United States Patent

[11] **3,632,484**

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[21] Appl. No. **6,326**
[22] Filed **Jan. 27, 1970**
[45] Patented **Jan. 4, 1972**

[54] **ELECTROLYTIC FACSIMILE-RECORDING PROCESS**
13 Claims, No Drawings

[52] **U.S. Cl.** **204/2**
[51] **Int. Cl.** **B21h 1/20**
[50] **Field of Search** 204/2

[56] **References Cited**

UNITED STATES PATENTS

2,063,922	12/1936	Elsey	204/2
3,332,857	10/1967	Lieblich	204/2
3,349,013	10/1967	Barnes	204/2

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ABSTRACT: Process of electrolytic facsimile-recording employing a silver or silver-alloy anode and a recording medium comprising paper impregnated with an aqueous solution of a formaldehyde reducing agent, wherein the impregnant includes a substance which will render soluble silver salts normally present during electrolytic facsimile recording in an insoluble form. The solubilizing substance may be an alkali metal salt of thiosulfate, thiocyanate or cyanide or an excess quantity of sodium formaldehyde sulfoxylate.

ELECTROLYTIC FACSIMILE-RECORDING PROCESS

This invention relates to the art of electrolytic recording, and in particular to an improved electrolytic recording medium or paper.

Recording paper of the electrolytic type is generally marked by passing the paper between a positive eroding metal anode electrode and a negative noneroding cathode electrode. The paper is impregnated with an electrolytically conducting solution containing a marking agent. When a voltage is applied between the electrodes and current is passed through the recording paper, metal ions are introduced into the paper from the anode and reacted with one or more of the ingredients of the paper impregnant to form a colored mark on the recording paper.

In order to be acceptable for facsimile-recording purposes, the recording paper preferably should be white initially and should have the ability to produce marks having a density which is at least close in linear relationship to the current passed through the paper. The density of the marked area should be variable uniformly in a range from white for zero current flow through grays for currents of intermediate magnitude to black for currents of maximum value. The mark preferably should be black so as to provide a good contrast with the white background.

There should also be a minimum of bleeding or fringing of the mark so as to provide good resolution. The unmarked paper while stored in moist condition in sealed containers for extended periods of time prior to use should remain stable without chemical decomposition of its ingredients which would cause discoloration of the paper or affect the reproducibility of results without recorder adjustment. Further, the marked recording paper should not become discolored, give off unpleasant or other odors, or be subject to the transfer of the mark to adjacent materials. The marked recording paper should be insensitive to light even after being repeatedly run through any of the conventional duplicating machines involving exposure to ultraviolet or other strong light sources.

In the prior art Elsey U.S. Pat. No. 2,063,922 has taught the use of silver anodes with a paper containing formaldehyde. This is of little practical utility because of the volatility of formaldehyde, and because the mark is diffuse.

In two more recent patents, Lieblich U.S. Pat. No. 3,332,857 and Barnes et al. U.S. Pat. No. 3,349,013, modifications have been proposed to overcome the aforementioned difficulties with the use of formaldehyde per se as taught by Elsey. Lieblich suggests the use of bisulfite addition compounds of formaldehyde and both Lieblich and Barnes et al. have taught the use of formaldehyde sulfoxylates. These materials will be generally referred to herein and in the appended claims as formaldehyde reducing agents.

Both of the latter disclosures are of practical utility but suffer from limitations of recording speed in the case of sodium formaldehyde bisulfite, and in short storage life in the case of sulfoxylate.

Despite the advantages which are claimed for formulations in the above disclosures, over the prior art of producing the mark by a steel anode with a paper containing hydroxyphenolic compounds; the latter is still used for the greater part of the commercial market.

This invention relates to the art of producing print by electrolysis of a silver or silver alloy anode into a moist paper containing a formaldehyde reducing agent.

It has been found that the novel effect that many formaldehyde reducing agents can be rendered commercially useful and effective if compounds which readily form precipitates with silver salts in aqueous solutions are excluded or rendered inactive. This is contrary to the teaching of Elsey who attempted deliberately to precipitate the silver salts formed during electrolysis.

Copending patent application Ser. No. 723,568 now U.S. Pat. No. 3,539,457, discloses the use of calcium and strontium salts of formaldehyde sulfoxylates which have this effect by causing the precipitation of sulfites formed in the decomposition of the sulfoxylate.

It has now been found that precipitation is not the only method by which the interference of these decomposition products may be avoided. Compounds which render soluble in water the sulfites and halides of silver, and which may be incorporated in the impregnant, are effective.

For example, if a paper is sensitized by impregnating it with the following solution:

Formaldehyde, Sodium Bisulfite Addition Compound		40 g.
Sodium nitrate		100 g.
Sodium carbonate		20 g.
Water	to make	1 liter

and an attempt is made to print on this paper by drawing it between a silver anode and a platinum cathode to which a voltage of 18 volts DC is applied, a mark is formed of optical density 0.5. The current is 0.10 ampere at first contact of the electrodes but falls rapidly to 0.04 amperes. The mark formed is considered to be insufficiently dense for normal printing.

By repeating this experiment except that 50 g. sodium thiosulfate is included in the solution, a mark is formed of optical density 1.2, and the current is 0.12 ampere throughout the printing process. Such a mark is ideal for printing.

It can be demonstrated that sodium thiosulfate has no printing properties per se by repeating the second experiment, but omitting the formaldehyde sodium bisulfite compound. No mark is formed.

It is well known that sodium thiosulfate solutions will dissolve silver salts which are insoluble in water, and this effect is used in photographic fixing. It is considered that the effect observed in the above experiment is due to a similar effect. In particular the sulfite of silver is only very slightly soluble in water but is soluble in aqueous solutions of thiosulfates, thiocyanates and cyanides. It has been established experimentally that the thiocyanates and cyanides exhibit the effect in recordings which were found with thiosulfate. Cyanides are of no practical value in the case of a paper which has to be handled, because of their toxicity, and in this regard it is preferred to use thiosulfates and thiocyanates of sodium and potassium, although cyanides may be useful in certain limited applications. Mixtures of these compounds are also effective.

An example of a recording paper which produces excellent print in commercial electrolytic recorders is:

Absorbent paper with the following solution:	1,000 grams, impregnated
Sodium nitrate	100 grams
Formaldehyde sodium bisulfite addition compound	40 grams
Sodium carbonate	20 grams
Sodium thiosulfate	60 grams
Water to make	1 liter

Other formaldehyde compounds behave similarly. In the case of sodium formaldehyde sulfoxylate, it is observed that papers prepared with low concentrations have excellent recording properties shortly after preparation, but that these properties deteriorate rapidly, even when the stabilizers reported by Barnes et al. are used. As the concentration is increased, the quality of print deteriorates but the stability of the paper improves. However, when thiosulfate or thiocyanate is added, the printing properties are excellent at the higher concentrations of sulfoxylate.

An example of such a paper is

Absorbent paper the following solution:	1,000 grams, impregnated with
Potassium nitrate	85 grams
Sodium formaldehyde sulfoxylate	132 grams
Sodium thiosulfate	52 grams
Sodium borate	23 grams
Water to make	1 liter

It is also found that very high concentrations of sodium formaldehyde sulfoxylate can be used, and papers with such formulations have excellent storage qualities.

Further, the unexpected effect that sodium formaldehyde sulfoxylate itself acts as a solubilizing agent for silver sulfite may be demonstrated by the following experiment:

Two solutions are prepared as follows:

	Solution A	Solution B
Sodium formaldehyde sulfoxylate	7.5 grams	15 grams
Sodium sulfite	2 grams	2 grams
Water to make	100 ml.	100 ml.

To each of these solutions was added a solution of 5 grams of silver nitrate in 100 ml. of water. It was observed that in the case of solution A, a white precipitate formed, the precipitate slowly turning black. In the case of solution B a slight precipitate formed, but immediately redissolved. The solution slowly became colored and deposited a fine, intensely black precipitate. This is interpreted as showing that excess sodium formaldehyde sulfoxylate will dissolve silver sulfite. This allows the complete reaction of the silver salt with the formaldehyde. In the case of solution A, particles of the precipitate react only at their surface.

Commercial sodium formaldehyde sulfoxylate contains a relatively large amount of sulfites, sulfates and sulfides. To operate effectively in these formulations, the commercial product must be purified. In the literature are described methods of recrystallization, none of which yields a product which is substantially better in this application than the original product. To provide a product suitable for the papers, a method of recrystallization has been developed. In accordance with this method, commercial sodium formaldehyde sulfoxylate is recrystallized by dissolving 2 kg. of the commercial product in 1 liter of 1 percent sodium carbonate solution by heating the mixture to 80° C. on a water bath. The resulting solution is filtered hot to remove insoluble impurities, and allowed to cool to room temperature in a closed vessel. The sodium formaldehyde sulfoxylate separates as ⅛–¼-inch transparent crystals, which are recovered by filtration. The purified sodium formaldehyde sulfoxylate is not dried, but is allowed to drain, and immediately made into the impregnant solution. By this method, the sodium carbonate retards decomposition of the sodium formaldehyde sulfoxylate during recrystallization and draining. In order to prepare an impregnant of exact composition it is necessary to assay the solution and to adjust the strength accordingly. This assay may be made by the well-known method of reducing iodine to iodide ions.

It has been determined that for proper operation of the effect three molecules of sodium formaldehyde sulfoxylate are required for each silver atom dissolved from the anode.

In a typical application where a recorder is printing at 300 lines per minute, each line is 0.012 inch wide, and the current is 250 milliamperes; it is calculated that the minimum concentration of sodium formaldehyde sulfoxylate in the impregnant is 120 g./l.

In the application of this solvation effect, and contrary to the teaching of Barnes et al., concentrations of sodium formaldehyde sulfoxylate in excess of 120 grams per liter are used in the impregnant.

The greater the concentration of sodium formaldehyde sulfoxylate, the longer is the life of the paper. The upper limit of concentration of sodium formaldehyde sulfoxylate is the limit of its solubility which is about 300 g./l. In order that the paper may lose some of its moisture without sodium formaldehyde sulfoxylate crystallizing, it is preferred to use less than 250 grams per liter. Within these limits of 130–250 grams per liter, a precise concentration is selected for each application according to the desired storage properties, and economic considerations.

A paper, for example, of the following formulation may be prepared:

Absorbent paper	1,000 grams, impregnated with the following solution:
Sodium formaldehyde sulfoxylate recrystallized	130 grams
Sodium nitrate	100 grams
Sodium carbonate	20 grams
Water to make	1 liter

An example of a recording medium having longer storage life than the above example above is:

Absorbent paper	1,000 grams, impregnated with the following solution:
Sodium formaldehyde sulfoxylate	250 grams
Sodium nitrate	45 grams
Sodium borate	10 grams
Water to make	1 liter

These papers have excellent recording characteristics. No aging period is required for the medium to reach maximum activity. The medium is ready for use as soon as the solution has saturated the fibers of the absorbent paper.

What is claimed is:

1. In a process of electrolytic recording employing an anode including silver and a recording medium comprising paper impregnated with an aqueous solution of a formaldehyde reducing agent; the improvement which comprises incorporating in said impregnant a substance which will render soluble silver salts normally present during electrolytic recording in an insoluble form, said substance being incorporated in sufficient quantity to solubilize said silver salts.

2. The improvement of claim 1 wherein said substance is selected from the group consisting of alkali metal thiosulfates, thiocyanates and cyanides and mixtures of same.

3. The improvement of claim 2 wherein said substance is present in from about 2–10percent by weight of the impregnant.

4. The improvement of claim 2 wherein said substance is selected from the group consisting of sodium and potassium thiosulfates.

5. The improvement of claim 2 wherein said substance is selected from the group consisting of sodium and potassium thiocyanates.

6. The improvement of claim 1 wherein said substance comprises sodium formaldehyde sulfoxylate in concentrations from about 13–25 percent by weight of the impregnant.

7. The improvement of claim 6 wherein said sodium formaldehyde sulfoxylate has been purified by recrystallization from an aqueous solution of an alkaline buffer to at least substantially eliminate sulfite, sulfate and sulfide salts therefrom.

8. A composition for an electrolytic recording medium for use in a recording process in which silver is electrolytically oxidized and subsequently deposited as a black or dark-colored precipitate, which comprises an absorbent paper impregnated with an aqueous solution of a substance which will render soluble silver salts normally present during electrolytic recording in an insoluble form, said substance being incorporated in sufficient quantity to solubilize said silver salts.

9. The composition of claim 8 wherein said substance is selected from the group consisting of alkali metal thiosulfates, thiocyanates and cyanides, and mixtures of the same.

10. The composition of claim 9 wherein said substance is present in from about 2–10 percent by weight of the impregnant.

11. The composition of claim 8 wherein said substance is selected from the group consisting of sodium and potassium thiosulfates.

12. The composition of claim 8 wherein said substance is selected from the group consisting of sodium and potassium thiocyanates.

13. The composition of claim 8 wherein said substance is sodium formaldehyde sulfoxylate in concentrations between about 13–25 percent by weight of the impregnant.

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