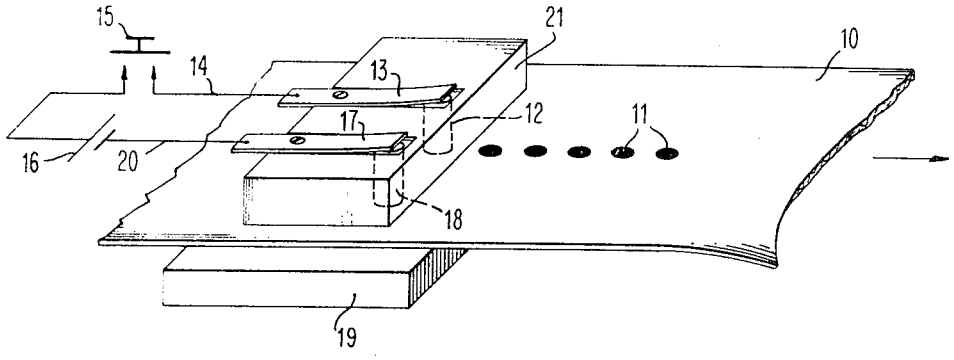
Aug. 21, 1973 A. AMBROSIA ET AL 3,753,869
ELECTROCHEMICAL RECORDING METHOD
Filed Dec. 20. 1971

FIG. 1



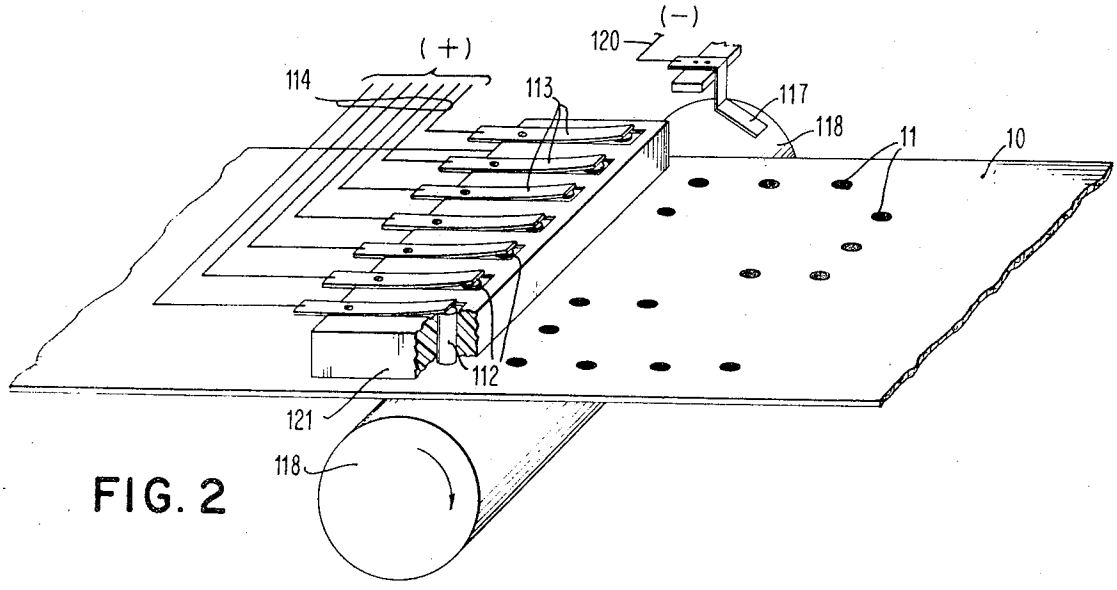


FIG. 2

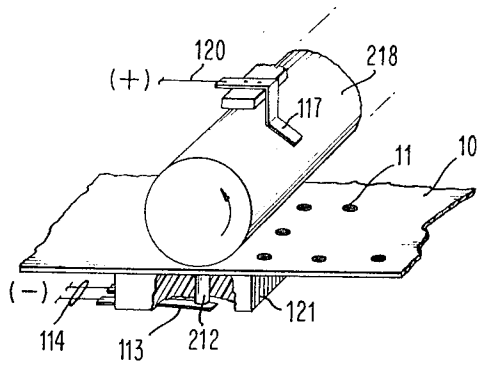


FIG. 3

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3,753,869

ELECTROCHEMICAL RECORDING METHOD

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Int. Cl. B41M 5/20
U.S. Cl. 204—2 18 Claims

ABSTRACT OF THE DISCLOSURE

A dot matrix electrochemical recorder printing by electrolysis which includes plural silver electrode pins which rub against a paper recording medium impregnated with a conductive salt selected from an alkali, ammonium fluoride and ammonium oxalate alone with a reducing agent selected from ascorbic acid, stannous chloride, stannous sulfate, potassium hydroxide, and some reducing phenols and amines, such as paraaminophenol.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to electrochemical processes and products and more particularly to electroprinting by electrolysis.

Description of the prior art

Heretofore printing by electrolysis has included paper media impregnated with an electrolytically-conducting solution containing water, a soluble salt such as alkali metal or ammonium nitrates and sulfates plus a reducing agent such as ascorbic acid or erythorbic acid. An anode of silver or its alloys with a cathode of platinum, platinum alloys, steel, etc. were taught.

Alternatively, paper has been impregnated with alkali metal halides of potassium bromide and iodide plus ammonium nitrate with a reducing agent of pyrocatechin, formaldehyde, gallic acid, acetaldehyde, "hydroquinine," pyrogallol, etc. Metol and sodium sulfite and ammonium nitrate were employed to prevent oxidation of the pyrocatechin reducing agent by air.

Other prior art has required external application of heat to render the medium markable electrically.

Prior art includes U.S. patents as follows: 3,402,109; 2,063,992; 2,776,251; and 1,918,492.

Alkali chlorides, bromides and iodides fail to provide dark or black printing because they form an insoluble yellow film at the electrode. We have discovered that those chemicals interfere with providing a good black mark by interfering with the reduction of the silver. They bind the silver into an insoluble compound, thereby inhibiting printing of marks which are acceptable. Marks so produced are illegible.

With respect to reducing agents used heretofore, pyrocatechin is a strong reducer but it is very unstable and will turn paper yellow. Gallic acid is not readily soluble and would tend to produce yellowing of paper. "Hydroquinine" produces a strong discoloration in paper and is very unstable. Pyrogallol has similar problems to pyrocatechin, discolors radically turning paper brown and is toxic. Erythorbic acid is unstable. Formaldehyde is toxic, very volatile and hard to retain on paper, and has a strong objectionable odor. Acetaldehyde has similar problems to formaldehyde.

Sulfate silver salts are only slightly soluble and tend to remove silver from solution tending to limit reduction of silver. Thus soluble alkali or ammonium sulfates are undesirable. Nitrates oxidize the silver ions and interfere with reduction of silver. Thus alkali or ammonium nitrates are also undesirable as soluble salts.

SUMMARY OF THE INVENTION

In accordance with our invention, a porous electrochemical recording medium is provided for recording data. The porous medium is impregnated with an aqueous solution of a conductive salt selected from potassium fluoride, sodium fluoride, lithium fluoride, ammonium fluoride and ammonium oxalate.

A reducing agent can be included in the medium selected from ascorbic acid, stannous chloride, stannous sulfate and potassium hydroxide and some reducing phenols and amines to provide immediate reduction of cations.

In a preferred form of this invention the porous medium is impregnated with a percentage of material to water by weight of 5–100% (preferably 20%) of hydrated $KF2H_2O$ and 1–10% (preferably 2%) of ascorbic acid. In a further preferred embodiment 0.1–2% (preferably 0.5%) of sodium sulfite is employed.

In another form a porous electrochemical latent marking recording medium is provided for providing recordings of data. The porous medium is impregnated with an aqueous solution of a conductive salt selected from fluorides of potassium, sodium and lithium as well as ammonium fluoride or oxalate. Such recordings may be latent images which can yield marks upon adding a reducing agent or upon hydrolysis.

An object of this invention is to provide marks on an electrochemical recording medium with improved printing quality.

Another object is to minimize discoloration of the recording medium.

Another object is fast printing.

A further object is prolonged conductivity of the medium.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows electrical marking apparatus for marking a medium impregnated with an electrochemical solution with dots selectively.

FIG. 2 shows apparatus for providing plural dot markings with plural electrodes and a lower drive roller electrode.

FIG. 3 shows apparatus comprising the reverse of FIG. 2, with the plural electrodes below and the drive roller electrode marking the top of the recording medium.

DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 shows a porous recording paper medium **10** supported on plate **19**. Marks in the form of dots **11** have been made on medium **10** by periodically passing electrical current through positive electrode **12** which is in electrical contact with spring **13** at its opposite end, which is connected by wire **14**, and switch **15** to the positive terminal of battery **16**. The negative terminal of battery **16** is connected by line **20** through spring **17** to pin **18** which contacts the medium **10** to provide a complete "electrochemical cell" through the electrolyte contained in the medium **10**. The electrode **12** is composed of silver, a metal or a metalloid that dissolves releasing ions into the paper when a potential is applied between it and the reference electrode.

In FIG. 2 a plurality of positive lines are connected through springs **113** to marking pins **112** which are equally spaced across medium **10** in carrier **121**. The medium **10** is supported by drive roller-electrode **118** which is connected through contact strip **117** and line **120** to negative potential. Each pin **112** is periodically and selectively energized to mark the medium **10**.

FIG. 3 shows a version in which the potentials of the electrodes in FIG. 2 are reversed to place the roller on

top. The roller **218** will be a marking electrode (silver, etc.).

The recording medium **10** preferably comprises a porous paper, which can retain strength when impregnated with an aqueous solution of a conductive salt, a reducer and a stabilizer.

The electrochemical marking system of this invention is similar to an electrochemical cell. There is an electrically soluble electrode **12** of silver, molybdenum or lead. There is an electrolyte and a reference electrode **18**. The paper, substrate or medium **10** is carrier for the electrolyte. In the systems of FIGS. 2 and 3 a printing system can use two soluble electrodes simultaneously to intensify the marking action from both sides of the paper **10**.

This depends upon the nature of the electrodes. Metals tend to dissolve in suitable electrolytes when they are pulsed anodically yielding positive ions to the paper (Ag^+) whereas nonmetals dissolve and produce marks on the paper when they are pulsed cathodically yielding negative ions (PbO_2^-, TeO_2^-). Therefore a cell combining both kinds of electrodes will be marking at both terminals on both paper sides.

Referring specifically to a silver - fluoride - ascorbic acid printing cell, the mechanism of the marking action involves two consecutive steps:

(A) Electrical dissolution of silver to silver ions which enter into the paper.
(B) Reduction of silver ions back to metal form (printed mark).

The fact that the two steps of the reactions above occur in series is important, because the nature of the electrolyte is such that it will enhance and will not interfere with either electrochemical mechanism.

THE CHEMICAL (ELECTROLYTE) SYSTEM

The chemical system is a liquid (aqueous) solution which is applied to the paper. This liquid is made up of a mixture of three components: (a) conductive salt; (b) silver reducing compound and (c) stabilizer.

The recommended composition is as follows:

(a) Conductive salt 20% hydrated potassium fluoride ($KF.2H_2O$)
(b) Silver reducing compound 2% ascorbic acid
(c) Sodium sulfite 0.5%

The percentages relate to the weight of components with respect to the weight of water employed.

(a) The conductive salt

Potassium fluoride which is present in the system in a large amount (20 grams in 100 grams of water) gives the paper good conductivity. Therefore, when a small voltage is applied between the silver and reference electrodes **12** and **18** current flows easily across the paper. As a result of this current flow, silver is dissolved from the positive electrode **12** in the form of silver ions (Ag^+). If no other substance were present in the paper, the paper location in which the silver ion was generated would not be visible (although it would remain there as a latent image). To print an immediately visible spot, a reducing substance is necessary.

(b) Silver reducing compound

Silver reduction is the process by which the soluble, colorless silver ion is converted to insoluble (black) silver metal

$$Ag^+ + e = A_g \text{ (metal)}$$

There are a few compounds that can produce such an effect. They are described below.

Vitamin C (ascorbic acid) is an excellent reducing compound, under certain conditions. Ascorbic acid is very stable in solid form, but when dissolved in water, it tends to decompose slowly with time producing a yellow color. This decomposition is mainly due to the action of oxygen of the air dissolved in the water. The optimum amount of ascorbic acid in the system is: 2 grams of ascorbic acid in 100 grams of water (already containing the conductive salt, 20 grams of potassium fluoride). However, a stabilizer has to be added to the system to prevent the air oxidation of ascorbic acid.

(c) Stabilizer

This is a substance that should be present in very small amounts to prevent the air decomposition of the ascorbic acid. It was found that sodium sulfite (0.5 gram in 100 grams of water) gives a stable printing system.

The ratio of ascorbic acid to sodium sulfite is very important and it should be held at about 3 to 4. If excess ascorbic acid is present, discoloration of the paper occurs (yellowing). If excess sodium sulfite is present, the printing reaction is very slow.

RANGES OF COMPOSITION USEABLE

It has to be understood that the above is an optimum system composition. However, the printing system will still generate acceptable marks varying the composition in the following ranges:

Potassium fluoride: between 5% to 100% of water in grams
Ascorbic acid: between 1% to 10% of water in grams
Sodium sulfite: between 0.1% to 2% of water in grams

ALTERNATIVES IN THE CHEMICAL COMPOSITION

There are several compounds that can enter in the composition of the chemical system (either performing the function of conductive salt, reducing compound or stabilizer), to replace the described above.

The conductive salt can be described in general as a substance highly soluble in water and which also gives a silver salt. Potassium fluoride, sodium fluoride, ammonium fluoride, lithium fluoride (in general all soluble fluorides) perform well as conductive salts. Conductive salts of high solubility in water but that form insoluble silver salts (such as sodium or potassium chloride, sodium or potassium iodide) are not very suitable.

In fact, when silver is the active printing electrode **12**, no other alkali halide will work in the system as a conductive electrolyte. Further, even traces of other alkali halides (chloride, bromide or iodide) will interfere preventing or curtailing the printing action. The reason for this is (as stated above) that any alkali halide (chloride, bromide or iodide), except fluoride, binds the silver ions into an insoluble compound and stops the printing reaction.

The electrolyte formulation should be such that it will provide free existence of silver ions on the paper, without binding them into insoluble silver salts of undissociated silver complexes. In other words, the electrolyte should be such that it will form a highly soluble and ionized silver salt. Fluorides are compounds that give the most soluble silver salts known, whereas chloride, bromide, and iodide give very insoluble, un-ionized silver salts. Other species that yield soluble silver compounds yet in complex undissociated (non-ionized) form cannot be present either. Examples of the latter are EDTA, carbonates, phosphates and sulfides. This restriction defines the electrolyte composition within narrow limits, because there are only few known silver species that meet the re-

quirement without discoloring the paper. Another species that works well is ammonium oxalate, although it reacts more slowly than fluorides.

The electrolyte (chemical system) should be free of ions which react with ascorbic acid, thus preventing step B (reduction of silver). Therefore, oxidants such as nitrates, perchlorates and chlorates, in the electrolyte would stop the marking action because they will destroy the ascorbic acid which is involved in reduction of silver ions back to metal form in the paper.

We have found experimentally that carbonates, phosphates, nitrates, chlorides, etc. fail to produce the effects of the fluorides, i.e. speed of printing, black printing and prolonged conductivity.

The system should provide remnant conductivity on the paper so that no characters are lost when printing is stopped momentarily. Hydrated fluoride salts provide this property.

For greatest speed the electrolyte should provide both electrical dissolution (step A) and reduction of the ions (step B).

The fluorides catalyze the anodic silver dissolution permitting a printing reaction in the microsecond range.

THE SILVER REDUCING COMPOUND (ALTERNATIVES)

As stated above, ascorbic acid is most suitable as a reducing compound.

Such a compound in general should be a substance that is stable in aqueous solutions and that is capable of converting silver ions into metallic silver in milliseconds. The reducing compound can be either inorganic or organic.

Among the inorganic reducers, a stable substance capable of reducing metals ions to a lower valence state, can perform this function. Stannous chloride, stannous sulfate, or traces of potassium hydroxide can replace the ascorbic acid.

Other organic compounds suitable as substitutes for ascorbic acid include stable reducing phenols and amines, in place of ascorbic acid which do not discolor paper. Such substitutes include paraaminophenol, phenylhydrazine and metol (methyl-2-paraaminophenol).

THE STABILIZER (ALTERNATIVES)

This should be a compound that prevents oxidation by air of the reducer. Sodium sulfite is optimum. However, very good results were obtained by replacing sodium sulfite by sodium hydrosulfite or paraformaldehyde.

ELECTRICAL SYSTEM

Using the recommended formulation, excellent black printing is achieved using 9 volt, 1 millisecond pulses. At higher voltages the speed of the reaction increases. For example, at 35 volts, reaction times of 200 nanoseconds are achieved.

ELECTRODES

The system includes a printing electrode (e.g. silver) and a reference electrode. To achieve dot printing at least one of the electrodes (printing or reference) has to assume a discrete shape (stylus).

In general, the printing electrode **12** can be composed of a metal or a metalloid that dissolves releasing ions into the paper when a potential is applied between it and a reference electrode. Among the metals are silver, molybdenum (dark blue mark), and chromium (yellow mark). In the case of using a metal as the marking electrode, this should be the positive terminal **12** of the printing cell.

Metalloids are tellurium, tellurium, lead-alloys, and tin-lead alloys. In this case, the marking electrode is the negative terminal of the printing cell.

REFERENCE ELECTRODE

The nature of the reference electrode **18** is of secondary importance. Preferably it should be made of a noncorroding material, such as stainless steel, gold, platinum, etc. However, other materials, such as copper, nickel, palladium, and even silver are satisfactory.

Both the "active" (printing) anode **12** and "passive" (reference) cathode **18** can be made of silver.

This has the advantage that it allows printing at will on either side of the paper. It may also be useful in the design of special electronic logic circuitry using transistorized drivers of either polarity. For example, in FIG. 2 or FIG. 3 the print material may be extracted either from a single large silver surface or from discrete styli.

CATHODIC PRINTING

The printing material (active electrode) can also be cathodically dissolved. Lead-tin alloys produce good marks. In this case, there is need only of potassium fluoride in the electrolyte because as soon as Pb dissolves as plumbite ion (PbO_2^-), thereafter it immediately hydrolyzes back into lead metal. The presence of tin on the electrode enhances the dissolution of lead.

DUAL PRINTING ELECTRODES

The combination into a single system of anodic and cathodic dissolution creates marks on both sides of the paper simultaneously. For example, the positive silver electrode and the negative tellurium electrode with KF and ascorbic acid operate well. A lead-tin alloy can be substituted.

Systems such as those above can be used to intensify the marking action produced at very low voltages (under 2 volts).

PRINTING ARRANGEMENTS

In the context of the prior art shown, only configurations using discrete silver electrodes have been used, where the size of the marked spot depends on the surface of the silver electrode. Printing of dots is achieved, independent of the active electrode area and in spite of the fact that the printed material is carried over a large single silver surface such as that of drum or roller **218** in FIG. 2. Referring to FIG. 3, one would expect that when the large silver roller **218** is the active (+) electrode, a spot as large as the surface of the paper in contact with the roller would be obtained. However, due to the peculiar properties of electrochemical systems involving a plane and a point electrode, the distribution of the lines of force is such that they concentrate around the point electrode **212**. Such electrochemical fields emanating from a point permit controlling the size of marks by controlling the size of the inert electrode **112**.

Electrolyte	Pulse time, msec.	Pulse voltage, volts	Mark density	Percent mark density transmittance
20% KF	1	10	0.35	45
2%-ascorbic acid	10	10	0.77	17
Do	1	40	0.92	12
20% Na NO_3	1	10	0.23	58
2%-ascorbic acid	10	10	0.52	30
Do	1	40	0.62	24
20% Na Br	1	10	No mark	
2%-ascorbic acid	10	10	No mark	
Do	1	40	No mark	
20% NaI	1	10	No mark	
2% ascorbic acid	10	10	No mark	
Do	1	40	No mark	
20% Na Cl	1	10	No mark	
2%-ascorbic acid	10	10	No mark	
Do	1	40	No mark	

The data in the above table was obtained by treating various samples of identical paper with equivalent amounts of the chemicals used. Then, marks were made using a silver electrode, with a system including silver as the positive electrode, plus paper containing the electrolyte, and including platinum as the negative electrode.

The resulting marks were analyzed for density and transparency with an optical densitometer. It is seen that highest density and faster reaction speed are obtained with the disclosed chemicals.

What is claimed is:

1. A recording medium and a silver marking electrode comprising,
   a silver electrode,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein an aqueous solution of a conductive salt as the electrolyte selected from the group consisting essentially of ammonium fluoride, ammonium oxalate and the fluorides of potassium, sodium, and lithium, said solution including a reducing agent for reducing cations free from oxidizing agents for minimizing time for reducing cations.

2. A recording medium and an electrode for marking said medium comprising,
   a silver electrode,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein a solution of 5% to 100% hydrated potassium fluoride $KF2H_2O$ as the electrolyte, 1% to 10% ascorbic acid as weight percentages of the weight of water in the solution for a reducing agent for cations, said solution being substantially free from oxidizing agents, for minimizing time for reducing cations.

3. A recording medium and electrode in accordance with claim 2 wherein said hydrated potassium fluoride comprises substantially 20 grams per 100 grams of water, and said ascorbic acid comprises substantially 2 grams per 100 grams of water.

4. A recording medium in accordance with claim 2 wherein sodium sulfite is included as 0.5 gram of sodium sulfite per 100 grams of water.

5. A recording medium in accordance with claim 2 wherein said solution includes 0.1% to 2% of sodium sulfite.

6. A recording medium and a silver marking electrode comprising,
   a silver electrode,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein an aqueous solution of a conductive salt as the electrolyte selected from the group consisting essentially of ammonium fluoride, ammonium oxalate and the fluorides of potassium, sodium, and lithium, in combination with an aqueous solution of a reducing agent for reducing cations selected from the group consisting essentially of stannous chloride, stannous sulfate, ascorbic acid, potassium hydroxide, stable reducing phenols and stable reducing amines which avoid staining said medium, said solution and said reducing agent being substantially free from oxidizing agents in order to minimize time for reducing cations.

7. A recording medium and a silver marking electrode comprising,
   a silver electrode,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein an aqueous solution of a conductive salt as the electrolyte selected from the group consisting essentially of ammonium fluoride, ammonium oxalate and the fluorides of potassium, sodium, and lithium, in combination with an aqueous solution of a reducing agent selected from the group consisting essentially of stannous chloride, stannous sulfate, ascorbic acid, potassium hydroxide, paraaminophenol, phenylhydrazine and metol (methyl-2-paraaminophenol), said solution and said reducing agent being substantially free from oxidizing agents in order to minimize time for reducing cations.

8. A recording medium and electrode in accordance with claim 1 wherein said reducing compound is free from the oxidizing agents consisting essentially of nitrates, perchlorates, and chlorates.

9. A recording medium and electrode in accordance with claim 8 wherein said reducing compound comprises ascorbic acid.

10. A recording medium and electrode in accordance with claim 8 wherein said solution includes sodium sulfite.

11. A recording medium and electrode in accordance with claim 9 wherein said solution includes sodium sulfite.

12. A recording medium and electrode in accordance with claim 2 wherein said reducing agent is substantially free from oxidizing agents including nitrates, perchlorates and chlorates.

13. A recording medium comprising,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein an aqueous solution of a conductive salt as the electrolyte selected from the group consisting essentially of ammonium fluoride and ammonium oxalate.

14. A recording medium in accordance with claim 13 wherein said solution includes reducing cations free from oxidizing agents.

15. A recording medium comprising,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein an aqueous solution of a conductive salt as the electrolyte selected from the group consisting essentially of ammonium fluoride and ammonium oxalate in combination with an aqueous solution of a reducing agent selected from the group consisting essentially of stannous chloride, stannous sulfate, ascorbic acid, potassium hydroxide, stable reducing phenols and stable reducing amines which avoid staining said medium.

16. A recording medium comprising,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein an aqueous solution of a conductive salt as the electrolyte selected from the group consisting essentially of ammonium fluoride and ammonium oxalate, in combination with an aqueous solution of a reducing agent selected from the group consisting essentially of stannous chloride, stannous sulfate, ascorbic acid, potassium hydroxide, paraaminophenol, phenylhydrazine and metol (methyl-2-paraaminophenol).

17. A recording medium comprising,
   a porous electrochemical medium for providing markings for recording data, said porous medium including impregnated therein an aqueous solution of a conductive salt of high solubility in water serving as the electrolyte and which yields a soluble compound when the anion combines with a silver electrode intended for providing markings to record data on said medium, said anion being selected from anions having a low tendency to oxidize silver and providing a soluble compound in water with silver, and said solution including a reducing agent for reducing silver.

18. A recording medium and marking electrode comprising,
   a silver marking electrode,
   a porous electrochemical medium for recording data with said silver marking electrode, said porous medium including impregnated therein an aqueous solu-

tion of a conductive electrolyte salt selected from the group consisting of ammonium fluoride, ammonium oxalate and the fluorides of potassium, sodium, and lithium, said electrolyte anions forming a soluble compound with silver in said medium,

said solution including ascorbic acid as a reducing agent whereby silver ions passing into said electrolyte from marking electrodes remain in solution in said electrolyte and are reduced to metal form in said medium by said ascorbic acid at high speed without delay because of the solubility and ionization of silver fluoride and silver oxalate.

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