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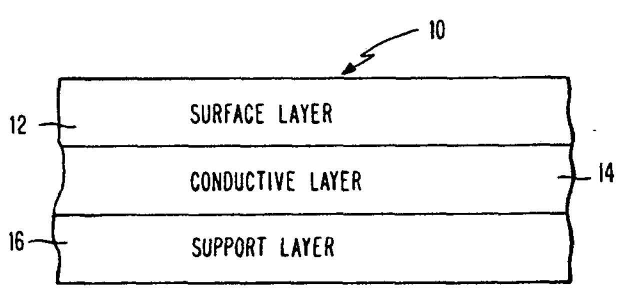
(54) Electrolytic printing method and apparatus.

(57) The recording medium (10) includes three distinct layers: The surface layer (12) incorporates a leuco dye that is responsive to low voltage pulses of amplitude and duration that would be compatible with voltages used by modern integrated circuit chips. The middle layer is a conductive layer and the bottom or support layer is made from any suitable insulating material.

The printing apparatus is supplied with write (18) and ground (20) electrodes of predetermined surface area that will contact the recording medium. The spacing or distance of the electrodes along the plane of the recording medium is also predetermined.

By proper selection of the thickness of the surface layer (12), the areas of the write and ground electrodes (18, 20) and their lateral spacing, low level electrolytic printing will be assured. A sufficient quantity of current is forced to flow into the surface and conductive layers beneath the write electrode means and thereby effects acceptable printing. Preferably, pulses of no more than 15 V amplitude will cause printing when at least 75 percent of the current delivered will be constrained to flow into the conductive layer (14).



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ELECTROLYTIC PRINTING METHOD AND APPARATUS

This invention is directed to apparatus for low voltage electrolytic printing on a recording medium as well as to a method. It is particularly concerned with the provision of a recording medium that includes a surface layer containing an electrochemically sensitive compound, which medium is particularly suitable for employment in low voltage electrolytic printing apparatus that has been adapted to take advantage of the properties of said recording medium.

The concept of electrically generated printing has sparked interest since the 1840's. Most attempts at utilizing an electrically initiated reaction by which printing could be accomplished required relatively high voltages, in the order of 150 to 250 V as that term is used herein, saturated or completely wetted paper and/or consumable electrodes. It was, therefore, necessary to employ various recording medium configurations which would be satisfactory for use in and which would meet the requirements of these prior art printing systems. As a result, all of these known recording mediums were intended to be employed in either a dry, relatively high voltage printing system or in a wet printing system wherein the recording medium was thoroughly saturated. There were also some attempts at hybrid printing systems and recording mediums therefor which attempted to reconcile and/or compensate for the disadvantages of both the dry and saturated printing approaches. However, like all compromise situations, these efforts were either too expensive to employ or unsatisfactory in performance.

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United States Patent No. 2 358 839 to Wagner teaches a "wet" electrolytic printing arrangement wherein the recording paper is impregnated with 100 cm^3 of water prior to recording. The current in a recording stylus is modulated in accordance with the instantaneous density of the subject to be reproduced and forms an image thereof in the recording paper. The resultant image is of improved sharpness due, in part, to the limited amount of moisture which remains after printing.

Another example of prior art electrically-based printing is found in United States Patent No. 2 833 677 to Baumlein which also describes one type of paper system or recording medium that was usable in a dry, high voltage class of printer. In that arrangement, an insulating paper layer is sandwiched between an upper metalized layer and a conductive backing. Sparks are created and traverse an air gap between the write electrode and the upper conductive layer to impinge thereon causing vaporization of the metalized layer lying in the spark path. This exposed the contrasting insulating layer beneath the vaporized metalized layer to thereby form a visible or printed track.

Also of interest is United States Patent No. 3 974 041 to Haruta et al which discloses an image recording medium having a recording layer which contains an image forming component and at least one reducing agent in an electrically conductive matrix composed of at least one zeolitic water containing compound. The zeolitic compound is one which contains water in cavities formed within its structure, yet still seemingly appears to be in a dry state. Recording takes place using a tungsten stylus and the zeolitic compound containing recording medium across which a voltage of 150 V is impressed.

The foregoing and other similar prior art examples of electrically induced or stimulated printing worked satisfactorily. However, their underlying operative processes still required significant wetting of the recording medium, the use of a relatively high voltage to achieve printing and/or the frequent replacement of the print electrodes due to their consumption in the printing process itself. Such requirements were obviously major impediments to a commercially successful printer which utilized electrically initiated printing, particularly those printing arrangements which could take advantage of and fully utilize the capabilities of integrated circuit chips.

The present invention intends to provide a remedy by providing a recording medium which is particularly suitable for use by low voltage printing apparatus adapted to efficiently utilize said medium.

The present invention also intends to provide a recording medium which is constructed to exhibit, in conjunction with the geometry of the printing apparatus electrodes and their spacing, a predetermined vertical resistance component through the surface layer thereof. Such recording medium may also require only low levels of energy input compatible with those needed by high density integrated circuit chips yet permits high resolution printing.

In addition, the present invention intends to enable low level energy printing on a responsive recording medium that facilitates the use of a low cost, integrated print head that will exhibit significantly improved operating life over that of the prior art.

These and other objects of the present invention are achieved by providing a layered recording medium having a topmost surface layer, an insulating support layer and a conductive layer sandwiched therebetween, all of appropriate thickness and low voltage printing apparatus adapted to employ said recording medium. The surface layer includes a binder, a leuco dye which is responsive to low levels of electrical energy and electrochemically converted thereby to a visible dye, a dye stabilizer, pigment and an electrolyte. The surface layer is constructed to insure, in conjunction with the area and spacing of the apparatus' electrodes, that sufficient current to effect full dye visibility passes vertically therethrough into the conductive layer.

The thickness of the surface layer is also a factor in building the recording medium to function correctly when subjected to the relatively low voltage and energy levels that are associated with large scale and very large scale integrated circuit chips. It is constructed with the purpose of providing an effective print medium that affords a low resistance path for a high percentage of current flow vertically through the surface layer directly under the print electrode and then into the conductive layer from where it returns to its source, given the spacing and geometry of the electrodes involved. The result is intended to pass at least 75% of the supplied current through the surface layer directly beneath the print electrode into the conductive layer.

Embodiments of the invention are illustrated in the attached drawing in which

Figure 1 schematically illustrates a cross-sectional view of a recording medium fabricated in accordance with the present invention; and

Figure 2 shows a schematic representation of the recording medium's electrical characteristics as affected by those of a low voltage printing apparatus which has been adapted to utilize said medium therein.

As used herein, the phrases "low voltage" or "low electrical energy" or their equivalent means that a voltage pulse of no more than 25 V amplitude is applied for an appropriate time to the print electrode. Preferably, for reasons to be explained hereinafter, the "write" pulse should not be greater than 15 V. The phrases "high voltage" or "high electrical energy" or their equivalent, as previously noted, means that a voltage pulse of between 150 and 250 V is to be applied to the print electrode.

Figure 1 depicts a paper system that has been fabricated in accordance with the present invention. This paper system or recording medium 10 includes a surface layer or coating 12, a conductive layer 14 and a base or support layer 16. These layers are joined together by known techniques which form no part of the present invention. As fabricated however, the paper system 10 described herein can be utilized in the form of rolled, cut sheet or fan-folded medium.

The surface layer 12 is typically about 5 to 50 µm thick. It includes five main components, one of which is a pigment of appropriate color, generally a clay. The clay component is selected, as needed, to enhance or reduce the brightness, whiteness and/or absorbtion of the surface layer 12 as would be appropriate to the end use. The surface layer 12 also includes as components thereof, a leuco dye, a dye stabilizer, a binder, and an electrolyte. It is applied by coating the surface of the conductive layer 14 with a predetermined proportion of its components.

A leuco or 1-dye is one whose chromophore is not visible under ordinary room conditions. It can, however, be permanently shifted into the visible spectrum if a pulse of sufficient energy is applied thereto for an appropriate period. The nature and use of such dyes for printing at low energy levels is described in United States Patent Application Serial No. which was filed in the name of W. E. Bernier. The leuco dye selected for use in and by the present invention is to be compatible with and responsive to the voltage and concomitant energy levels associated with large and very large scale integrated circuits. These LSI and VLSI chips will typically require bus and driver voltages on the order of no more than 25 V (preferably 15 V) and power drain of about 2.0 W, an energy level which was intolerable in prior art printing systems and for prior art recording mediums. The definition of printing apparatus and of a recording medium that is particularly suitable to be printed on at this rather low energy level permits the use of an integrated print head and very significantly lowers, if not eliminates with the use of appropriate print electrodes, the consumption of the print electrodes.

Several formulations have been tried for the surface layer 12. Examples of these are shown in Table I, as follows:

TABLE I

EXAMPLE	COMPONENT	COMPONENT TYPE	% BY WEIGHT
A	leucodye, electrolyte & stabilizer	*	50
	binder	starch	20
	pigment	clay	30
B	leucodye, electrolyte & stabilizer	*	50
	binder	starch	5
	pigment	BaSo4	45
C	leucodye, electrolyte & stabilizer	*	50
	binder	vinyl/ethylene copolymer	20
	pigment	clay	30

* a leuco dye/electrolyte dispersion in water which consists of 1.0% benzoyl leuco-methylene blue, 4.5% NH_4Br and 5.0% KBr. The dye stabilizer used is methylene 0.1% ascorbic acid leaving 89.4% water as the remainder.

As will be evident, the use of a material within the surface layer 12 that is electrochemically responsive to low levels of electrical energy is extremely advantageous.

The conductive layer 14 is generally formed from a thin metal foil, such as aluminum, about 1000 Å (0.1 μm) thick or from a coating of electrolyte such as NaCl or other suitable salt. As will be hereinafter discussed, the thickness of the conductive layer 14 is not critical to the printing mechanism. However, it should be kept to a minimum to avoid giving the recording medium too thick a feel or appearance as well as to hold down cost.

The support layer 16 serves merely, as its name states, to support the surface layer 12 and conductive layer 14. It will typically be about 15 to 50 μm thick and be fabricated from commonly available paper. As an insulator, the support layer 16 will not play an active role in the printing process except to prevent current from leaking off the conductive layer 14.

A printing arrangement which would utilize a recording medium fashioned in accordance with the present invention is schematically illustrated in Figure 2. As shown therein, the recording medium 10 is brought beneath a print stylus or electrode (anode) 18 by any suitable conventional transport mechanism, which is not shown. The print stylus 18 may be formed of tungsten, which shows some degree of consumability in use, or of a ruthenium oxide coated member, which compound is very stable and exhibits little or no tendency to chemically enter into the printing process. The ground electrode (cathode) 20 would be fabricated from a similar, if not identical, material and is separated from the write electrode 18 by a distance L. Both the write electrode 18 and the ground electrode 20 are assumed to have the same diameter D, since both will likely be fashioned of the same stock material and thereafter coated if appropriate.

As opposed to the dry, high voltage prior art printing process mentioned above, an electrode voltage V+ of not more than 25 V, and preferably of not more than 15 V, is applied thereto. The 15 V limit is highly desirable since it is compatible with and would therefore permit the use of LSI or VLSI integrated circuit chips right in the print head itself. A simplified equivalent electrical circuit of the paper system 10 is shown in Figure 2.

A control circuit 22 is coupled between the voltage source V+ and the write electrode 18. This control circuit can be of conventional design and serves to form and then selectively forward voltage pulses of appropriate amplitude and width or duration to the write electrode 18. The control circuit 22 would, of course, be forming pulses pursuant to printing desired text and/or graphics as directed by a source therefor to which it is coupled by an input line or bus 24.

There are three main resistances that can possibly affect or enter into the printing process: R_1, the horizontal resistive component through the surface layer 12 between the electrodes 18 and 20; R_2, the vertical resistive component through the surface layer 12 between the electrodes 18 and 20 respectively and the conductive layer 14; and R_3, the total resistance along or through the conductive layer 14 from the current entry to exit points therein. In the dry, high voltage prior art printing processes, the applied print voltage was significantly higher than is presently comtemplated and the R_1 resistance component of the utilized recording mediums was never a factor as sufficient excess current was available to flow into and through the conductive layer and then back through the surface layer to the cathode. In the wet processes of the prior art, the surface layer was saturated with water or similar fluid and thereby rendered sufficiently conductive for printing purposes. This meant that the surface layer resistance R_1 was lowered considerably and so excessive current and so excessive current also was made available to insure sufficient current flow into and through a conductive layer, if present, to insure that printing would take place.

The resistance R_1 is equal to the resistivity R_s of surface layer 12 times L divided by the product of D and T_s, the thickness of layer 12. The resistance R_2 is equal to the resistivity R_s multiplied by the thickness T_s and then divided by the area of the electrodes 18 and 20. Resistance R_3 is determined by summing L and D, which sum is then multiplied by the resistivity R_c of the conductive layer and that total then divided by the product of D and T_c, the thickness of the conductive layer 14. These resistive relationships would be expressed as:

$$R_1 = (R_s \cdot L)/(D \cdot T_s) \qquad (1)$$

$$R_2 = (4 \cdot R_s \cdot T_s)/(\pi \cdot D^2) \text{ and} \qquad (2)$$

$$R_3 = (R_c \cdot (L + D))/(D \cdot T_c). \qquad (3)$$

The resistivity of the conductive layer 14, assuming it was formed of aluminum, would be 2.8×10^{-6} ohm-cm. This number is very, very small when contrasted with a typical surface layer resistivity of 10 ohm-cm and would be if compared to most other, if not all, conductive materials that are usable to form the conductive layer 14. Thus, the effects of R_3 will be negligible and can be ignored for purposes of analyzing the electrical resistive characteristics of the recording medium as influenced by the printing apparatus in which it is employed.

The current through each branch of the schematic circuit shown in Figure 2 is given in

$$I_s \cdot R_1 = I_c \cdot (2R_2 + R_3). \quad (4)$$

Rearranging to solve for the current ratio yields

$$\text{RATIO} = I_c/I_s = R_1/2R_2 \text{ (since } R_3 \text{ is negligible)} \quad (5)$$

which becomes, through substitution for R_1 and R_2,

$$\text{RATIO} = \frac{R_s \cdot L \cdot \pi \cdot D^2}{D \cdot T_s \cdot 8R_s \cdot T_s} \quad (6)$$

or the following by simplification

$$\text{RATIO} = (\pi \cdot L \cdot D)/(8T_s^{\,2}). \quad (7)$$

If L is 3 mils (76.2 µm), D is 10 mils (254 µm) and T_s is 2 mils (50.8 µm), then

$$\text{RATIO} = 2.94. \quad (8)$$

The total or equivalent resistance R_t of two resistors R_a and R_b in parallel is equal to their product divided by their sum, or

$$R_t = (R_a \cdot R_b)/(R_a + R_b) \qquad (9)$$

Applying equation (8) to the schematic circuit shown in Figure 2 and substituting shows that $R_a = R_1$ and $R_b = (2R_2+R_3)$ can be equated. However, with R_3 being treated as negligible $R_b = 2R_2$, so that

$$R_t = (R_1 \cdot 2R_2)/(R_1 + 2R_2). \qquad (10)$$

Extending equation (4) gives

$$I_tR_t = I_sR_1 = I_c\ (2R_2+R_3) \qquad (11)$$

or, with R_3 being treated as negligible,

$$I_tR_t = I_sR_1 = I_c2R_2. \qquad (12)$$

Therefore, the ratio of the current I_c that will flow through the conductive layer 14, the vertical current component that also flows through each of the resistances R_2, to the total current I_t is

$$I_c/I_t = R_t/2R_2 \qquad (13)$$

which becomes, through substitution for R_t from equation (10),

$$I_c/I_t = R_1/(R_1 + 2R_2). \qquad (14)$$

Dividing the right side of equation (14) by R_1 and using the substitution for the quotient RATIO developed in equation (7), gives

$$I_c/I_t = 1/(1+1/\text{RATIO}) = 1/(1+1/2.94) = 0.746. \quad (15)$$

It can be seen from equation (15) that about 75% of the total current available will flow vertically through resistance R_2 from the print electrode 18 through the conductive layer 14 given the particular geometry and spacing of the electrodes. More importantly, the presence of a conductive layer 14 insures that a greater magnitude current will flow through the surface layer 12 than if there were no conductive layer provided at all. This conclusion is verified by the following

$$I_s \text{ (without layer 14)} = I_t \text{ or } I_t/I_s = 1.00; \quad (16)$$

$$I_t \text{ (with layers 12 \& 14)} = V(1/R_1+1/2R_2); \text{ and} \quad (17)$$

$$\begin{aligned} I_t/I_s &= R_1(1/R_1+1/2R_2) = 1 + R_1/2R_2 \\ &= 1 + \text{RATIO} = 3.94 \end{aligned} \quad (18)$$

which indicates that, for this particular exemplary configuration, the presence of a conductive layer 14 draws almost four times the total current through the surface layer 12.

It is therefore important when building a recording medium that is to be used in a low energy electrochemical printing system in accordance with the present invention to insure that current flow from the print electrode to a conductive layer under the surface layer of the recording medium, the vertical current component through the surface layer, is maintained about equal to or greater than 75% of the total current flow from the print electrode. As explained above, this is accomplished by selecting a recording medium and a surface layer therefor which, in conjunction with an appropriate printing apparatus electrode arrangement, are compatible with and conducive to low energy printing. Thus, the inclusion of a conductive layer in the recording medium, the proper selection of surface layer thickness and components thereof and the choice of appropriate electrode surface area and spacing insures that satisfactory low level energy printing will, in fact, take place. Further, such printing takes place with minimal halo or fringing beneath the write electrode 18 due to the large vertical current component.

In order to facilitate and expedite printing, a liquid applicator 26 may be provided. The applicator 26 is adapted to uniformly meter out very small quantities of liquid, preferably water, over the surface layer 12 of recording medium 10, just prior to its passing under the write electrode 18.

CLAIMS

1. Apparatus for printing with low energy levels, characterized by

   a recording medium (10) having a surface layer (12) including a leuco dye, a support layer (16) and a conductive layer (14) sandwiched between said surface and said support layers,

   a write electrode (18) and a ground electrode (20) having predetermined surface areas and being positioned to contact said surface layer (12) of said recording medium (10), said ground electrode being spaced apart from said write electrode by a predetermined distance,

   wherein the thickness of said surface layer (12), the area of and the distance between said write and said ground electrodes (18, 20) are selected to constrain a sufficient percentage of the writing current delivered to said write electrode (18) to flow through said surface layer (12) into and through said conductive layer (14) and back through said surface layer to said ground electrode (20) to form a visible mark in said surface layer (12) beneath said write electrode (18).

2. The apparatus according to claim 1, wherein the thickness of said surface layer (12), the area of and the distance between said write and said ground electrodes (18, 20) are predetermined to constrain at least 75 percent of the current delivered to said write electrode (18) to flow through said surface layer (12).

3. The apparatus according to claim 1, further including a source of electrical energy and control means (22) coupled between said source and said write electrode (18), said source being adapted to provide low voltage pulses of durations up to approximately 0.5 milliseconds.

4. The apparatus according to claim 3, wherein said control means (22) is adapted to pass only voltage pulses having an amplitude of less than 25 V to said write electrode (18).

5. The apparatus according to claim 3, wherein said control means (22) is adapted to pass only voltage pulses having an amplitude of less than 15 V to said write electrode (18).

6. A method for electrolytic printing with low energy levels on a recording medium (10) having a surface layer (12) of predetermined thickness and including a leuco dye, a support layer (16) and a conductive layer (14) sandwiched between the surface and the support layers, said method being performed by an electrolytic printing apparatus including a write electrode (18) having a predetermined surface area contacting said recording medium (10) as it passes and a ground electrode (20) having a predetermined surface area, said ground electrode (20) being separated from the write electrode (19) by a predetermined distance, both electrodes contacting said recording medium as it passes,

characterized by providing low voltage pulses having amplitudes that are compatible with those required by integrated circuit chips and of durations no greater than 0.5 milliseconds,

and selecting the thickness of the surface layer (12), the area of and the distance between the write and the ground electrodes (18, 20) such that a sufficient percentage of the current delivered to the write electrode (12) flows through the surface layer into and through the conductive layer (14) and back through the surface layer to the ground electrode (20) to form a visible mark in the surface layer (12) beneath the write electrode (18).

7. The method according to claim 6, wherein the thickness of the surface layer (12), the area of and the distance between the write and the ground electrodes (18, 20) are selected so that at least 75 percent of the current flows through the surface layer (12).

8. The method according to claim 6, wherein the amplitude of the low voltage pulses provided is limited to a maximum of 25 V.

9. The method according to claim 6, wherein the amplitude of the low voltage pulses provided is limited to a maximum of 15 V.

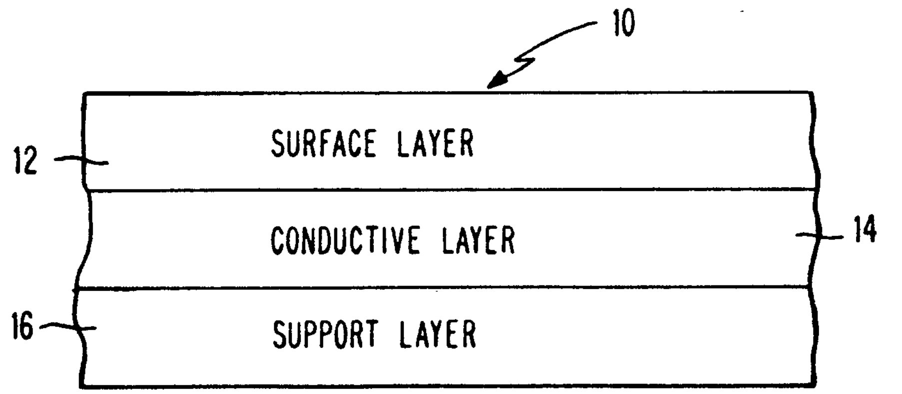
10
12
SURFACE LAYER
CONDUCTIVE LAYER
14
16
SUPPORT LAYER

FIG. 1

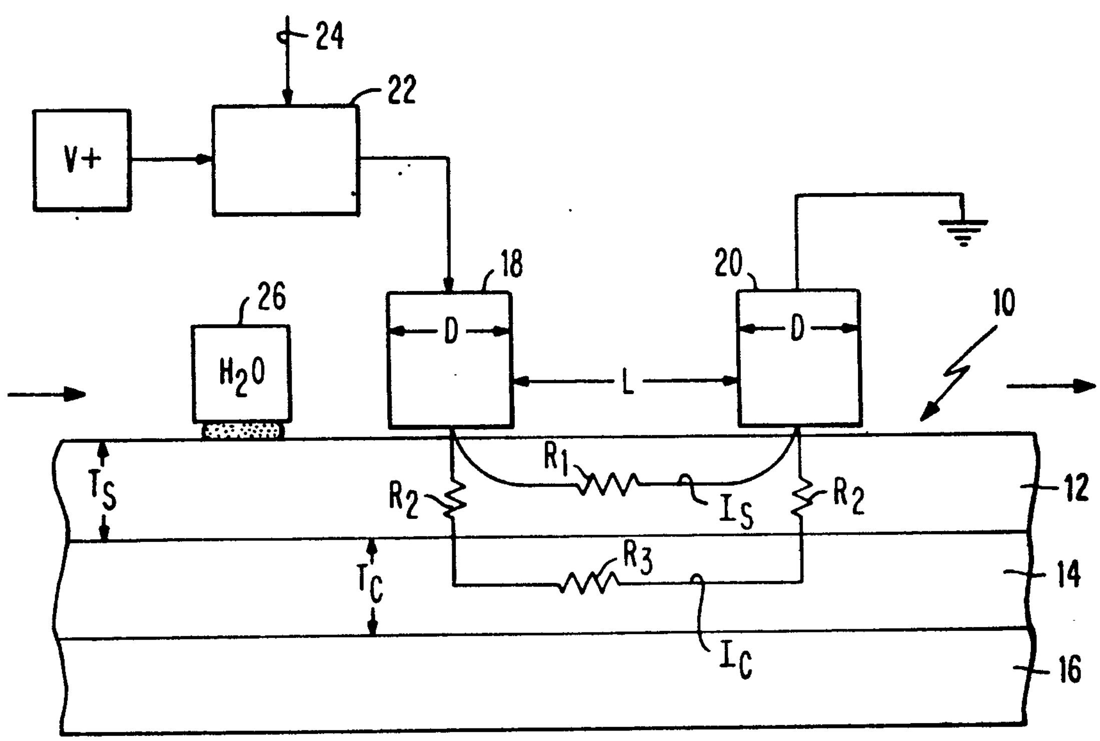
24
22
V+
18
20
26
H_2O
D
D
L
10
T_S
R_1
R_2
I_S
R_2
12
R_3
T_C
14
I_C
16

FIG. 2