

[54] **MULTICOLOR PERMANENT AND ERASABLE PRINTING**

[75] Inventor: **Carlos J. Sambucetti**, Mohegan Lake, N.Y.

[73] Assignee: **International Business Machines Corporation**, Armonk, N.Y.

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Primary Examiner—James W. Moffitt

Assistant Examiner—Jay P. Lucas

Attorney—Richard C. Sughrue et al.

[57] **ABSTRACT**

An electro-chemical printing system operable in either a permanent printing or erasable printing mode. A single electrode may function as both the permanent marking electrode and the erasable marking electrode simply by reversing the polarity of the potential applied to the electrode. Provision is also made for erasing erasable markings. A salt bridge may be provided between a reference electrode and the recording medium to prevent a counter-mark during erasing.

7 Claims, 3 Drawing Figures

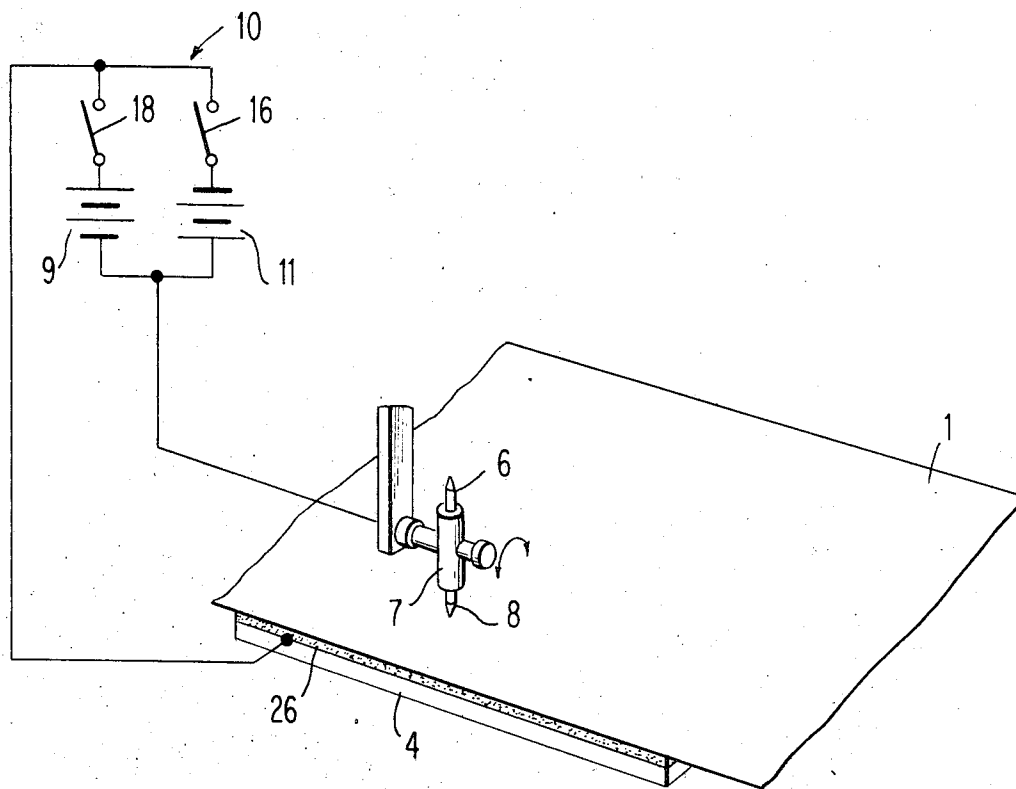


FIG. 1

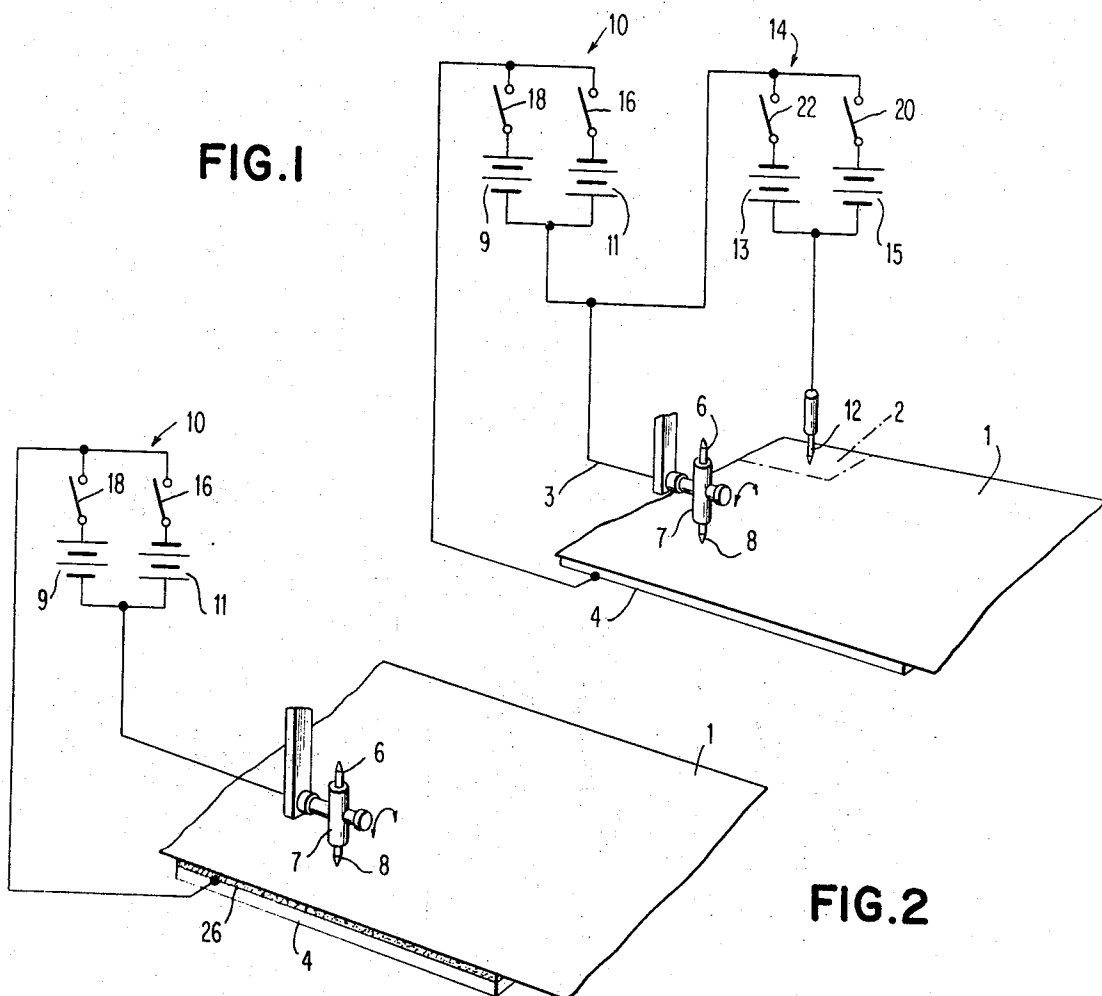


FIG. 2

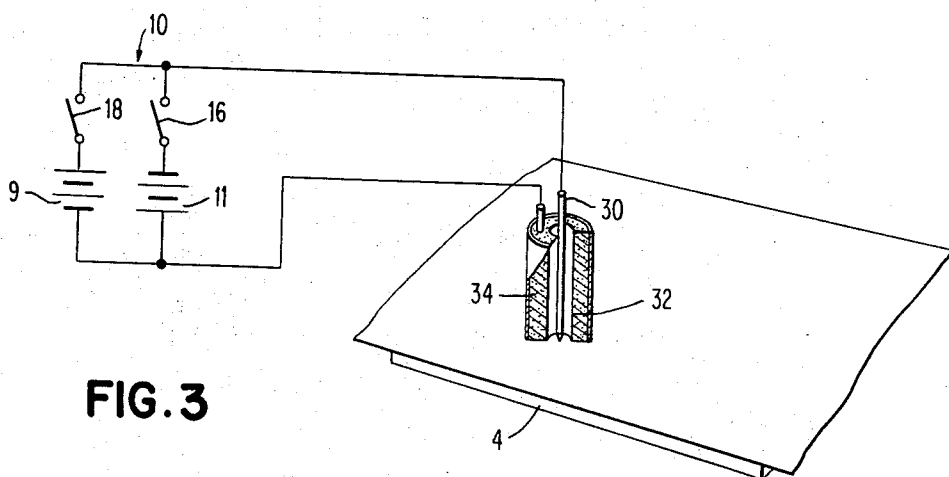


FIG. 3

MULTICOLOR PERMANENT AND ERASABLE PRINTING

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is in the field of electro-chemical printing systems.

2. Description of the Prior Art

Various systems employing electro-chemical printing are available. These systems can be broadly classified into those which provide permanent markings and those which provide non-permanent or erasable markings.

In the former type system, a porous recording medium, such as paper, is impregnated with a conductive salt (electrolyte) such as ammonium fluoride, ammonium oxalate, or potassium fluoride or the like and a reducing agent such as ascorbic acid, stannous chloride, stannous sulfate, or the like. Printing is effected through the use of a silver or silver alloy anode and a cathode of platinum, platinum alloy, gold, steel, etc. When current is caused to flow between the anode and the cathode through the conductive recording medium, a portion of the silver anode dissolves releasing ions into the paper. The reducing agent causes the reduction of the silver ions back to metal form thereby producing a permanent printed mark. When a silver anode is used, the mark appears black in color. An example of such a permanent marking system is disclosed in pending U.S. Pat. application Ser. No. 209,930, filed Dec. 20, 1971, to Ambrosia et al., assigned to the same assignee as the invention disclosed herein.

An example of an erasable system can be found in U.S. Pat. No. 2,927,834, to S.L. Solar, issued Mar. 8, 1960. In such a recording system, the recording medium is impregnated with an electrolyte, as is the case with the permanent marking system, and a pH indicator. When the impregnated medium is subjected to an electric current of one polarity, the pH of the impregnant is varied to provide a colored mark. The color of the mark will vary depending upon the specific pH indicator used. More specifically, when a substantially neutral electrolyte is subjected to current flow, acidification is brought about at the positive electrode while the area about the cathode becomes alkaline. Depending upon whether an acidic indicator or a basic indicator is included with the electrolyte, a color mark will appear on the recording medium at either the area about the cathode or the anode.

In many instances, it is extremely desirable to be able to selectively, permanently or erasably record information on a common recording medium with a single printing apparatus. Often, there is associated with information of a permanent nature, information which is of a transient nature only. While the permanent information would be permanently recorded on the recording medium, the non-permanent information should be erasably printed. In map plotting, for example, permanent terrain features should be permanently marked on the recording medium, while transient features such as the position of railroad cars moving along tracks permanently noted on the map should be erasably indicated. Also, in the field of computer plotting of graphics, both permanent and non-permanent markings are often required. In the area of strip recordings, multiple strip plots are often recorded to visually display the results of a plurality of measurements made over a variety

of test runs. In many instances, it is desirable to permanently record only selected plots. Thus, a relatively simply constructed and inexpensive recording system having the capability of providing both permanent and non-permanent markings on a common recording medium would be a highly desirable tool to workers in the many fields utilizing visual recording apparatus.

With respect to the erasable system, there is the problem of the counter-mark produced when the system is in its erase mode. Assuming a base indicator has been added to the electrolyte, in response to a current pulse passing through the recording medium between the cathode (marking electrode) and anode (reference electrode), a color mark appears on the recording medium in the vicinity of the cathode. To erase this mark, the potential on the cathode and anode are reversed so that the cathode now becomes the anode (erase electrode) and the anode the cathode (reference electrode). Although the mark previously produced disappears, a new mark called a counter-mark appears at the new cathode. Since the recording medium is translucent, the electrodes cannot be placed in alignment on opposite surfaces of the recording medium, for a counter-mark appearing on the bottom surface of the medium would be seen from the top surface.

Prior techniques for solving this problem call for the use of a so-called sacrificial area with a reference electrode in contact therewith. This area is located on the recording medium a distance from the recording area. Obviously, this technique results in a considerable waste of recording medium since the sacrificial area cannot be used for recording data and must be discarded. Other, more serious problems are also encountered with this approach. Optimally, the marking/erasing electrode and reference electrode should be as close together as possible. Ideally, the electrodes should be placed in alignment on opposite sides of the recording medium. When a sacrificial area is used, the erase electrode and the reference electrode must be spaced relatively far apart, and thus erasing becomes difficult because the conductivity between electrodes becomes much less than that available when the current is passed directly through the thickness of the recording medium. To compensate, high erasing potentials must be used. Further, the reaction time of the system is slower. When the same reference electrode is used during the non-permanent marking mode of operation, the distance between the marking electrode and reference electrode is also great and thus high marking potentials are required.

Further, in the area of graphic recording, a large marking area is needed and the marking electrode rapidly moves in an essentially unpredictable manner to various X Y coordinates on the marking area. This means that the distance between the marking/erasing electrode and the reference electrode is not only large but varies considerably as the marking electrode traces out the graphic illustration. Thus, the conductivity at the marking spots varies considerably. To overcome this problem, the marking and erasing voltages must be made variable and dependent upon the position of the marking/erasing electrode.

SUMMARY OF THE INVENTION

The present invention overcomes the above-indicated disadvantages associated with conventional electro-chemical printing systems by providing a sys-

tem which can operate in either a permanent or erasable recording mode of operation. In addition, an embodiment of the inventive system is disclosed which solves the counter-marking problem without using sacrificial areas. As a result, the marking/erasing and reference electrodes can be located close to each other and indeed they may be located in alignment on opposite sides of the recording medium.

Briefly, the dual operating mode feature is attained by impregnating a recording medium, such as paper, with an electrolyte such as potassium fluoride, ammonium fluoride, ammonium oxalate or the like along with both a reducing agent such as ascorbic acid, stannous chloride, stannous sulfate or the like, and an electrochromic material such as a Redox system or a pH indicator. The marking/erasing electrode is in the form of a permanent or erasable marking electrode element and an erase electrode element positioned in a holder which is rotatable to place either of the electrode elements into contact with the recording medium. The marking electrode element is formed from silver or its alloys while the erase electrode element is formed from platinum or its alloys. A reference electrode is also provided. The silver marking electrode element acts as either a permanent or erasable marking electrode merely by changing the polarity of the potential supply thereto.

To solve the counter-mark problem there is provided a conductive salt bridge positioned between the reference electrode and the recording medium. The salt bridge provides the necessary conductivity but as the electrolyte in the salt bridge does not contain any electrochromic material, it will produce no marking at either polarity.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates one embodiment of the dual mode electrochemical printing system of the present invention;

FIG. 2 illustrates a second embodiment of the dual mode printing system featuring a salt bridge for overcoming the counter-marking problem; and

FIG. 3 shows a further embodiment of the invention illustrating another form of the salt bridge.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 illustrates one embodiment of the permanent or erasable electro-chemical printing system of the present invention. Recording medium 1, which may be porous paper, is positioned over a conductive base 4 of platinum, gold or platinum or gold plated mylar or epoxy boards. Other suitable conductive materials may be used for the base. The recording medium, which may for example, be in the form of a continuous roll of paper (not shown) with the paper being unrolled and pulled across the base 4, as needed or individual sheets or a continuous loop, is impregnated with a conductive salt such as potassium fluoride, ammonium fluoride, ammonium oxalate or the like, a reducing agent such as ascorbic acid, stannous chloride, stannous sulfate or the like and an electrochromic material such as a pH indicator or a Redox system. Preferably, an electrochromic material is used which produces a color in response to a basic condition of the electrolyte. Examples of suitable pH indicators are given in the above referenced Solar patent.

To effect either a permanent or an erasable mark, there is provided a silver or silver alloy marking element 8 coupled to reversible polarity sources 10 and 14 through a rotatable conductive electrode element holder 7. The reversible polarity sources 10 and 14 are illustrated as being formed by pairs of batteries 9, 11 and 13, 15. In fact, any D.C. source of potential which can reverse the polarity of its out-put potential may be used. It should be noted that the electrode element 8 is electrically connected to only one of the sources 10, 14 at any instant of time to accomplish marking or erasing. The significance of the provision of the two reversible polarity sources will be explained below. Also attached to the holder 7 is an erase electrode element 6 made of platinum or its alloys. Two reference electrodes, one used to the exclusion of the other, are provided in the form of electrode 12 positioned over a sacrificial area 2 of the recording medium 1 and the conductive base 4.

To effect a permanent mark, the holder 7 is rotated so that the silver electrode element 8 is in contact with the recording medium 1 and either switch 16 or 20 is closed so that the silver electrode is provided with a potential positive with respect to the reference electrode. If switch 16 is closed, the reference electrode takes the form of the conductive base 4, while if switch 20 is closed, the reference electrode takes the form of electrode 12. When switch 16 is closed, current will flow directly through the thickness of the recording medium. Since the distance between the reference electrode in the form of base 4 and marking electrode element 8 is small, a dense black mark will appear. On the other hand, if switch 20 is closed, the distance between the marking electrode element and reference electrode is increased, thereby decreasing the conductivity between electrodes. As a result, a less dense mark may appear. In either case, the mark appears as a result of the creation of positive silver ions which flow to the paper and are there reduced by the reducing agent back to metal form.

To provide a non-permanent or erasable mark, the same silver electrode element 8 may be used. In this case, either switch 18 or 22 would be closed so that the marking electrode element 8 appears at a negative potential with respect to the reference electrode. When switch 18 is closed, the top surface of the recording medium 1 in the vicinity of the electrode element 8 becomes alkaline. This condition is noted by a color mark produced as a result of including an electrochromic material in the medium impregnant. The color of this erasable mark will generally differ from that provided as a result of a permanent mark. The particular color will depend upon the particular electrochromic material used.

To erase a non-permanent mark, holder 7 is rotated so that the erase electrode element 6 is positioned in contact with the recording medium 1. In addition, switch 20 would be closed whereby electrode element 6 is at a potential positive with respect to reference electrode 12. When this occurs, the erasable mark produced by the silver electrode element 8 is erased while a counter-mark is produced in the sacrificial area 2 in the vicinity of the reference electrode 12. Reference electrode 4 would not be used during the erasing process since recording medium 1 is translucent and thus a counter-mark produced on the bottom surface of me-

dium 1 during the erasing process would be visible from the top surface.

A difficulty may arise if an erasable mark is produced using the conductive base 4 as the reference electrode. As previously set forth, in such a case, the conductivity between the marking electrode element 8 and the base 4 is strong and thus an intense mark would be produced. To effect erasing, reference electrode 12 must be used for the reasons indicated above. Since the distance between electrode 12 and the erase electrode element 6 is much greater than the distance between electrode element 8 and base 4, the conductivity decreases and thus unless the potential of battery 14 is made substantially greater than that of battery 9, a complete erasure may not result. Therefore, it would be preferable to use source 14 when creating and erasing erasable marks. On the other hand, it may be preferable to use source 10 and base 4 as the reference electrode when producing permanent marks.

Thus, the purpose for the dual reversible sources 10 and 14 becomes clear. Although their use is not essential to the primary teachings of the present invention, they do provide an advantageous flexibility in the system. When not required, source 10 may be removed and both permanent or erasable markings produced using only source 14 and reference electrode 12.

Although the marking electrode element 8 has been specified as consisting of silver or its alloys, this electrode can be composed of any metal which dissolves releasing ions into the recording medium. Among these metals, in addition to silver, are molybdenum and chromium. The reference electrode has been indicated as being either of gold or platinum. Other materials may be utilized such as stainless steel, copper, nickel or palladium. Further, it is also possible to use the erase electrode element 6 as a marking electrode for producing erasable marks.

FIG. 2 illustrates a second embodiment of the invention wherein the problems associated with the use of a sacrificial area on the recording medium are alleviated. As will be recalled from above, when a non-permanent mark is erased using the system illustrated in FIG. 1, a sacrificial area 2 must be provided so that the counter-mark does not appear in the recording area. To solve the counter-mark problem without the use of a sacrificial area, the embodiment of FIG. 2 is provided. Like elements in FIG. 1 and FIG. 2 carry common numerical designations. FIG. 2 differs from FIG. 1 in the provision of a non-metallic conductive interface 26 between the conductive base 4 acting as a reference electrode and recording medium 1. This conductive non-metallic interface is preferably comprised of a salt bridge containing an electrolyte but no electrochromic material. The salt bridge provides a high conductivity non-metallic reference terminal in contact with the recording medium and this new terminal will produce no mark on the medium regardless of its polarity with respect to the erase electrode.

The salt bridge may be a system formed of three components, water, a conductive salt (electrolyte) and an organic protein that gels, such as gelatin or agar. Depending upon the relative amounts of salt and agar, different consistencies and conductivity can be obtained. Excellent salt bridges are obtained using 5 grams agar and 30 grams calcium chloride per 100 grams of water. Other salts are known that can replace the chloride ions such as nitrates, sulfates and fluorides. As a matter

of fact, fluoride can be used as a common electrolyte for both the conductivity on the paper, that is, the recording medium and the salt bridge. Formation of the salt bridge using these materials can be accomplished by heating distilled water to the boiling point, adding agar until a perfect solution is formed and then the required amount of conductive salt. The bridge can be applied to the conductive base 4 as a thin film and let cool to harden. Thus, the salt bridge is formed of a solidifying gel containing the electrolyte which provides excellent conductivity while not causing markings on the recording medium at either polarity.

To protect the salt bridge against physical damage which may occur as the recording medium passes thereover, there may be provided a conductive non-metallic protective film situated between the salt bridge and the recording medium. This protective film may take the form of a layer of wet paper or cellophane.

In operation of the system of FIG. 2, permanent markings can be formed in the manner disclosed with respect to FIG. 1. That is, switch 16 is closed and marking electrode element 8 is placed in contact with the recording medium 1. Since the marking electrode element 8 is at a positive potential with respect to the reference electrode, in the form of base 4 and salt bridge layer 26, ions of the electrode material are released into the paper where they are reformed into the metal to produce a permanent mark. Erasable marks are provided by opening switch 16, closing switch 18, and retaining electrode element 8 in contact with the recording medium 1. In this situation, electrode element 8 is at a potential negative with respect to the reference electrode, causing the area on the top surface of the medium 1 in the vicinity of electrode element 8 to become alkaline. Due to the electrochromic material in the medium, a color mark appears. To erase this non-permanent color mark, holder 7 is rotated so that erase electrode element 6 is in contact with the medium 1 and switch 16 is closed. Since the erase electrode element 6 is at a positive potential with respect to the reference electrode, the area about the electrode becomes acidic and the color mark disappears. Were it not for the non-metallic conductive interface 26, the underside of recording medium 1 would be in contact with the metallic base 4 and a counter-mark would appear. However, the imposition of the interface 26 containing no color indicators, prevents a counter-mark from appearing.

FIG. 3 shows a third embodiment of the invention wherein both the marking/erasing electrode and the reference electrode are located close to each other on the same surface of the recording medium 1. Like elements in FIGS. 1, 2 and 3 are designated by common numerical designators. The marking/erasing electrode 30 may be formed of platinum or its alloys and is located in a hollow core of a cylinder formed of insulating materials such as teflon. Surrounding this core is a cylindrically shaped salt bridge 34. Base 4 in this instance may be formed of non-conductive material or an insulation layer could be positioned between it and medium 1. Operation of this configuration is identical to the operation of the embodiment of FIG. 2. With electrode 30 being platinum only erasable marks can be made. Permanent marks can be provided by interchanging a silver electrode for the platinum electrode.

In operation, when the inside platinum electrode 30 is negative with respect to the potential of the conduc-

tive salt bridge 34, marking occurs. When the polarity is reversed, and the inside platinum electrode becomes positive with respect to the salt bridge, erasing occurs with no counter-marking. Such an arrangement permits the marking and erasing at low voltages because of the close proximity between the electrode 30 and the reference electrode 34.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. An electro-chemical printing system comprising:
 - a recording medium impregnated with a conductive salt, a reducing agent and an electrochromic material,
 - a marking electrode composed of a metal that dissolves releasing ions when a first polarity potential difference is applied between it and a reference electrode for forming a permanent mark on said medium, said marking electrode producing an erasable mark when a second polarity potential difference, opposite said first polarity potential difference, is applied between it and said reference electrode,
 - an erase electrode,
 - a reference electrode, and
 - a reversible polarity potential source coupled between said marking and erase electrodes and said reference electrode.
2. The electro-chemical printing system of claim 1 wherein said marking electrode is composed of silver and said erase and reference electrodes are composed

of platinum.

3. The electro-chemical printing system of claim 2 wherein said electrochromic material is a pH indicator.

4. The electro-chemical printing system of claim 2 wherein said electrochromic material is a Redox system.

5. The electro-chemical printing system of claim 2 further including a conductive rotatable electrode holder holding said marking and erase electrodes and being coupled to said potential source.

6. An electro-chemical printing system comprising: a recording medium formed of a porous material impregnated with potassium fluoride, ascorbic acid and an electrochromic material,

a silver mark electrode, for generating permanent or erasable marks on said medium and positioned on a first surface thereof

a platinum mark/erase electrode positioned on said first surface

a reference electrode positioned on said medium, and

a reversible polarity potential source coupled between said reference electrode and said mark and mark/erase electrodes,

whereby a permanent mark is produced by said mark electrode when it is at a positive potential with respect to said reference electrode and an erasable mark is produced by said mark electrode when it is at a negative potential with respect to said reference electrode.

7. The printing system of claim 6 further including a rotatable electrode holder wherein are mounted said mark and mark/erase electrodes.

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