United States Patent [19]

Thompson

[11] **3,875,032**

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[54] **METHOD FOR CONTROLLING A SILVER-RECOVERY PLATING SYSTEM**

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[52] **U.S. Cl.** **204/109,** 204/231

[51] **Int. Cl.** **C22d 1/12,** B01k 3/02

[58] **Field of Search** ..... 204/109, 228, 231, DIG. 7

[56] **References Cited**

UNITED STATES PATENTS

3,551,318 12/1970 Snook et al. 204/294

3,751,355 8/1973 Mandroian 204/109

FOREIGN PATENTS OR APPLICATIONS

1,144,756 3/1969 United Kingdom 204/228

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[57] **ABSTRACT**

The plating current in a system for recovering silver from photographic fixing solution is controlled in response to the threshold voltage required to pass plating current in the solution, and to the variation of current flow at voltages near the threshold as the silver ion concentration in the solution varies.

1 Claim, 2 Drawing Figures

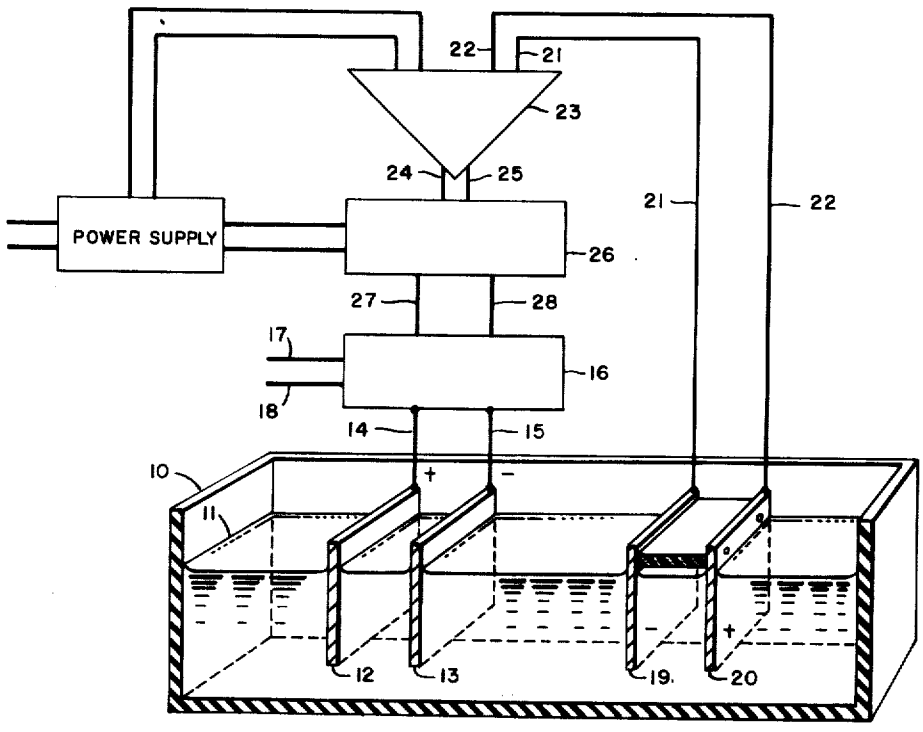
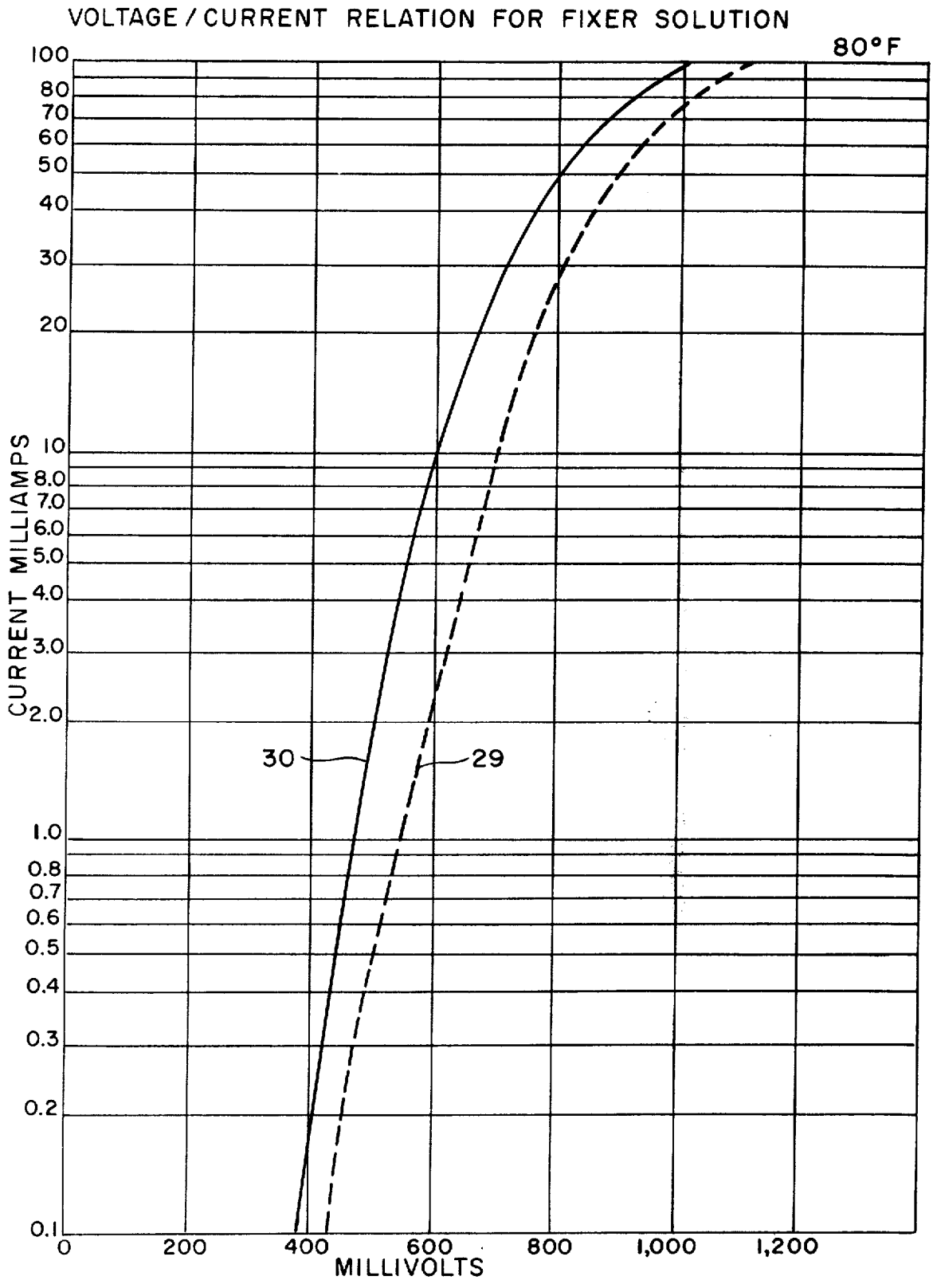


Fig. 1


VOLTAGE / CURRENT RELATION FOR FIXER SOLUTION
80°F
CURRENT MILLIAMPS
100
80
70
60
50
40
30
20
10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
30
29
0
200
400
600
800
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MILLIVOLTS

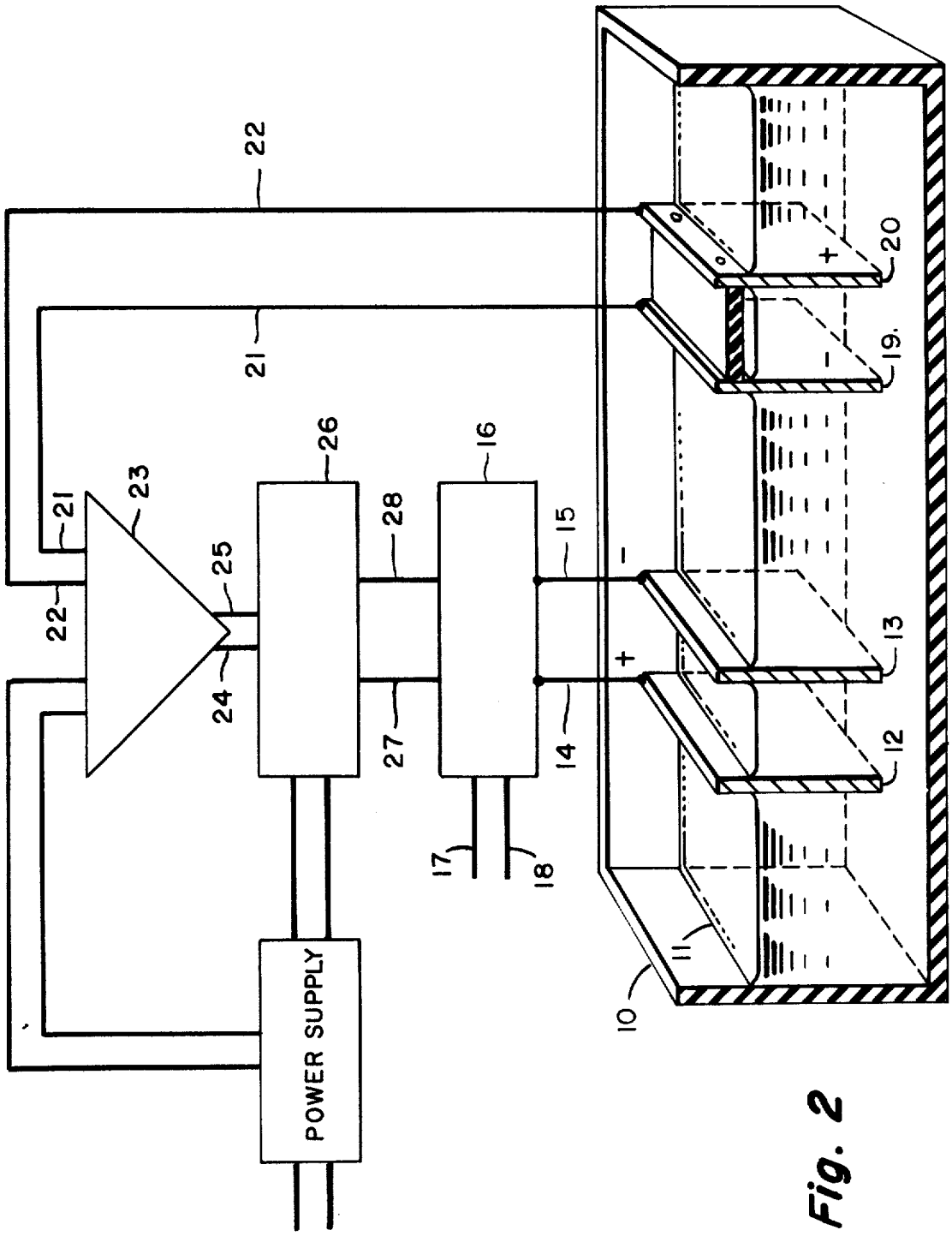

22
21
20
19
26
16
23
21
28
15
25
22
13
24
27
14
12
17
18
11
10
POWER SUPPLY

Fig. 2

METHOD FOR CONTROLLING A SILVER-RECOVERY PLATING SYSTEM

BACKGROUND OF THE INVENTION

Photographic film normally has silver bromide or silver chloride suspended in an emulsion that is coated on a film or paper substrate. Exposure of this film to light, followed by subjecting the film to a chemical developing bath, converts the silver bromide or chloride to metallic silver. The degree to which the bromides and chlorides are converted to metallic silver is related to the intensity of the impingement of the light at a particular area. The remaining silver bromide or chloride that has not been converted by the initial exposure of the film in the camera must be removed before it has the opportunity to react to subsequent light impingement. Any such subsequent exposure would turn the entire film black, and destroy the initial image.

The excess silver compounds are removed by a solvent which has little or no effect on the converted metallic silver image, but has a great affinity for the remaining silver halide compounds. This solvent is referred to as the "fixing bath," and continued use of this bath results in the accumulation of a considerable amount of silver. This silver can be recovered from the solution in a variety of ways, one of these being a variant of the conventional plating procedure. This process has the advantage of a low operating cost, potentially high purity of the recovered metal, and the possibility of re-using the fixing bath after the silver has been removed.

The purity of the recovered silver can be seriously impaired by malfunction of the equipment. The typical fixing bath includes a considerable amount of sodium or ammonium thiosulfate, and contains pH buffers and other stabilizers. The thiosulfate ion is sensitive to the passage of electric current through the bath, although the current will show a definite preference to silver ions. Reduction of the concentration of silver ions produces a tendency for some of the current to transfer between the electrodes via the thiosulfate ions, resulting in the disintegration of these ions into sulfide ions and other complex ions of varying nature. This decomposition prevents further use of the fixing bath, as the sulfide ions attack the plated silver to produce a silver sulfide. The resulting impairment of the purity of the silver is accompanied by the release of a very obnoxious gas containing hydrogen sulfide, resulting in the unsatisfactory performance of the recovery unit at low silver ion concentrations.

Attempts have been made to control the principal plating current in the recovery system as the silver is plated out, and the concentration of silver ions is progressively reduced. One approach has been to monitor the plating current as a function of the change in voltage between the plating electrodes as the silver is plated out. The difficulty with this procedure is that there is no direct relationship between the voltage change and the silver ion concentration. Changes in electrode area, solution concentration, temperature, and other variables will cause a device operating on this principle to be erratic. It has also been proposed to monitor the principal plating current as a function of the color of the silver deposit, the color being altered by the appearance of sulfide on the electrode. Any such correction or control tendency can only occur after some damage has already been done to the deposited silver. Variations in the transmission of light through the solution will also make such a unit erratic. A third approach appears in the U.S. Pat. No. 3,551,318. In the device disclosed in this Patent, a voltage generating device is immersed in the fixing solution. This device functions much like an electrolytic battery cell, and generates about 0.4 volts when no silver ions are present in the mixture. The output voltage of this cell is reduced to about 0.2 volts by an increase in silver ion concentration. This voltage variation is used as a control factor to adjust the principal plating current. In this type of device, an inherent problem is present in the required purity of the silver element of the control cell. If this element becomes contaminated by sulfide ions or other materials, this device also becomes very erratic. The resulting deviation from proper control function can easily turn the principal plating current full on, which will proceed to decompose the solution in the absence of a high concentration of silver ions. This type of device has also shown a tendency to be sensitive to variations in temperature.

SUMMARY OF THE INVENTION

The present invention provides a method for controlling the principal plating current of a silver-recovery system as a function of the threshold voltage required to pass current through the fixing solution at the particular degree of ion concentration that may exist at a given moment. This threshold voltage will vary in an opposite relationship to the silver ion concentration. By establishing a voltage preferably somewhat less than the threshold voltage corresponding to zero silver ion concentration, the amount of current flow across auxiliary control electrodes will be directly related to the silver ion concentration. When the principal plating current is controlled by this relationship, the quantity of the principal plating current in amperes can be held down to the point where substantially all of it will be carried by the silver ions, and thus will not involve the thiosulfate ions. A somewhat more complicated arrangement providing the same end result is to use a conventional detecting device programmed to determine the existing threshold voltage of the solution as it varies. This voltage can then be used as the control factor in regulating the main plating current.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a chart showing the relationship between the control electrode voltage and the resulting current.

FIG. 2 is a schematic diagram showing the relationship of the components of the plating system, including the control device.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The tank **10** will normally contain a quantity of fixing solution indicated at **11.** The principal anode **12** and cathode **13** are immersed in this solution, and are provided with DC potential via the leads **14** and **15** from the current supply **16.** Line voltage is supplied to this unit at the connections **17** and **18.**

The auxiliary cathode **19** and anode **20** function as control electrodes. These are separated by an insulating block, and at least part of both of these electrodes is immersed in the solution **11** within the tank **10.** The leads **21** and **22** connect the control cathode **19** and

anode **20**, respectively, to the comparator **23**. This comparator is a standard device, and applies a fixed voltage across the control cathode and anode **19** and **20**. This pre-set voltage causes a certain current to flow, depending upon the silver content of the solution **11** at the moment. This current varies with the silver ion content. The comparator produces a signal related to this flow of current, and this signal is applied through the leads **24** and **25** to the phase or pulse control device **26**. This unit may be of the SCR, or triac type, according to preference. The signal delivered through the leads **27** and **28** from the phase control unit **26** to the current supply unit **16** regulates the output of the main plating current delivered to the recovery anode and cathode **12** and **13** respectively. Silver of high purity will be deposited upon the cathode **13** which is preferably of relatively thin stainless steel that can be flexed to snap the accumulated silver free. A very small quantity of silver will also accumulate on the cathode **19**. Under most circumstances, the principal electrodes will operate at a current level in the neighborhood of 15 amperes, whereas that across the control electrodes will be approximately 0.0015 amperes. Under typical conditions of operation, the main cathode **13** will be stripped of silver perhaps every other week, with the control cathode being cleared of its silver accumulation about once a year.

Referring to FIG. **1**, the dotted curve **29** indicates the voltage-current relationships in a solution in which there are substantially no silver ions. The full line curve **30** shows the related relationship in a solution which has a substantial quantity of silver ions present. It is highly significant that a threshold voltage is necessary before any current whatever will pass in the solution. This threshold voltage varies with the degree of silver ion concentration, and a voltage across the control electrodes less than the zero-current voltage (threshold) associated with the dotted curve **29** will result in eliminating any tendency to involve the thiosulfate ions in the electrolysis, even at the lowest degrees of silver ion concentration. Even when a control voltage is slightly above the threshold voltage corresponding to zero-silver ion concentration, the use of this voltage at the control electrodes produces such a negligible degree of electrolysis as to produce no serious contamination problem.

I claim:

1. A method of controlling the plating current in a silver-recovery system, said system including a tank normally containing a photographic fixing solution having a variable silver ion content, and also including a primary cathode and anode means normally immersed in said solution in said tank, and electric circuit means adapted to supply DC electric current to said primary electrode means, said method comprising:

immersing control cathode and anode means in said solution in said tank;

applying an electrical potential across said control cathode and anode means at a voltage adjacent to the threshold voltage required to induce a flow of current in said solution at zero silver content of said solution; and

controlling said electric circuit means to determine the current flow between said primary cathode and anode means as a function of the flow of current between said control anode and cathode means.

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