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Sambucetti

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[54] **ELECTROCHEMICAL MOLECULAR DISPLAY AND WRITING**

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[52] **U.S. Cl.**................**350/160 R**, 350/267, 350/312, 317/231, 340/336, 40/28 C

[51] **Int. Cl.**..**G02f 1/28**

[58] **Field of Search**......................350/160, 267, 312; 317/231; 340/336; 40/28 C

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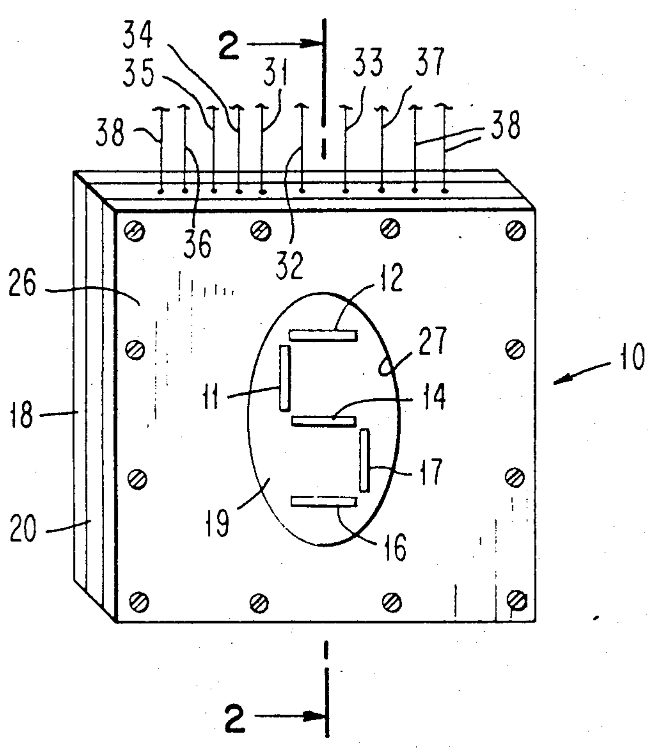
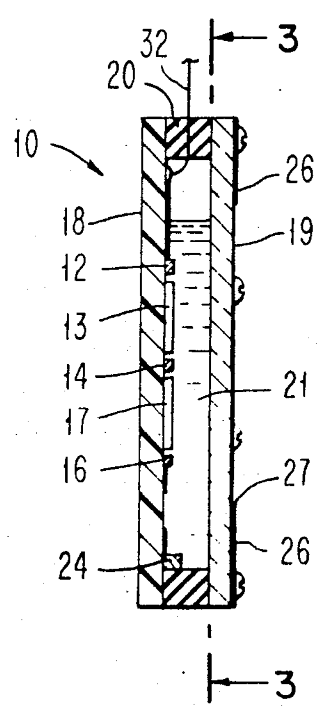
[57] **ABSTRACT**

An electrochemical, electrically-controlled reversible character patterns which can be erased. The apparatus includes a substrate carrying highly reflective display electrode strips which can be electrically addressed selectively to present characters. Characters are displayed by producing a cloud of iodine molecules obscuring certain electrode segments or strips composed of a noble metal or the like normally visible through a transparent cover in the absence of an iodine cloud. An electrolyte capable of undergoing an electrochemical reduction-oxidation reaction yields a molecular, highly non-reflective film on the display electrode strips to selectively obscure the selected display strips from view to present different characters to the viewer. Satisfactory electrolytes include organic polar iodide compounds including ammonium, arsonium, and phosphonium iodides. Preferably, the electrolyte includes pentavalent nitrogen iodides with a radical selected from the choline group such as acetylcholine, propionylcholine and butyrylcholine iodides. The iodine molecules provided in the film tend to remain near the electrode for a substantial period of time to provide "short-term" memory. If gelatine or other water soluble substances are added to the electrolyte, which substances are inert, transparent, and which retard migration of ions, then the duration of the memory provided by the system is extended according to the concentration of such substances. Alternatively, iodine lines can be used to form characters where the gold background is present everywhere and dark lines are written upon the display electrodes which normally are not distinguishable from the background optically. In still another alternative, the form of this invention electrolyte carried in a paper can be used to provide electrochemical writing upon the paper.

22 Claims, 4 Drawing Figures





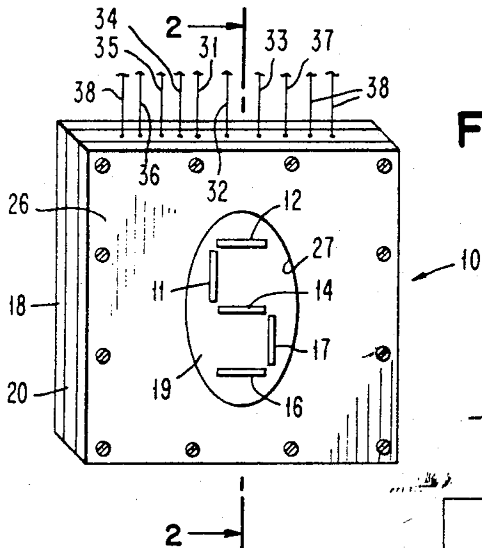


FIG. 1

FIG. 3

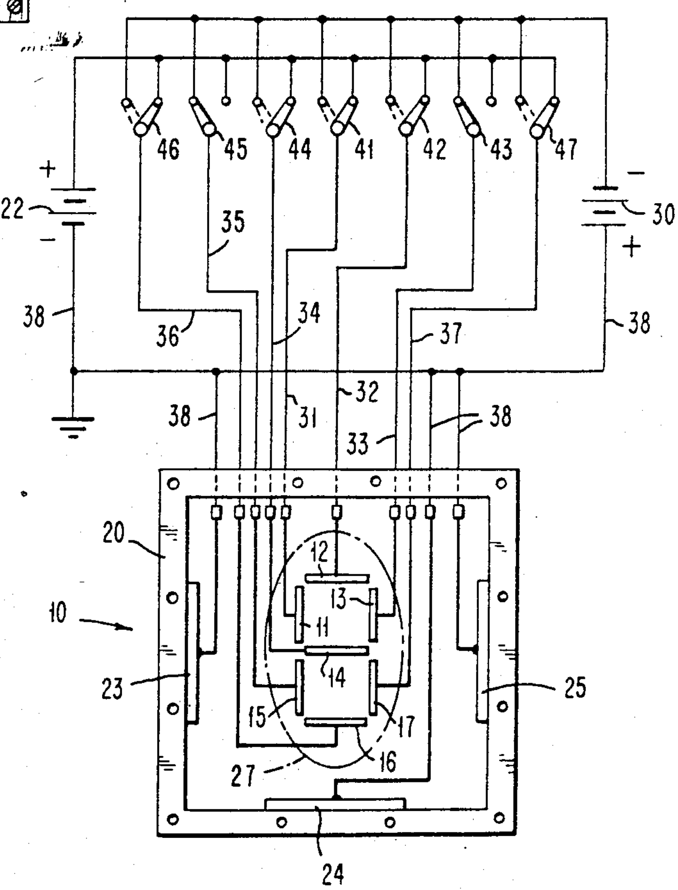


FIG. 2

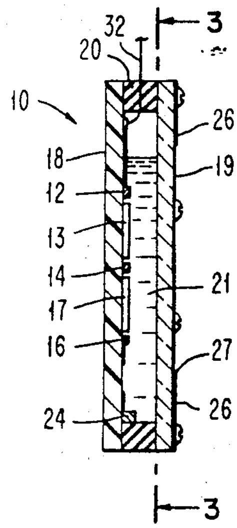
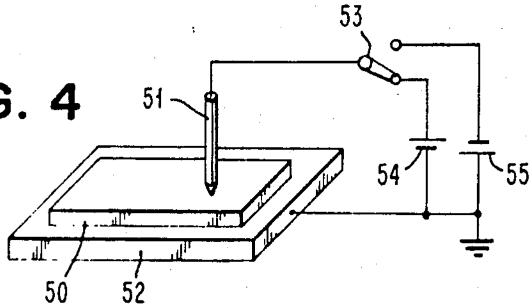


FIG. 4



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ELECTROCHEMICAL MOLECULAR DISPLAY AND WRITING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of electrochemical display and writing devices providing changeable signs exhibiting patterns under electrical control.

In addition, this invention relates to chemical, electrical and wave energy electrolytic apparatus and a method for providing an electrochemical display and for electrochemical writing.

In addition, this invention relates to electrically operated registers including an electrochemical display apparatus combined with data storage.

2. Description of the Prior of

Electrochemical cells have been employed for the purpose of providing electrochemical displays by means of electrochemical plating or by use of reactive electrodes which are tarnished by a reaction between the electrode and the electrolyte. However, the prior art available has not suggested use in displays of inactive or noble metal electrodes without reaction of the electrodes or plating of the electrodes. A problem with both of these techniques of display regardless of the anions and cations employed is that while the chemical reactions may be reversible, they are only partially reversible from the point of view of their implementation in displays. The problem which occurs is that the electrodes become coated with oxides of materials upon their surfaces which gradually blacken the display surfaces even if the underlying electrode is a noble metal an other less reflective or different colored metals are electroplated thereon.

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide an electrochemical display method and device in which the electrodes do not react with the electrolyte and are not plated but with which an optical effect is provided by electrochemical means.

Another object of this invention is to provide an electrochemical display or sign which exhibits memory and which provides a high quality display with long life and a corresponding method.

Still another object of this invention is to provide an electrode structure which is economical and which employs a minimum of noble metal material without bleeding of a base metal through a noble metal material layer which is used as the display electrode.

In accordance with this invention, an electrochemical display apparatus is provided including a pair of electrodes, one of said electrodes including a surface composed of a noble metal selected from gold, platinum, iridium and rhodium, and an electrolyte providing a reversible reduction-oxidation reaction providing a change in the reflection characteristics in connection with the one electrode. A corresponding method is provided. Preferably the electrolyte comprises an organic polar iodide compound selected from the group including ammonium, arsonium, and phosphonium compounds. Preferably, the electrolyte is a pentavalent nitrogen compound of the general formula

$$\left[\begin{array}{c} R_3 \\ | \\ R_2\text{—}N\text{—}R_4 \\ | \\ R_1 \end{array}\right]^{+} I^{-}$$

where R_1, R_2, R_3, and R_4 are selected from hydrogen, alkyl, and aromatic groups which can be simple and substituted. The choline groups can be selected from acetylcholine, propionylcholine and butyrylcholine iodides, and electrolyte concentration varies from 0.5 to 20 percent by weight in water, and the electrolyte concentration is approximately 2.5 percent by weight in water.

Preferably, a soluble, non-reactive material is added to the electrolytic solution for retarding motion of substances in the electrolyte, which can be gelatine added to the electrolytic solution in sufficient concentration to increase viscosity. One electrode includes a basic layer of copper supported upon a substrate, an intermediate layer of palladium and an outer layer of gold. The palladium is electrodeposited upon the copper base and gold is plated upon the palladium. The other of the electrodes comprises a reference electrode composed of silver and silver iodide.

In another aspect, radiation reflection is controlled by apparatus including a pair of electrodes. At least one of the electrodes has a surface adapted for reflection of radiation. The surface is composed of an inactive substance. Electrical terminals are connected to said electrodes. An electrolyte provides a reversible reduction-oxidation reaction to produce at the one electrode (when current flows between said electrodes in one direction) a reaction product having an optical characteristic of absorbing light to a substantial degree when adjacent to the one electrode. A container holds the electrodes and the electrolyte.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a perspective view of a display device constructed in accordance with this invention.

FIG. 2 shows a vertical section taken along line 2—2 in FIG. 1.

FIG. 3 shows a section taken along line 3-3 in FIG. 2 of the display device of FIGS. 1 and 2 connected in an electrical circuit for providing a display of various alphanumeric characters. FIG. 4 is an writing apparatus embodying this invention.

DETAILED DESCRIPTION OF THE DRAWINGS

Referring to FIGS. 1-3, an electrochemical display device 10 includes a plurality of anodes 11-17, composed of a gold surface over a layer of palladium upon a layer of copper on a printed circuit board 18. The copper had been etched to form separate display electrodes before palladium and gold were added. A transparent cover 19 composed of glass or lucite, and a gasket 20 between the board 18 and the cover 19 are included. An electrolyte 21 is contained within the space enclosed by the cover 19, the gasket 20 and the board 18. The electrolyte 21 comprises an aqueous or water-alcohol solution of organic iodide compound, preferably one of the pentavalent nitrogen compounds in which iodine is attached to the nitrogen as follows:

$$\left[\begin{array}{c} R_2 \\ | \\ R_1\text{—}N\text{—}R_3 \\ | \\ R_4 \end{array}\right]^{+} I^{-}$$

Preferably, the compound should be highly soluble in water. The preferred choice of an electrolyte comprises acetylcholine iodide or propionylcholine iodide preferably having a weight concentration in water of 2 to 6 percent.

$$\left|\begin{matrix} CH_2-N(CH_3)_3 \\ | \\ CH_2OCOCH_3 \end{matrix}\right|^+ I^-$$

The display electrodes **11–17** are connected by wires **31–37** to switches **41–47** and through them to the anode of battery **22**, whose cathode is connected via lines **38** to the reference electrodes **23, 24** and **25** in the display device **10**. The reference electrodes **23, 24** and **25** composed of silver and silver iodide are spaced about the device **10** so that the display electrodes **11–17** are substantially equidistant from a reference electrode so that the time required for each electrode to change "color" is substantially the same as every other electrode. Thus, the display will be presented over all of the display electrode segments **11–17** substantially at once rather than appearing in a fragmented fashion over a period of time, here and there.

When current is passed from battery **22** through display electrode **11–17** (which becomes an anode) through the electrolyte, and the reference electrodes **23, 24** and **25**, a film of molecular iodine (I_2) is formed adjacent to that display electrode (**11–17**) and remains in juxtaposition therewith. However, the film is subject to diffusion with time which varies inversely as a function of the concentration of the electrolyte and as a function of the viscosity of the solution. Display electrodes **11–17** should have rugged surfaces to insure better adherence of the film formed on them. When switches **41** to **47** are reversed, display electrodes **11–17** become cathodes and the current is reversed to dissipate the iodide cloud. All of the cover **19** except for the area over anodes **11–17** has a mask **26** thereover to highlight the characters through frame **27**.

Because of the wetting nature of the pentavalent nitrogen organic solution, the iodide film has a strong covering power on the surface of the display electrodes **11–17** and does not show any bleeding effects. Bleeding refers to rapid visible migration of the iodine molecules away from the strip **11–17**. Wetting enhances both resolution, where one is writing characters with iodine, and memory, because line with is not spread and dispersal is slower.

Simultaneously, with formation of the film at the display electrode **11–17**, serving as an anode, the cathodic reaction at reference electrodes **23, 24** and **25** consists in the discharge of an alkyl ammonium cation which prevents hydrogen gas evolution, if the voltage is kept below 1.5 volts. As a consequence of the electrochemical reactions, the display electrode segments **11–17** (anodes) assume a dark brown color, whereas the reference electrodes (cathodes) retain their usual color although they are not visible, in any event.

If, under the same voltage, the polarity of the cell is reversed by switches **41–47**, the film at the electrodes **11–17** vanishes in the solution and it is formed again at the reference electrodes **23, 24** and **25**. The process can be repeated many times without affecting the conditions of pure gold surface of display segments **11–17** at all. In fact, the noble metal does not participate in the reaction and acts only as an interface for electron exchange between the external circuit and ions in solution.

The display electrodes **11–17** can be manufactured by electrochemically etching a printed circuit board to form the underlying electrode structure and perform an additional step of etching with acid in such a manner as to produce small pockets or holes in the surface. Then the palladium can be added by electrodeposition and then the gold can be deposited to yield corresponding plated pockets in which iodine film will be trapped for longer periods of time to lengthen memory.

The electrode reactions for the build up and erasing of the film are:

$$\text{(Transparent) } 2I^- + 2e \rightleftarrows I_2 \text{ (Film)}$$

Essentially, the electrolyte system consists of a certain amount of

$$\left|\begin{matrix} & R_2 & \\ & | & \\ R_1- & N & -R_3 \\ & | & \\ & R_4 & \end{matrix}\right|^+ I^-$$

dissolved in water. R_1, R_2, R_3 and R_4 can be either alifatic (methyl, ethyl, . . . , etc.) or aromatic groups (phenyl, benzoyl groups) either the same or different. For example, both trimethyl-phenyl ammonium iodide and dimethylethyl-benzoyl ammonium iodide work reasonably well. However, if the resulting compound is not readily soluble in water, it is necessary to use water-alcohol or other solvent mixtures.

Best results are obtained when one of the radicals belongs to the choline group. For example, acetylcholine and propionylcholine iodides are excellent, especially when the aqueous concentration is maintained between two to 6 grams percent.

$$\left|\begin{matrix} CH_2-N(CH_3)_3 \\ | \\ CH_2OCOCH_3 \end{matrix}\right|^+ I^-$$

Acetylcholine Iodide Legend

To achieve improved memory, the solution of electrolyte includes 3 percent by weight of gelatin, which increases persistency of the film by enhancing its adherence to the electrode surface.

I. Variations in pentavalent nitrogen compound formulation

Starting with the basic formula

$$\left|\begin{matrix} & R_3 & \\ & | & \\ R_1- & N & -R_2 \\ & | & \\ & R_1 & \end{matrix}\right|^+ I^-$$

The simplest compound of pentavalent nitrogen is one of which all R groups are hydrogen, which is ammonium iodide

$$\left|\begin{matrix} & H & \\ & | & \\ H- & N & -H \\ & | & \\ & H & \end{matrix}\right|^+ I^-$$

This compound works in the cell and the free iodine forms at the anode (writing) and erases when the display segment **11–17** is made a cathode. However, the film does not adhere to the electrode and there is considerable bleeding of the film around the display segment **11–17**.

Similar behavior is observed with trimethyl and triethylammonium iodide. Use of the choline group as one of the radicals of the pentavalent nitrogen formulation, is possible with varying complexity of the substituted choline molecule. Acetylcholine iodide, propionyl choline iodide, butyrylcholine iodide and benzoylcholine iodide cause the electrolyte to be a very efficient wetting agent and the brown film produced upon writing remains strongly attached to the character surface of the electrode **11–17**.

A second observation is that acetylcholine iodide and propionylcholine iodide are both very satisfactory. As the molecular weight of the compound increases, for example, with butyrylcholine iodide, the solubility in water of the compound decreases and besides the film produced in writing erases less readily.

Acetylcholine iodide and propionylcholine iodide electrolytes are operative within a temperature range from 0°C to 85°C although memory is poor at the higher temperature due to the high energy level of the iodine molecules. The optimum temperature range for these two electrolytes is 10°C at which the electrolyte tends to gell and 50°C at which the electrolyte evaporates and memory deteriorates.

With increasing molecular weight and complexity, for example, with benzoylcholine iodide, the compound is insoluble in water and is unsatisfactory as an electrolyte in that case. However, water-alcohol mixtures of benzoylcholine iodide are soluble and good writing-erasing effect is obtainable.

The pentavalent nitrogen choline compounds are satisfactory in mixtures in which the solvent is a solvent such as methanol, ethanol, acetone, D.M.S.O. Two problems arise in these mixtures: (a) the solvent tends to evaporate, and (b) the film produced in writing dissolves more rapidly to provide a shorter memory.

Pentavalent nitrogen compounds with iodide produce a good writing and erasing display effect. This occurs in pure aqueous solutions or in water-solvent mixtures. Compounds containing the choline group are most suitable because bleeding of the film disappears and the duration of the memory is much enhanced.

II. Other iodide compounds without pentavalent nitrogen

Simple inorganic iodides (potassium iodide, lithium iodide, lanthanum iodide, etc.), show poorer film adherence and memory and a great deal of gas evolution. Organic compounds in which nitrogen is substituted by arsenic such as methyl-tri-phenyl arsonium iodide do not dissolve in water. Water-alcohol mixtures of this compound did show a poorer reversible writing-erasing effect.

Methyl triphenyl phosphonium iodide shows considerable hydrolysis decomposition. Besides arsenic and phosphonium compounds, other compounds containing sulfur instead of nitrogen such as ethyl-methyl sulfonium iodide, yield poor results.

III. Optimum cell chemistry

Acetylcholine iodide or propionylcholine iodide give excellent results. A concentration of 2.5 grams of acetylcholine iodide in 100 grs. of water gives fast speed with a memory duration of less than 1 minute. To increase memory or permanency of the presence in the display of the film, gelatin is added to the solution. The amount of gelatin is not critical. A concentration of 1 percent grams of gelatin increases the memory to about 5 minutes, but the solution is still fluid. A concentration of 10 grams percent of gelatin allows working with a solid electrolyte.

One can evaluate the active mass of electrolyte involved in the writing of a given character as well as the percentage loss of iodine film per character as a function of the time that a character is "on" before electrical erasing occurs.

To distinctly write a character of 0.08 square inch surface area (made of 7 mm × 1 mm segments) requires depositing 8×10^{-6} grams of iodine. The electrolyte solution around each character has available 0.7 grams of iodine, and allows writing $(0.7/8)\ 10^6$ characters. Studies indicate that only 50 percent of the iodine film migrates to the solution as free iodine. The rest reconverts back to iodide available for further writing. Therefore, the number of characters that can be written, assuming that each one is left alone to dissipate totally in the electrolyte (process that takes more than 3 minutes) is twice as much or $(2 \times 0.7/8)\ 10^6$ characters.

Iodine migration studies indicate that the percentage loss of iodine is linear during the first 20 seconds, then the curve flattens out and total migration occurs after 3 minutes. In the first 20 seconds, the percentage loss is approximately 0.5 percent per second. As a display for a card punch verifier, a very fast operator can punch and verify an **80** column card in about 20 seconds, thus producing roughly 10^5 character/8 hour day.

Assuming for such applications that 10 percent of the film will be lose per character on an average (loss will be maximum for the first character of an **80** column card, and minimum for the 80th character), the approximate life of the electrolyte (without the regeneration) will be:

$$\frac{2\times 0.7/8\ 10^6}{10^5}\times 10 = 140 \text{ days}$$

IV. Improvements in Acetylcholine Iodide Cells

Changes in cell structure: The cell reference electrode can be a gold bar placed alongside or around the gold-plated character. The problems associated with this are that when writing iodine on a character at voltages over 1.5 (to obtain faster writing) gas is evolved at the gold reference. Also, when erasing a character, the iodine film is transferred to the gold reference thus allowing far more iodine migration and dispersion in the electrolyte.

Substitutes for a gold reference electrode of a different material include aluminum metal, which during the character erasing cycle is superior because the iodine film erased from the gold character does not reform on the aluminum surface. During the writing cycle, gas evolution occurs on the aluminum reference as it does no gold.

A reversible reference electrode which acts as a carrier and reservoir for iodide ions is the silver, silver iodide electrode shown in the preferred embodiment. The element is simply made of silver surface which is coated with a crystal layer of silver iodide. The coating is applied by electrolysis in the same acetylcholine iodide electrolyte. The mechanism for writing and erasing with this reference electrode is:

$$\underset{\substack{\text{silver iodide}\\ \text{(insoluble)}}}{AgI} \underset{\text{erasing}}{\overset{\text{writing}}{\rightleftarrows}} \underset{\substack{\text{silver}\\ \text{(insoluble)}}}{Ag^{\circ}} + \underset{\substack{\text{iodide}\\ \text{ions}}}{I^{-}}$$

When writing on the gold character strips (character (+) and reference (−)) iodide ions enter the solution from the AgI reference while other iodide ions leave it to form the film of iodine on the gold. During erasing, the film of iodine over the gold is converted back to iodide, and the reference silver and iodide regenerate the AgI layer. Both end products of the reference electrode reactions are insoluble (silver and silver iodide) except for the iodide ions which are produced or captured by the reference.

a. The silver, silver iodide electrode allows writing iodine on gold characters as faster speeds (voltages over 2 volts) without gas evolution, because the dissociation for AgI occurs preferentially to the electrolysis of water.

b. Erasing also occurs with no gas evolution at the reference. If the erasure is voltage-controlled at the gold character in order to stop current flow where the gold surface is iodine free, the problem of gas generation is solved altogether.

c. Short circuiting the reference overnight with a gold bar placed in a cell containing substantial amounts of free iodine, completely purges the cell of dispersed iodine, while forming more AgI at the reference.

The reversible writing process in these cells consists in the electrical generation of sufficient iodine to form a character. In the erasing process the film is electrically reduced back to iodide. If, during the interval between writing and erasing there were no exchange between the film and the solution, all the iodine film produced on writing would be electrically recovered by erasing and the solution would last indefinitely.

However, molecular iodine is soluble in solutions of iodide (which is the main ion in the electrolyte) and, therefore, when the film is deposited and the character is left "on," there is a gradual process of migration of the molecules from the film to the solution. This phenomenon produces two effects; (a) the film tends to vanish with time even without electrical erasing, so that memory is limited. This is not a critical limitation because memory times of up to thirty minutes are easily achieved. (b) this dissolution of the iodine film by interaction with iodide from the electrolyte forms an iodine-iodide complex in which part of the iodine is in free form and therefore no longer available for writing. This tends to remove iodide ions from the electrolyte producing a gradual exhaustion which limits the electrolyte life. The exhaustion process will depend on the initial concentration of iodide, on the number of characters written per unit time and on the interval lapsed between writing and erasing.

If the operation of the display is such that the characters are electrically erased a few seconds after being displayed, then the amount of iodine lost by migration is minimum and the cell life is considerably longer.

Employing the current required to erase the film from the display as a source of memory, a computer or other data processing device can read the display by providing a potential for erasing and measuring the re-

sultant current for the various display electrodes **11–17.**

In electrochemical displays it is desirable that some means be provided for altering the appearance of the display in response to an electrical signal. This can be done by changing the reflection of the light or the color or both. For example, it is desirable to provide a surface that is visible to the observer. It is also desirable to provide a structure which will permit changing the appearance of the surface being viewed from light reflecting to light absorbing and to provide that change at such a speed that the process is compatible with the speed of data processing or data transmission devices. Electrochemical displays permit patterns of information to be presented in sizes as small as fractions of an inch in character size to several inches in character size. They also permit the display system to be operated at low applied voltages which are compatible with semiconductor or transistor circuits.

In addition, such displays permit the use of arrays of characters made by photoetching as is done in connection with printed circuits. A dot raster form of character can be provided by means of providing large numbers of dots connected by means of arrays of horizontal and vertical conductors. Such displays are flat. An application of this type of technology is that a keyboard may be used to enter the data upon the display, and then, if the display includes memory, the computer system may extract the data from the memory in the display and erase the display at the same time.

Another embodiment of this invention is shown in FIG. **4.** The above electrochemistry can be applied to printing upon a paper **50** (or other similar material) impregnated with one of the above suggested electrolytes, with a writing electrode **51** on one side of the paper **50** and a reference electrode **52** on the other side of the paper **50** so that iodine molecules can form in the paper at the noble metal electrode **51** in an electrochemical printer which employs electrodes in direct contact with the paper **50.** Switch **53** connects the electrodes in circuit with batteries **54** and **55** which provide currents in reverse directions for writing and erasing.

If the printed circuit board **18** is the same color as the surface of the display segments **11–17,** then when the iodine cloud or film is formed upon the segments, it will write a line rather than obscuring one. In essence, then one can write white on black or black on white.

I claim:

1. An electrochemical data presentation apparatus including:

a. a pair of electrodes,

b. one of said electrodes comprising a data presentation electrode including a noble metal selected from gold, platinum, iridium and rhodium,

c. a fluid medium for selectively obscuring said data presentation electrode from view, said medium containing an electrolytic compound providing an electrochemical reversible reduction-oxidation reaction product composed of free molecules of an anion changing the light transmitting characteristics of said medium as a function of the proportion of said compound comprising said reaction product,

d. a container holding said electrodes and said medium containing said electrolytic compound,

e. said reaction product when produced being present in said medium adjacent to said data presentation electrode, and

f. said reaction product being suspended in said fluid medium.

2. An electrochemical data presentation apparatus including:

a. a pair of electrodes,

b. one of said electrodes comprising a data presentation electrodes including a noble metal selected from gold, platinum, iridium and rhodium,

c. a medium for presentation of indicia, said medium containing an electrolytic compound providing an electrochemical reversible reduction-oxidation reaction product changing the transmission characteristics of said medium,

d. a container holding said electrodes and said medium containing said electrolytic compound, and

e. said electrolytic compound comprising an organic polar iodide compound selected from the group including ammonium, arsonium, and phosphonium compounds.

3. An electrochemical data presentation apparatus including:

a. a pair of electrodes,

b. one of said electrodes comprising a data presentation electrode including a noble metal selected from gold, platinum, iridium and rhodium,

c. a medium for presentation of indicia, said medium containing an electrolytic compound providing an electrochemical reversible reduction-oxidation reaction product changing the transmission characteristics of said medium,

d. a container holding said electrodes and said medium containing said electrolytic compound, and

e. said electrolytic compound comprising a pentavalent nitrogen compound of the general formula

$$\left|\begin{array}{c} R_3 \\ | \\ R_2-N-R_1 \\ | \\ R_1 \end{array}\right|^{+} I^-$$

where R_1, R_2, R_3 and R_4 are selected from hydrogen, alkyl, and aromatic groups including both simple and substituted forms.

4. Apparatus in accordance with claim 3 wherein said choline groups are selected from acetylcholine, propionylcholine and butyrylcholine iodides.

5. Apparatus in accordance with claim 4 in which the concentration of said electrolytic compound varies from 0.5 to 20 percent by weight in solvent.

6. Apparatus in accordance with claim 4 wherein the concentration of said electrolytic compound is approximately 2.5 percent by weight in solvent.

7. An electrochemical data presentation apparatus including:

a. a pair of electrodes,

b. one of said electrodes comprising a data presentation electrode including a noble metal selected from gold, platinum, iridium an rhodium,

c. a medium for presentation of indicia, said medium containing an electrolytic compound providing an electrochemical reversible reduction-oxidation reaction product changing the transmission characteristics of said medium,

d. a container holding said electrodes and said medium containing said electrolytic compound, and

e. said medium comprising an electrolytic solution of said electrolytic compound and a soluble, non-reactive material added to said electrolytic solution for retarding motion of substances in said electrolytic solution.

8. Apparatus in accordance with claim 7 wherein said non-reactive material is gelatine added in sufficient concentration to increase viscosity of said solution.

9. An electrochemical data presentation apparatus including:

a. a pair of electrodes,

b. one of said electrodes comprising a data presentation electrode including a noble metal selected from gold, platinum, iridium and rhodium,

c. a medium for presentation of indicia, said medium containing an electrolytic compound providing an electrochemical reversible reduction-oxidation reaction product changing the transmission characteristics of said medium,

d. a container holding said electrodes and said medium containing said electrolytic compound, and

e. said one electrode including a basic layer of copper supported upon a substrate, an intermediate layer of palladium and an outer layer of gold.

10. Apparatus in accordance with claim 9 with said palladium layer electrodeposited upon the copper base and said gold layer plated upon said palladium.

11. Apparatus in accordance with claim 2 wherein the other of said electrodes comprises a reference electrode composed of silver and silver iodide.

12. An electrochemical radiation reflection controlling apparatus including:

a. a pair of electrodes,

b. at least one of said electrodes having a light reflecting surface, said surface being composed of an inactive substance,

c. electrical terminals connected to said electrodes,

d. an electrolytic fluid comprising means for providing a reversible reduction-oxidation reaction to produce at said one electrode, when current flows between said electrodes in one direction a reaction product composed of free molecules of an anion having an optical characteristic of absorbing light directed towards said electrode to a substantial degree when said reaction product is suspended in said fluid adjacent to said one electrode,

e. and a container holding said electrodes and said electrolyte.

13. An electrochemical reflection controlling device including:

a. a pair of electrodes at least one of which is composed of noble metal material,

b. an electrolyte containing an organic compound of pentavalent nitrogen with an iodide ion combined in the compound,

c. at least one of said electrodes having a radiation reflecting surface,

d. electrical terminals attached to said electrodes,

e. and a container including said electrodes and said electrolyte.

14. A display device including

a. a pair of sets of electrodes, one set of electrodes comprising a printed circuit board including an etched copper pattern of electrode structures plated with palladium and then plated with gold,

b. an electrolyte containing an organic compound of pentavalent nitrogen with a negative iodide ion included in the compound and a choline group comprising a radical of a positive ion including the nitrogen,

c. a container including said electrodes and said electrolyte.

15. Apparatus in accordance with claim **14** wherein said compound is selected from a group including acetylcholine iodide and propionylcholine iodide.

16. An electrochemical display apparatus including:

a. a pair of electrodes,

b. one of said electrodes including a noble metal with high reflection characteristics selected from gold, platinum, iridium and rhodium,

c. and an electrolyte providing a reversible reduction-oxidation reaction product in said electrolyte adjacent to said electrode at the end of said reaction for absorbing radiation, said reaction product composed of free molecules of an anion and providing a change in the reflection from said one electrode,

d. and a container holding said electrodes and said electrolyte.

17. An electrochemical data presentation method including:

a. employing a pair of electrodes,

b. using one of said electrodes including a noble metal selected from gold, platinum, iridium and rhodium as a data presentation electrode,

c. and employing a medium for presentation of indicia, said medium containing an electrolytic compound yielding an electrochemical reversible reduction-oxidation reaction product suspended in said medium adjacent to said one electrode composed of free molecules of an anion for absorbing radiation and thereby changing the transmission characteristics of said medium to present data formed by passing direct current between said electrodes with a positive potential upon said one electrode.

18. A method in accordance with claim **17** including employing as said electrolyte an organic polar iodide compound selected from the group including ammonium, arsonium, and phosphonium compounds.

19. A method in accordance with claim **17** including employing as said electrolyte a pentavalent nitrogen compound of the general formula

$$\left|\begin{array}{c} R_3 \\ | \\ R_2{-}N{-}R_4 \\ | \\ R_1 \end{array}\right|^{+} I^{-}$$

where R_1, R_2, R_3 and R_4 are selected from hydrogen, alkyl, and aromatic groups which can be simple and substituted.

20. An electrochemical radiation reflection controlling apparatus including:

a. a pair of electrodes,

b. at least one of said electrodes comprising a display electrode having a surface adapted for reflection of radiation, said surface being composed of gold,

c. said one electrode including a basic layer of copper supported upon a substrate, an intermediate layer of palladium and an outer layer of gold, said palladium being electrodeposited upon the copper base, said gold being plates upon said palladium, the other of said electrodes comprising a reference electrode composed of silver and silver iodide,

d. an electrolyte, said electrolyte being a pentavalent nitrogen compound of the genera formula

$$\left|\begin{array}{c} R_2 \\ | \\ R_1{-}N{-}R_3 \\ | \\ R_4 \end{array}\right|^{+} I^{-}$$

where R_1, R_2, R_3 and R_4 are selected from hydrogen, alkyl, and aromatic groups which can be simple and substituted, said choline groups being selected to form acetylcholine, propionylcholine and butyrylcholine iodides, including a solvent containing water to form an electrolytic solution,

e. electrical terminals connected to said electrodes,

f. said electrolyte comprising means for providing a reversible reduction-oxidation reaction to produce at said one electrode for current between said electrodes in one direction, a reaction product having an optical characteristic of absorbing light to a substantial degree when adjacent to said one electrode,

g. a soluble, non-reactive material including gelatin being added to said electrolytic solution for retarding motion of substances in the electrolyte to increase viscosity,

h. and a container holding said electrodes and said electrolyte.

21. Apparatus in accordance with claim **1** wherein said electrolytic compound comprises an iodide and said reaction product comprises free molecules of iodine.

22. Apparatus in accordance with claim **1** wherein said electrolytic compound comprises an organic halide and said reaction product comprises free molecules of said halide.

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