer.

In another aspect, the invention is a method of making an electrode set, comprising ablating through a portion of a first metallic layer with a laser, to form an electrode pattern. The first metallic layer is on an insulating substrate.

In still another aspect, the invention is a method of making an electrode set ribbon, comprising ablating through a portion of a first metallic layer with a laser, to form a plurality of electrode patterns. The first metallic layer is on an insulating substrate, for example, a polymer. The electrode set ribbon comprises a plurality of electrode sets.

In yet another aspect, the present invention is an electrode set, comprising a first metallic layer, on an insulating substrate, comprising a plurality of electrodes. The first metallic layer has a feature size of less than 75 μm .

In yet another aspect, the present invention is a patterned laminate, comprising a patterned metallic layer on, and in contact with, an insulating substrate. The metallic layer comprises at least one of gold, platinum,

palladium and iridium. Furthermore, the insulating substrate comprises a polymer, and the patterned metallic layer has a feature size of less than 75 μm .

An advantage of the present invention is that it allows for the possibility of small feature sizes.

As used herein, the phrase "patterned laminate" means a multilayered structure that includes an overlayer through which an underlying layer is exposed, i.e. the overlayer has gaps and does not completely cover the underlying layer. The gaps or areas of exposure form the "pattern" of the patterned laminate. Furthermore, the term "pattern" means one or more intentionally formed gaps having a feature size, for example, a single linear gap having a constant width, where the smallest width is the feature size. Not included in the term "pattern" are natural, unintentional defects.

As used herein, the phrase "feature size" is the smallest dimension of a gap found in a pattern.

As used herein, the phrase "electrode pattern" is a pattern which when formed in a metallic layer includes at least two, for example 2 to 60, or 3 to 20, electrodes which are not electrically connected to each other, but each of which includes its own contact pad.

As used herein, the phrase "metallic layer" refers to a layer made of a material that is a metallic conductor of electricity, such as a pure metal or alloys.

As used herein, the phrase "electrode set" is a set of at least two electrodes, for example 2 to 60, or 3 to 20, electrodes. These electrodes may be, for example, a working electrode and a reference electrode.

As used herein, the phrase "ablating" means the removing of material.

Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of

the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein:

Figure 1 illustrates an electrochemical sensor strip of the present invention;

Figure 2 illustrates an exploded view of an electrochemical sensor strip of the present invention, more clearly showing each individual part;

Figure 3 illustrates an electrode set of the present invention;

Figure 4 illustrates another electrode set of the present invention;

Figure 5 illustrates still another electrode set of the present invention;

Figure 6 is a schematic of still another electrode set of the present invention;

Figure 7 is a schematic of an electrode set ribbon of the present invention;

Figure 8 is a schematic of a device of the present invention for making an electrode set ribbon of the present invention; and

Figure 9 is a block diagram of a process of the present invention for making a sensor strip of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 illustrates the assembled electrochemical sensor strip **12**, which includes a base **1**, the contact pads **9** and **9** that are part of the electrodes. The sensing region **10** of the electrodes is also illustrated.

Figure 2 illustrates an exploded view of a sensor strip **12**, which includes a base **1**, adhesive foil **2** for holding the base to the electrode

substrate **3**. The electrode set **16** is on the electrode substrate **3**, and is partially covered by a dielectric **5**. A cover **8** is attached to one end of the dielectric with adhesive tape **7**. A small gap **13** in the dielectric, and a space **14** in the adhesive tape, together with the cover and the electrodes, form a pocket inside of which may be place reagent **6** used to aid in electrochemically detecting and quantifying an analyte. This pocket can act as a capillary, drawing the fluid to be tested onto the sensing region **10** (not shown) of the electrodes. Alternatively, the cover may be absent, exposing the sensing region of the electrodes, and the sample may be directly applied onto this region.

Figure 3 illustrates an electrode set **16**, including two electrodes **4** and **4**. The electrodes have contact pads **9** and **9**, which are electrically connected to the sensing region **10** of the electrode. Also illustrated is dielectric **5** which covers the first and second electrodes, exposing only the sensing region and the contact pads.

Figures 4 and 5 illustrate two different electrode sets **16**, which each include a substrate **1**, and first and second electrodes **4** and **4**. The electrodes are separated by a gap **18** that prevents electrical contact between the two electrodes. For purposes of illustration, the regions of the electrodes which will become the sensing region **10**, and the contact pads, **9** and **9**, are shaded. The gap **18** corresponds to the feature size of this electrode set, since it is the smallest intentional feature. Figures 4 and 5 illustrate two different electrode patterns, one having a simple straight gap (Figure 4), and the other more complex and containing a rectilinear gap, forming a region of interlacing fingers of the two electrodes (Figure 5).

Figure 6 is a schematic of an electrode set of the present invention, including two electrodes **4** and **4**. The sensing region **10** of the electrodes contains interlacing fingers of the two electrodes, again a rectilinear gap. Also shown opposite the sensing region are the contact pads **9** and **9** of each electrode. The gap between the electrodes corresponds to the feature size, and may be 1 to 100 μm , preferably less than 75 μm , more preferably 5 to 50 μm , most preferably 10 to 30 μm . The gap passes completely through the

metallic layer so that the two electrodes are not electrically connected in the electrode set. The values for the dimensions illustrated in Figure 6 are for a single specific embodiment, and these values may be selected as need for the specific use. For example, the length of the electrode set may be 2.5 to 250 mm, the width may be 0.4 to 40 mm, the gap between the contact pads may be 1 μm to 5 mm, and the width of each contact pad may be 1 to 20 mm. The electrode pattern shown in Figure 6 (and other figures) is symmetric, however this is not required, and irregular or asymmetric patterns (or electrode shapes) are possible.

Figure 7 is a schematic of an electrode set ribbon **24**. The ribbon includes a plurality of panels **20**, each of which includes a plurality of electrode sets **16**. Also shown is the original metallic laminate ribbon **22** that is subject to laser ablation to form the electrode set ribbon **24**. The width of the ribbon is selected to accommodate the laser ablation system, and may be, for example, 40 to 0.4 inches. The ribbon may be any length, and is selected based on the desired number of electrode sets, and/or the ease of handling and transport of the ribbons. The size of each individual panel is selected to fit conveniently on the ribbon, and therefore each panel may contain 1 to 1000 electrode sets, preferably 2 to 20 electrode sets.

Figure 8 is a schematic of a device for producing electrode sets, in the form of an electrode set ribbon **24**. First a roll of metallic laminate ribbon **22** is fed through guide rolls **28** into a laser ablator **26**. In the laser ablator the metallic layer of the metallic laminate ribbon is ablated with the laser, in an electrode pattern, to form the electrode set ribbon **24**. The electrode set ribbon **24** is then passed through more guide rolls **28**, with a tension loop to adjust the tension of the ribbon, and through an optional inspection camera **30**, which may be used to check for defects. Next, optionally, the electrode set ribbon **24** may be laminated with an adhesive foil ribbon **32**, in a laminator **36**, to form a laminated electrode set ribbon **34**, which is then guided through guide rolls **28**, and rolled up.

Figure 9 is a block diagram of a process for making an electrochemical sensor strip of the present invention. As shown, in step **110** the metallic

lamine ribbon **22** is ablated by laser ablation to form an electrode set ribbon, and then laminated with adhesive foil ribbon **32** to form a laminated electrode set ribbon **34**. In step **120** the laminated electrode set ribbon **34** is screen printed with a UV curable dielectric **50**, which forms the dielectric **5** (not shown) of each sensor strip, forming a dielectric covered ribbon **38**. In step **130** the starting reagents **40** are compounded to form reagent **6**, and then in step **140** the reagent is applied onto the dielectric covered ribbon **38**, the ribbon is split into reels, each one panel wide, to form reagent covered panel reels **44**.

In step **150** the reagent covered panel reels **44** are covered with clear polyester roll **52** attach through double sided adhesive tape roll **54**, which forms the clear cover **8** (not shown) and adhesive tape **7** (not shown) of each sensor strip. The product of step **150**, clear covered panel reels **46**, are then split into individual sensor reels, each one electrode set wide, and laminated with a base substrate roll **56**, in step **160**, which forms the base **1** (not shown) of each sensor strip, to form sensor reels **48**. In step **170** the sensor reels are cut into individual sensor strips **12** (not shown) which are sorted and packed into vials **60**, each closed with a stopper **58**, to give packaged sensor strips **62**. In steps **150** and **160**, a liner is release in order to attach the base and cover.

A laser system capable of ablating the metallic layer, to form the individual electrode sets, is well known to those of ordinary skill in the art. Examples include excimer lasers, with the pattern of ablation controlled by lenses, mirrors or masks. An example of such a system is the LPX-400, or LPX-200, both from LPKF LASER ELECTRONIC, GMBH of Garbsen, Germany.

The metallic laminate is a metallic layer on the electrode substrate. The metallic layer may contain pure metals or alloys, or other materials which are metallic conductors. Examples include aluminum, carbon (such as graphite), cobalt, copper, gallium, gold, indium, iridium, iron, lead, magnesium, mercury (as an amalgam), nickel, niobium, osmium, palladium, platinum, rhenium, rhodium, selenium, silicon (such as highly doped

polycrystalline silicon), silver, tantalum, tin, titanium, tungsten, uranium, vanadium, zinc, zirconium, mixtures thereof, and alloys or metallic compounds of these elements. Preferably, the metallic layer includes gold, platinum, palladium, iridium, or alloys of these metals, since such noble metals and their alloys are unreactive in biological systems. The metallic layer may be any thickness, but preferably is 10 nm to 1 mm, more preferably, 20 nm to 100 μm , or even 25 nm to 1 μm . Figure 9 illustrates the process with a 50 nm gold film.

In the laser ablation process, the metallic layer may be ablated into an electrode pattern. Furthermore the patterned metallic layer may be coated or plated with additional metal layers. For example, the metallic layer may be copper, which is then ablated with a laser, into an electrode pattern; subsequently, the copper may be plated with a titanium/tungsten layer, and then a gold layer, to form the desired electrodes. Preferably, however, only a single layer of gold is used, which is directly in contact with the electrode substrate, since it allows for the entire elimination of wet chemical steps for the formation of the electrode sets.

The electrode substrate is formed from an insulating material, so that it will not provide an electrical connection between the electrodes of the electrode set. Examples include glass, ceramics and polymers. Preferably, the electrode substrate is a flexible polymer, such as a polyester or polyimide. An example of a suitable material would be the polyimide UPLEX from TECHNI-MET of Connecticut, which is available pre-coated with gold, palladium or platinum; or ULTEM 1000 (polyetherimide) from GE, available coated with copper.

A UV curable dielectric and which is screen printable, may be used to form the dielectric, for example the polymer composition 5018 dielectric composition from DuPont. The clear cover is a clear material that is inert to biological fluids, for example glass, polyethylene, polypropylene, polyvinylchloride, polyimide, or polyester. The clear cover may have markings. The adhesive tape is also a flexible polymer having a surfaces

covered with an adhesive; these materials are also well known to those of ordinary skill in the art.

The base is a supporting structure, and is preferably made of flexible polymer material, with a thickness sufficient to provide support to the sensor strip, for example polyester with a thickness of 6 mils. The adhesive foil may be made for the same types of compositions as the adhesive tape.

The reagent is optional, and may be used to provide electrochemical probes for specific analytes. The starting reagents are the reactants or components of the reagent, and are often compounded together in liquid form before application to the ribbons or reels. The liquid may then evaporate, leaving the reagent in solid form. The choice of specific reagent depends on the specific analyte or analytes to be measure, and are well known to those of ordinary skill in the art. For example, a reagent for measurement of glucose in a human blood sample contains 62.2 mg polyethylene oxide (mean molecular weight of 100-900 kilodaltons), 3.3 mg NATROSOL 250 M, 41.5 mg AVICEL RC-591 F, 89.4 mg monobasic potassium phosphate, 157.9 mg dibasic potassium phosphate, 437.3 mg potassium ferricyanide, 46.0 mg sodium succinate, 148.0 mg trehalose, 2.6 mg TRITON X-100 surfactant, and 2,000 to 9,000 units of enzyme activity per gram of reagent. The enzyme is prepared as an enzyme solution from 12.5 mg coenzyme PQQ and 1.21 million units of the apoenzyme of quinoprotein glucose dehydrogenase, forming a solution of quinoprotein glucose dehydrogenase. This reagent is described in WO 99/30152, pages 7-10.

The processes and products described include disposable biosensors, especially for use in diagnostic devices. However, also included are electrochemical sensors for non-diagnostic uses, such as measuring an analyte in any biological, environmental, or other, sample. Furthermore, also included is any patterned laminate, preferably a patterned laminate of a noble metal (gold, platinum, palladium, iridium, alloys thereof) in direct contact with an insulating substrate, such as a polymer. Such laminates can have a variety of electrical function, including use as electrodes, electrical wires or connectors, microwave reflectors, etc. Preferably, these patterned laminates

[illegible]

CLAIMS:

1. A method of making a patterned laminate, comprising:
ablating through a portion of a metallic layer with a laser, to form
a pattern in said metallic layer;
5 wherein said metallic layer is on, and in contact with, an
insulating substrate,
said insulating substrate comprises a polymer, and
said metallic layer comprises at least one member selected from
the group consisting of gold, platinum, palladium and iridium.
- 10 2. The method of Claim 1, wherein said pattern has a feature size
of less than 75 μm .
3. The method of Claim 1, wherein said pattern has a feature size
of 1 μm to 50 μm .
- 15 4. A method of making an electrode set, comprising:
ablating through a portion of a first metallic layer with a laser, to
form an electrode pattern;
wherein said first metallic layer is on an insulating substrate.
5. The method of Claim 4, further comprising applying a second
metallic layer on said first metallic layer.
- 20 6. The method of Claim 4, wherein said first metallic layer
comprises copper.
7. The method of Claim 4, wherein said first metallic layer
comprises at least one member selected from the group consisting of gold,
platinum, palladium and iridium.
- 25 8. The method of Claim 4, wherein said insulating substrate is a
polymer.

9. The method of Claim 4, wherein said pattern has a feature size of less than 100 μm .

10. The method of Claim 4, wherein said pattern has a feature size of less than 75 μm .

5 11. The method of Claim 4, wherein said pattern has a feature size of 1 μm to 50 μm .

12. The method of Claim 8, wherein said first metallic layer is in contact with said insulating substrate.

10 13. The method of Claim 12, wherein said first metallic layer comprises at least one member selected from the group consisting of gold, platinum, palladium and iridium.

15 14. A method of making an electrode set ribbon, comprising:
ablating through a portion of a first metallic layer with a laser, to form a plurality of electrode patterns;
wherein said first metallic layer is on an insulating substrate, and
said electrode set ribbon comprises a plurality of electrode sets.

20 15. The method of Claim 14, wherein said first metallic layer comprises at least one member selected from the group consisting of gold, platinum, palladium and iridium,

said insulating substrate is a polymer, and
said first metallic layer is in contact with said insulating substrate.

25 16. A method of making a sensor strip, comprising:
forming an electrode set by the method of Claim 4; and
cutting said substrate, to form a strip.

17. The method of Claim 16, further comprising applying a dielectric on a portion of said metallic layer.

18. The method of Claim 17, further comprising applying a reagent on a portion of said electrode set.

19. A method of making a sensor strip, comprising:
forming an electrode set ribbon by the method of Claim 14; and
cutting said ribbon into a plurality of strips;
wherein each of said strips comprises at least one of said
electrode sets.

20. The method of Claim 19, further comprising applying a dielectric on a portion of said metallic layer.

21. The method of Claim 20, further comprising applying a reagent on a portion of each of said electrode sets.

22. A patterned laminate, prepared by the method of Claim 1.

23. An electrode set, prepared by the method of Claim 4.

24. An electrode set, prepared by the method of Claim 7.

25. An electrode set, prepared by the method of Claim 13.

26. An electrode set ribbon, prepared by the method of Claim 14.

27. A sensor strip, prepared by the method of Claim 19.

28. A sensor strip, prepared by the method of Claim 21.

29. An electrode set, comprising:
a first metallic layer, on an insulating substrate, comprising a
plurality of electrodes,
wherein said first metallic layer has a feature size of less than
75 μm .

30. The electrode set of Claim 29, wherein said first metallic layer comprises at least one member selected from the group consisting of gold, platinum, palladium and iridium.

31. The electrode set of Claim 30, wherein said insulating substrate is a polymer.

32. The electrode set of Claim 31, wherein said first metallic layer is in contact with said insulating substrate.

33. A sensor strip, comprising:
the electrode set of Claim 32,
and a dielectric on a portion of said first metallic layer.

34. The sensor strip of Claim 33, further comprising reagent, on a portion of said first metallic layer.

35. Packaged sensor strips, comprising:
a plurality of the sensor strips of Claim 27, a vial, containing said plurality of said sensor strips, and
a stopper, sealing said vial.

36. Packaged sensor strips, comprising:
a plurality of the sensor strips of Claim 28, a vial, containing said plurality of said sensor strips, and
a stopper, sealing said vial.

37. Packaged sensor strips, comprising:
a plurality of the sensor strips of Claim 34, a vial, containing said plurality of said sensor strips, and
a stopper, sealing said vial.

38. A patterned laminate, comprising:
a patterned metallic layer on, and in contact with, an insulating substrate,

wherein said metallic layer comprises at least one member selected from the group consisting of gold, platinum, palladium and iridium,

said insulating substrate comprises a polymer, and

5 said patterned metallic layer has a feature size of less than

75 μm .

ABSTRACT

A method of making a patterned laminate includes ablating through a portion of a metallic layer with a laser, to form a pattern in the metallic layer, where the metallic layer is on and in contact with an insulating substrate. The patterned laminate may be patterned to form electrodes, and can be formed into an electrochemical sensor strip.

5

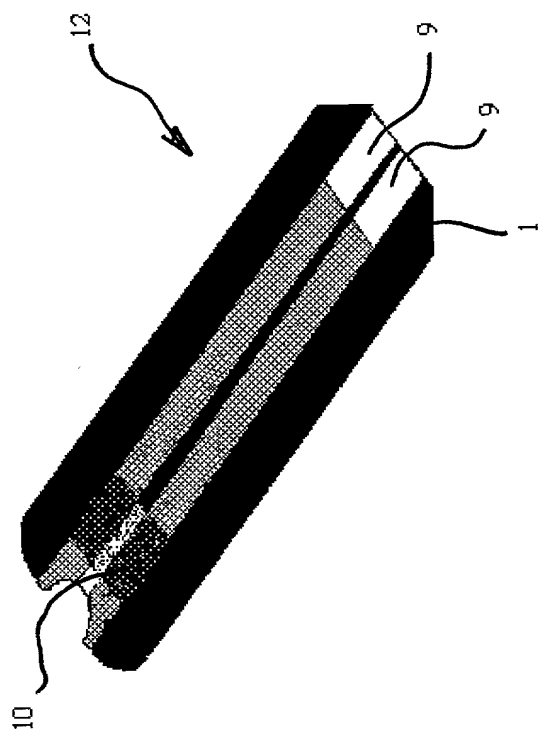
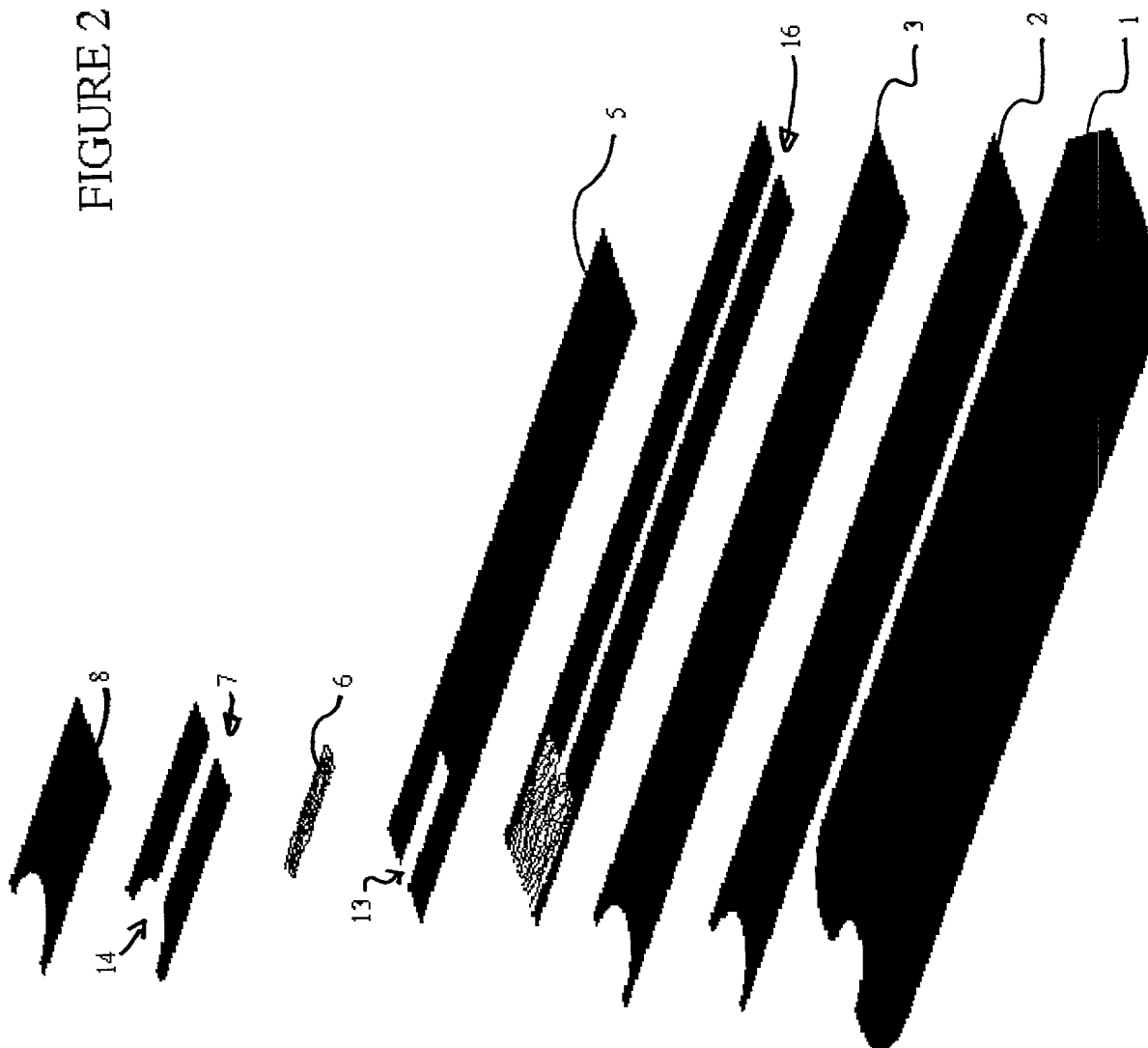
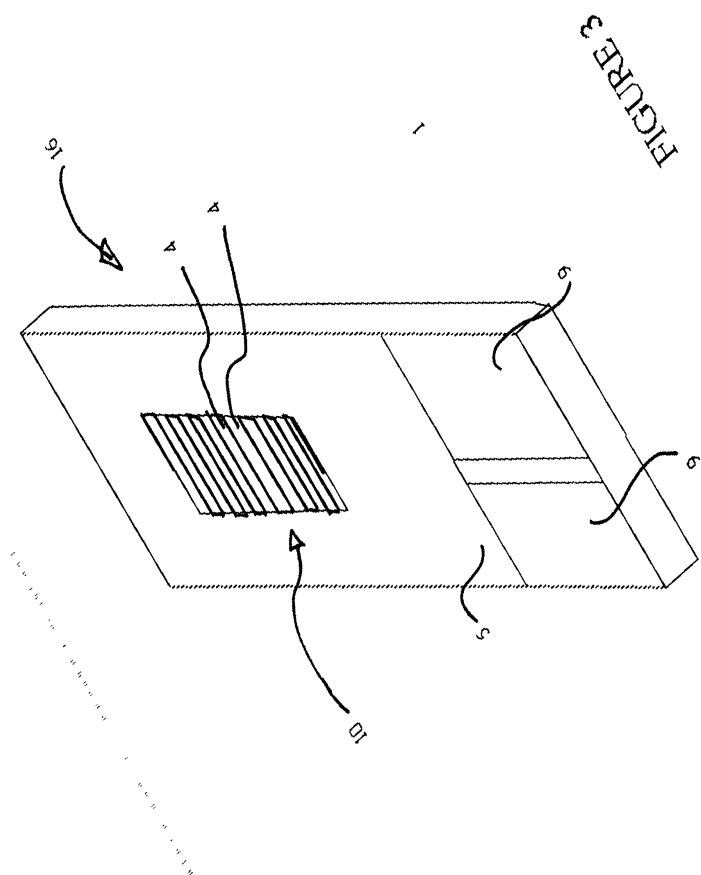


FIGURE 1





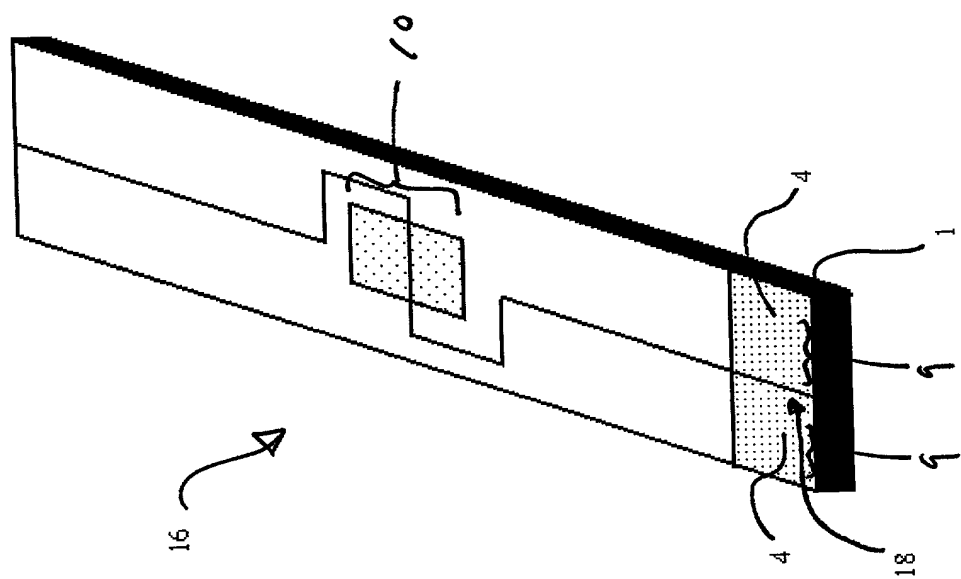


FIGURE 4

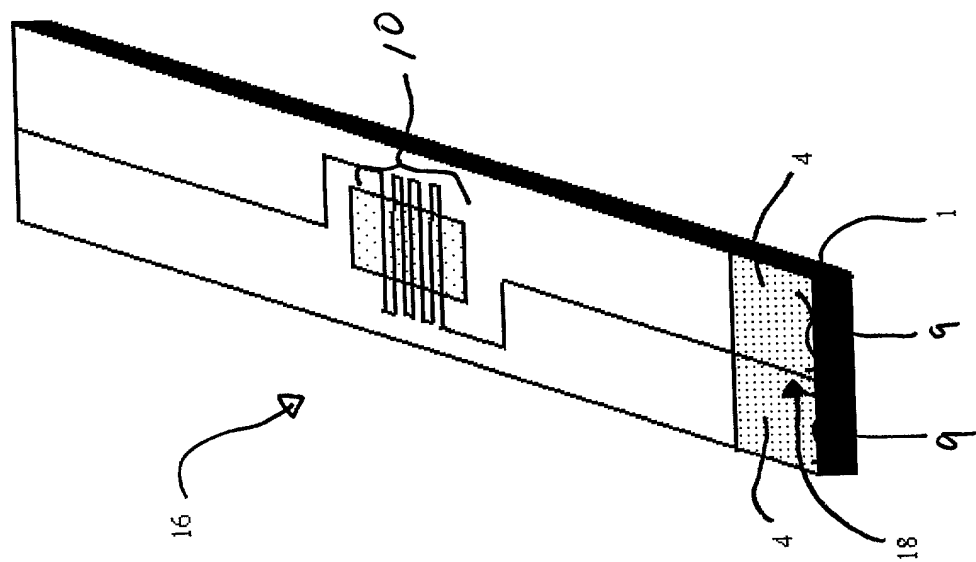


FIGURE 5

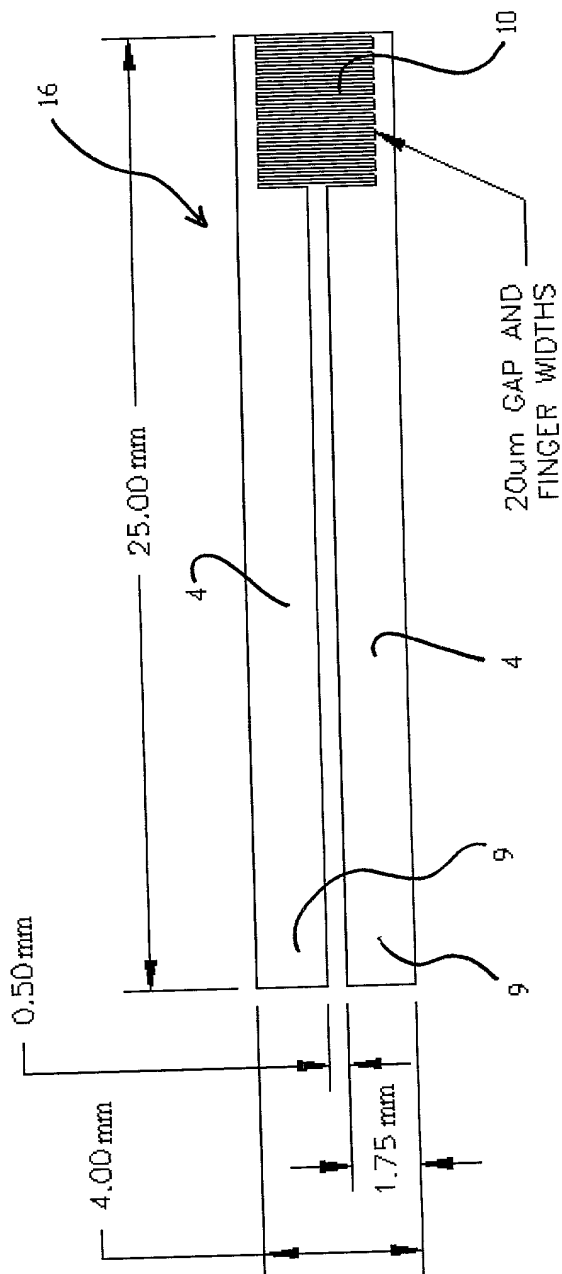


FIGURE 6

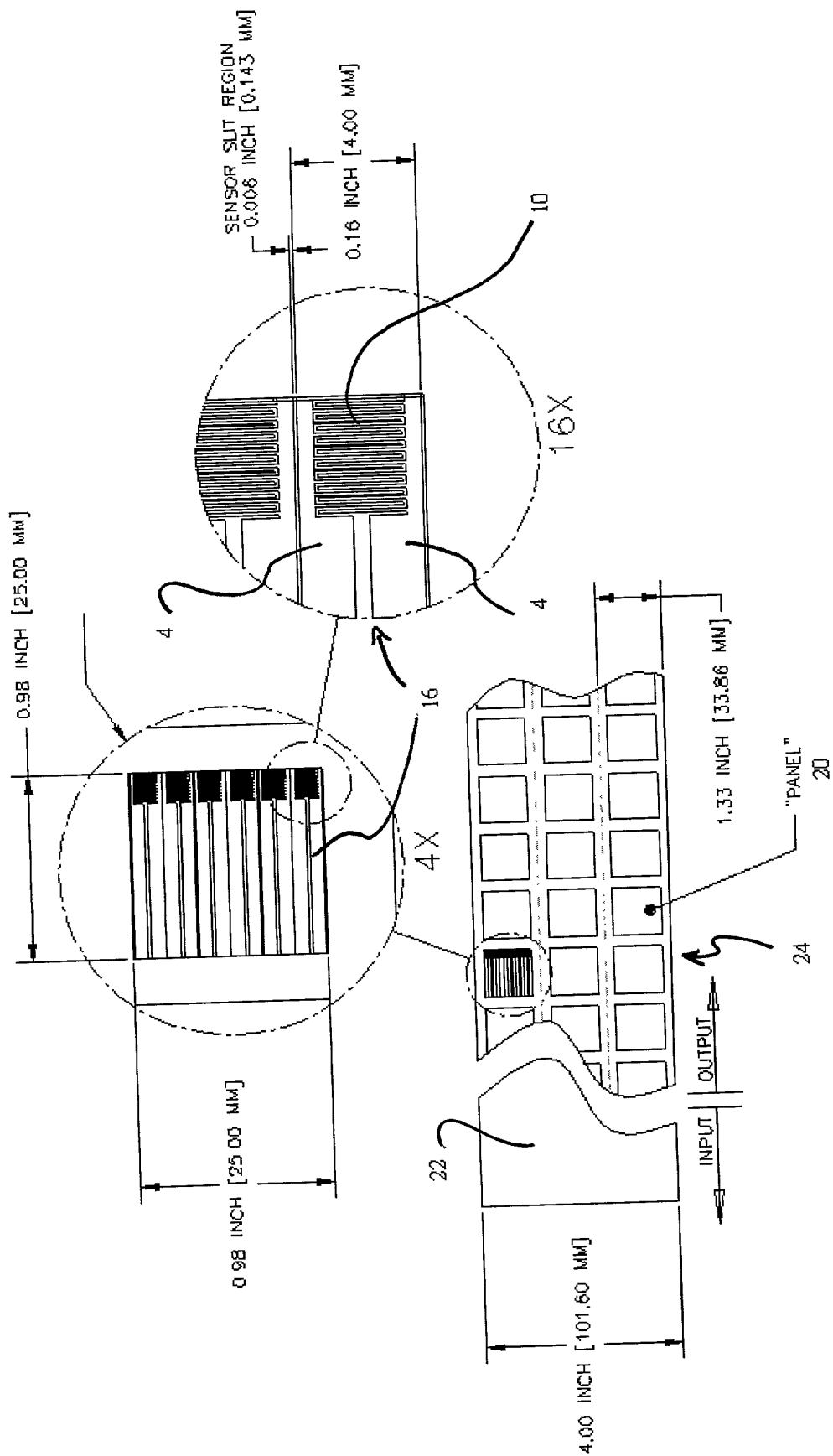


FIGURE 7

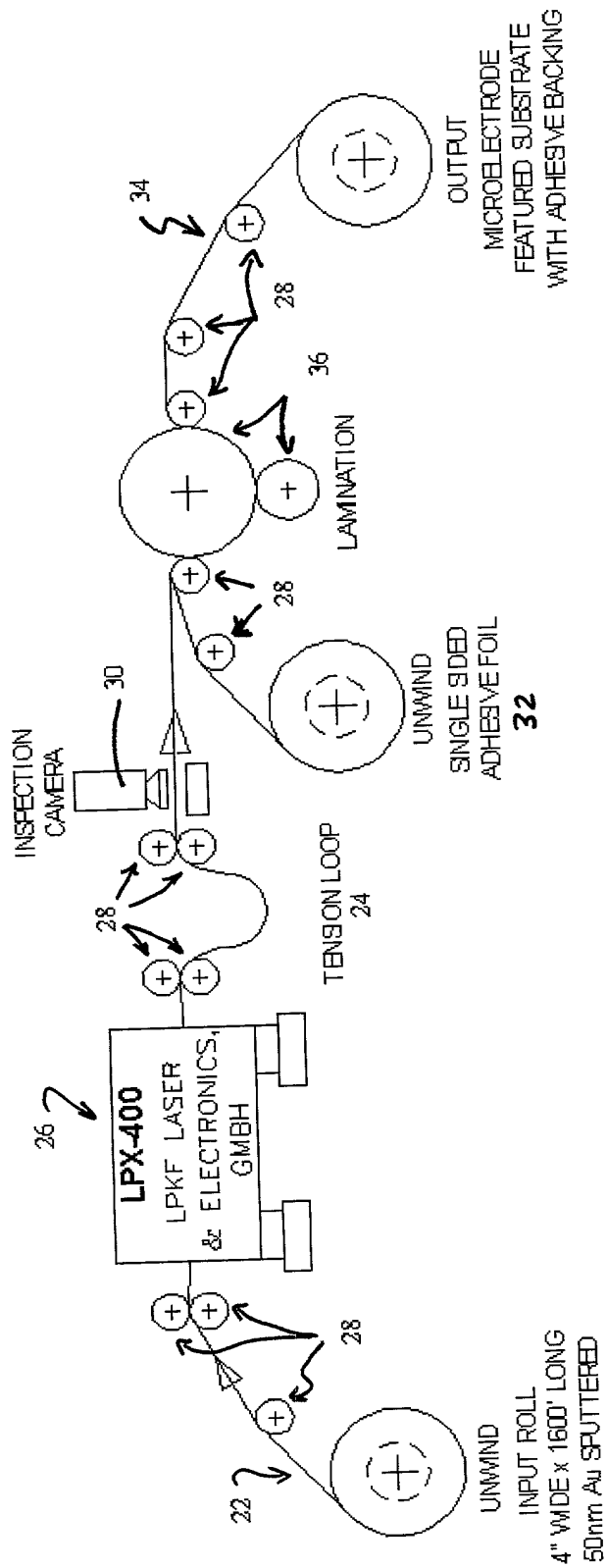


FIGURE 8

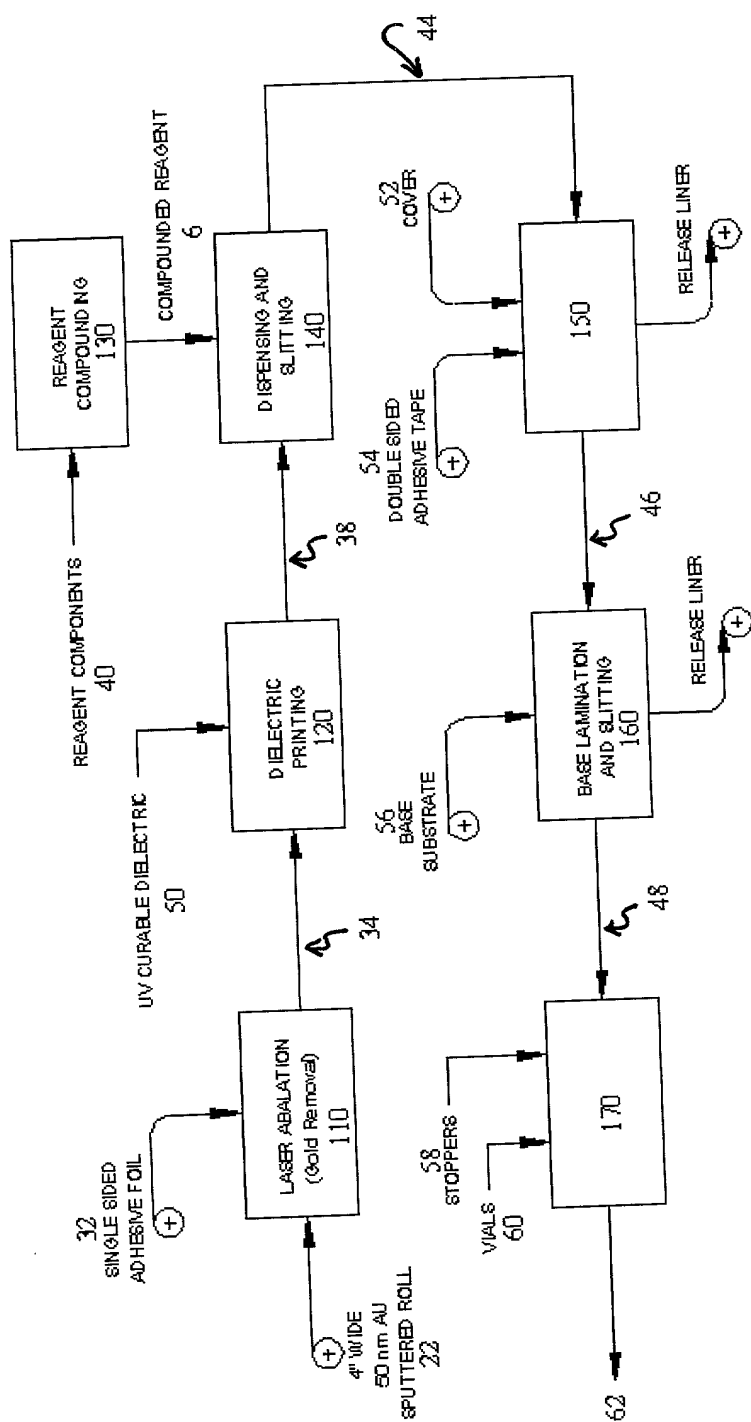


FIGURE 9