July 23, 1968 J. GAYNOR 3,393,617

RECORDING APPARATUS COMPRISING A PHOTOSENSITIVE MEMBER, A RECORDING MEMBER, AND AN ION EXCHANGE MEMBRANE

Filed Jan. 25, 1965

Fig. 1.

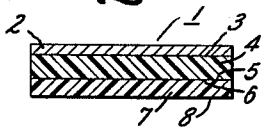


Fig. 2.

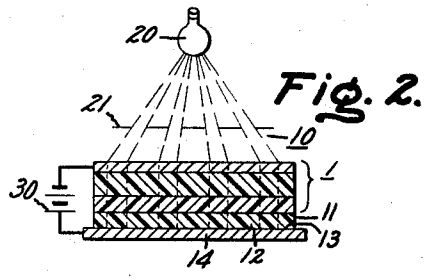


Fig. 3.

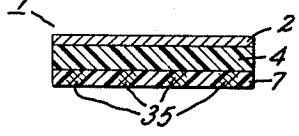
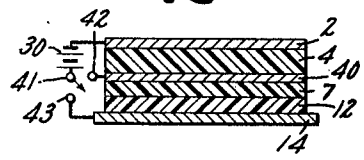


Fig. 4.



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United States Patent Office 3,393,617 Patented July 23, 1968

3,393,617

RECORDING APPARATUS COMPRISING A PHOTOSENSITIVE MEMBER, A RECORDING MEMBER, AND AN ION EXCHANGE MEMBRANE

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Filed Jan. 25, 1965, Ser. No. 427,695
1 Claim. (Cl. 95—1.7)

ABSTRACT OF THE DISCLOSURE

An apparatus is disclosed for recording an image on a recording medium including a stacked structure composed of a photosensitive layer, a recording layer, and an ion transport layer intermediate the photosensitive and recording layers. A pattern of radiation is imaged on the photosensitive layer to produce a change in electrical resistance in the irradiated portions of the photosensitive layer. Means are provided for applying an electrical potential across the stacked structure to cause current to flow through the photosensitive layer in proportion to the changed resistance. Such current causes selective migration of ions from the ion transport layer into contact and reaction with the recording layer to record a physically distinguishable image.

This invention relates to electrophotography and more particularly to electrophotography which employs the phenomenon of electromigration.

The term "electrophotography" was originally applied to the photographic process involving the use of a charged photoconductor which was then selectively discharged by exposure to light to form a remanent pattern of charges and developed by the use of electrostatically charged insulating powders. With continued work in this field, two branches have emerged—electrostatic electrophotography and electrolytic electrophotography. In the former, an image pattern is developed from an electrostatic charge pattern on the surface of a photoconductor, while in the latter, the distribution of currents which flow in a photoconductor when it is illuminated cause electrolytic reactions which produce a latent image which is developed by modified wet silver halide photographic techniques.

There are certain undesirable aspects inherent in both of these previously developed systems of electrophotography. For example, in the electrostatic systems now employed, a plurality of steps is required to produce an image, relatively high voltages are required to electrostatically charge the photoconductor and the blocking layer configuration which limits the quantum efficiency to one resulting in low photographic speed. In the electrolytic systems, cations as well as anions are electrodeposited during the electrolysis reaction and anodic gases may occur at the electrolyte-photoconductor interface whereupon, at high current densities, the entire interface may be disrupted or the photoconductor poisoned. Further, there is insufficient amplification in the electrochemical process to permit satisfactory direct development without further steps. It would be desirable to provide an electrophotographic process which avoids these difficulties, permits sufficient photon amplification for development with no further processing and enables the photosensitive element to be regenerated for further use.

It is therefore a principal object of this invention to provide an electrophotographic apparatus and process which instantly responds to an input signal to reproduce a recorded physically distinguishable image of a pattern of incident radiation.

A further object of this invention is the provision of

an information recording medium which may be erased and reused.

A yet further object of this invention is the provision of a novel method for instantaneously recording an image pattern of incident radiation in response to an input signal to produce a physically distinguishable image.

Briefly stated and in accordance with one embodiment of the invention, a multiple layer structure is provided wherein a photoconductor layer is provided with a transparent electrode on one face, its other face being in intimate contact with one face of an ion-sensitive recording layer, the other face of the recording layer being in intimate contact with one face of an ion transport layer, the other face of the ion transport layer being in electrical contact with a second electrode layer, and means to provide an electrical potential across the two electrodes. When an image pattern of radiation is projected or otherwise caused to impinge upon the transparent electrode and hence upon the photoconductor, those areas of the photoconductor which are illuminated lose electrical resistance in proportion to the level of illumination while those areas not illuminated retain a high electrical resistance. No recording takes place until an electrical potential is impressed between the two electrodes which produces an electrical current. When this occurs, the current flows through the conductive areas of the photoconductor in proportion to the relative conductivity of the several areas and ions are produced at the ion transport layer-recording layer interface in numbers proportionate to the current flow. A chemical reaction occurs at this interface to produce a physically distinguishable image pattern on either or both layers which has a point-to-point correspondence to the image pattern of the incident radition. The reaction ceases when the flow of current is interrupted when illumination is removed or the voltage turned off and the recording layer with the image thereon may be removed, the ion-transport layer regenerated by replacing the depleted ions and an unexposed recording layer member inserted in place for another exposure and development step. Depending upon the nature of the chemical reaction and the nature of the recording layer, the recorded image may be erased by reinserting the exposed recorded image in the apparatus, exposing the photoconductor to a uniform illumination, and applying a current of reversed polarity across the two electrodes.

The invention may be more readily understood in its various aspects and embodiments by recourse to the following description taken in conjunction with the accompanying drawing in which:

FIGURE 1 is a semischematic cross-sectional view of one form of an information recording medium according to the present invention;

FIGURE 2 is a semischematic cross-sectional view of the recording medium of FIGURE 1 assembled with the other operative elements of the recording apparatus of the invention;

FIGURE 3 is a semischematic cross-sectional view of the recording medium of FIGURE 1 after the recording step has been accomplished; and

FIGURE 4 is a semischematic cross-sectional view of a modification of the recording apparatus of FIGURE 2.

With particular reference to the drawings, one embodiment of a recording medium 1 is illustrated in FIGURE 1 in which a transparent electrically conductive film 2 is supported upon and contiguous with one surface 3 of a photoconductor layer 4. The opposite surface 5 of the photoconductor forms an interface with one surface 6 of a recording member 7 having an opposite surface 8.

In this embodiment, the transparent electrically conductive film 2 is a very thin layer of a metal or metallic salt which may be conveniently deposited on surface 3 by any of a number of well-known methods, such as by evaporation, for example. The photoconductor layer 4 may be made in any number of well-known ways. For example, if it is desirable to be able to remove the recording member 7 and replace it with another recording member, layer 4 may be made from an organic polymeric film matrix such as polystyrene, for example, containing a dispersion of fine particles of a photoconductive solid such as cadmium sulfide, or by the use of an organic polymeric film wherein the polymeric film material is photoconductive. On the other hand, if separability of layer 4 from member 7 is not desired, a photoconductive layer of a material such as, for example, cadmium sulfide may be applied to surface 6 of recording member 7 by evaporation, sputtering, or any other suitable technique, and then the transparent electrically conductive film 2 applied thereover. Recording member 7 is composed of or contains a substance which is chemically reactive to the presence of ions whereupon the chemical reaction, which may or may not be reversible, produces a change in the member which is physically distinguishable. For example, member 7 may be a polymeric film or sheet of paper containing a conventional acid-base indicator such as litmus or the like. The nature of these reactions and the manner in which they may be employed in the practice of this invention will be discussed in greater detail subsequently.

As shown in FIGURE 2, recording medium 1 is incorporated in the recording apparatus 10 by placing surface 8 of recording member 7 in contact with one surface 11 of an ion transport layer 12, the opposite surface 13 of which is in electrical contact with an electrically conductive layer or film 14. The ion transport layer 12 is composed of a material which acts as a source of ions and may be composed, for example, of an ion exchanger in the form of a resinous membrane. These membranes are well known, widely used in industry, and commercially available in forms in which the available ion is either a cation or an anion, depending upon the desired reaction. Also, depending upon the particular desired reaction, a specific ion may be selected.

When the recording apparatus 10 is assembled as in FIGURE 2 and a pattern of radiant energy is caused to impinge upon the transparent electrically conductive film 2 and to be transmitted therethrough to impinge as a pattern of light upon the surface 3 of photoconductor 4. This is schematically illustrated in FIGURE 2 wherein radiant energy source 20 provides a pattern of energy through screening member 21 which impinges as aforesaid upon film 2 and surface 3 of recording medium 1. Those areas of the photoconductor 4 which are exposed to the energy react to cause such areas and the photoconductive material directly beneath them to become electrically conductive to a degree which is proportionate to the intensity of the incident radiation. The areas and the material directly beneath them which are not exposed to the activating radiation remain in an essentially electrically nonconductive state. It should be noted that at this point, however, the only event which the radiation has produced is the formation of the pattern of electrically conductive paths in an essentially nonconductive matrix through the layer 4. When a current is caused to flow between the two electrically conducting layers 2 and 14 from a source schematically illustrated at 30, the flow of current selectively takes place through the pattern of electrically conductive paths in layer 4 and, following the shortest paths, progresses according to said pattern through recording layer 7 and through ion transport layer 12. Depending upon the polarity of the current and whether the ion transport layer 12 is a source of cations or anions, ions from the ion transport layer are electrically driven in a corresponding pattern to the surface 11 where they chemically react with surface 8 of recording member 7 to produce a corresponding pattern of reacted material, which pattern is physically distinguishable.

The recording medium 1 is then separated or removed from the recording apparatus 10 and, as shown in FIGURE 3, provides a recording of the pattern of incident radiation schematically shown as the areas 35.

If desired, recording member 7 may be removed from the recording medium 1 and replaced by a new or regenerated member for another recording operation. Additionally, it may be desirable to regenerate the ion transport member 12 by replenishing the depleted ions.

It should also be noted that while for the purpose of providing a disclosure of a working example of the invention, the recording member 7 has been described as located between the photosensitive layer 4 and the ion transport layer 12, the relative positions of member 7 and layer 12 may be reversed, if desired. In such an arrangement, ion transport layer 12 would be located between layer 4 and member 7 and ions would be electrically driven from layer 12 to the interface between layer 12 and member 7 to there react to form the record of the image pattern. Furthermore, while a separable recording medium and member have been disclosed, the structure shown in FIGURE 2 may be made as an integral, nonseparable body. In such a configuration, it is contemplated that it may take the form of a flexible tape which would be adapted to be moved past an exposure station where it might be exposed in either a continuous fashion or in a stepwise or frame by frame manner similar to conventional motion picture film, and a switching device may be used to synchronously interrupt the electric current flow in a manner analogous to the operation of the shutter of a motion picture camera. It will, of course, be obvious that either or both of the electrically conductive layers may be transparent. It is also contemplated that all of the several layers of the stacked array of sheet-like elements may be transparent with respect to the particular radiation employed. While for purposes of illustration, electrically conductive layer 2 has been disclosed as transparent, it will be appreciated that it may be opaque if electrically conductive layer 14 ion transport layer 12, recording layer 7, and photosensitive layer 4 are transparent and the radiation is accomplished through layer 14 instead of through layer 2, as has been illustrated in FIGURE 2. It should also be noted that the recording layer might also be composed of an ion transport or exchange membrane.

While the foregoing disclosure has involved the use of electrically driven ions to cause the formation of an image pattern by a chemical reaction, it is well known that many materials which are not, strictly speaking, ions may be caused to migrate in response to an electrical field. Since literally thousands of papers and books have been published concerning the phenomena of electromigration of materials by electrophoresis and electromatography, no detailed discussion of these techniques is deemed necessary or desirable at this point. Reference is made to "Ionography" by H. J. McDonald et al., The Year Book Publishers, Inc., Chicago, Ill., 1955, which discusses a very great many substances which may be caused to migrate under the influence of an electric field and, hence, are suitable for use in this invention.

As is well known, there are a large number of chemical reactions which depend upon the presence or absence of either cations or anions and very often upon the presence of very specific cations or anions. The following are some examples of the kinds of changes and reactions which may be used for recording images according to this invention. Volume changes in polyelectrolytes to produce an image by deformation, a change in pH brought about by the migration of hydrogen or hydroxyl ions to form opaque precipitates or to dissolve opaque compounds or cause a color change in an acid-base indicator, form

vat dyes from their leuco forms, catalyze chemical reactions such as esterification, aldol condensations and polymerizations. Relatively, small changes in the ionic content at the ion source-recording member interface can result in very large optical density differences because the migrating ion acts as the trigger for the reaction.

Similarly, a variety of chemical reactions are catalyzed by cations of metals such as copper, iron, nickel, cobalt, and manganese, and anions such as sulfate, phosphate, chloride, and bromide, among others. Furthermore, chelates which are highly colored may be formed from many of the metal ions. The coordination number varies from two to eight depending on the cation and its valence state, thereby effecting multiplication. Insoluble black compounds such as copper sulfide, lead sulfide, and iron sulfide, for example, have exceedingly high extinction coefficients and scatter light, even though the formation of such compounds provides little amplification. As a result, however, the formation of such compounds produces large optical density changes even in very small quantities. The formation of those charge transfer complexes which are black also have high extinction coefficients.

The production of images utilizing ion transport techniques as previously disclosed may be advantageously applied to the manufacture of so-called "printed circuit" modular elements. For example, recording layer **7** may be made as a thin film of metallic copper and layer **12** may be the source of an electromigratory material which chemically reacts with the copper to produce a reaction product which may be preferentially removed. This layer **12** may be, for example, a membrane which is a source of chloride ions. Upon exposure to an appropriate light pattern with an accompanying applied field, a pattern of copper chloride may be produced in the copper film which may be subsequently dissolved out with an acid such as hydrochloric acid, for example. Other similar electrically conductive or semiconductive materials may be so-treated and, indeed, if similar patterns of non-conductive materials are desired, analogous electrophotography solution techniques may be employed.

Further, certain organic molecules undergo reversible oxidation and reduction reactions with great ease with the transfer of an electron to or from the reacting species, such as, for example, the well-known quinone-hydroquinone couple. Polymers have been prepared from these compounds which retain the ability to oxidize or reduce compounds. Under the influence of a field, electrons or protons will migrate to the interface to there react with recording material in the recording layer to produce a physically distinguishable image. In addition, a solution of inorganic and/or organic ions may be solidified and stabilized by adding agar, gelatin, starch, and certain polar polymers such as, for example, polyvinyl alcohol or polyvinyl acetate. The ions will migrate through the solid under the influence of a current in accordance with their polarity.

Yet further, charged colloidal particles will also migrate in response to an applied electrical current or field. If amino acids are used as the reactive constituent in the recording layer, the ionophoretic layer serves as the source of the developable material. For example, the black dyes amido Black B and Sudan Black are very effective stains for amino acids. Furthermore, colloidal dispersions of, for example, copper, lead, or iron will react with a source of sulfide ion to produce black sulfides.

It will be appreciated that many of the foregoing changes and reactions may be utilized to produce image patterns which are distinguishable by means other than by observing or measuring a change in color. Changes in opacity or transmissivity to radiation of various kinds, changes in optical properties such as index of refraction or light scattering properties, changes in various electrical and magnetic properties, and other kinds of distinguishable physical changes to permit retrieval of the image pattern.

The recording apparatus illustrated in FIGURE 4 constitutes a modification of the apparatus shown in FIGURE 2, differing therefrom in the provision of electrically conductive layer **40** interposed between the photoconductive layer **4** and the recording layer **5**. Of course, if the ion transport layer **12** or a functionally equivalent layer which is the source of a reactive material which is capable of migration in response to an applied electric field is interposed between the recording layer and the photoconductor, the conducting layer **40** is interposed between the photoconductor and layer **12**. Layer **40** is characterized by having very good electrical conductivity in a direction parallel to the flow of current or the direction of the applied electric field and relatively poor conductivity in a direction perpendicular to the direction of the current or field. These sorts of properties are well known in thin evaporated films of silver, gold, tin, and indium, for example. A two-position switch **41** is connected as shown so that in a first position, a current or field may be applied between coating **2** and layer **40** by moving switch element **41** into contact with **42**. When switch element **41** is moved into contact with **43**, the current or field is applied between coating **2** and coating **14**. Layer **40** has at least two functions and, under certain conditions, three. The presence of the layer aids in the prevention of poisoning of the photoconductor by migration of ions or other polar particles from the recording layer or the layer containing particles capable of electromigration. Further, since the photoconductor may be exposed to radiation prior to the exposure which is desired to be recorded, undesired long lived carriers may be present which may be recorded as "noise." By completing the circuit between layer **2** and layer **40** just prior to making the desired recording, these unwanted stray carriers are swept out of the photoconductor lessening the amount of noise. Further, if the layer **2** is composed of a proper metal such as silver for CdS, for example, additional carriers are injected from the silver when it is illuminated and the use of the two electrodes **2** and **40** permits photon amplification.

Other conditions which are necessary to the advantageous practice of the invention are as follows:

The electrical resistance of the photoconductor must be higher than the resistance of the recording layer and the ion transport or equivalent layer when the photoconductor is not subjected to radiation;

When the photoconductor is irradiated, those areas which are illuminated must have electrical resistance lower than that of the two layers previously referred to; and

When the activating energy is a current, the use of a voltage pulse permits much higher instantaneous currents than a steady state voltage and eliminates the need of a mechanical shutter.

It will be obvious that many other variations may be made within the purview of this invention. For example, a continuous tape recording apparatus similar to that shown in FIGURE 2 of the application filed concurrently herewith in the names of James M. McQuade and Robert P. Hamlen, Ser. No. 427,694, entitled, "Recording Medium," and assigned to the assignee of this application, may be employed. As pointed out in this copending application, a great number of ionic reactions are possible in the practice of this invention to produce image recordings which are physically distinguishable by a number of techniques. It should be noted that when pictorial type images are recorded according to this invention, images having continuous tone are achievable.

From the foregoing disclosure and description, many variations within the ambit of the invention will readily occur to those skilled in the art. Therefore, it is not intended to limit the scope of the invention except as set forth in the appended claim.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A recording apparatus comprising in combination a sheet-like photosensitive member, a sheet-like recording member capable of change in at least one physically distinguishable characteristic in response to the introduction of ions, and a sheet-like ion transport member which is an ion exchange membrane and which provides a source of ions that can be caused to migrate in response to an applied electrical field assembled in a surface-to-surface stacked array such that each member is in intimate physical contact with its neighboring member and said recording member and said ion transport member share a common interface, means for imposing an image pattern of activating radiation upon the surface of said photosensitive member to produce a change in electrical resistance in the irradiated portions of said member, and means to apply an electrical potential across said stacked array to cause selective electromigration of the ions of said ion transport member into contact and reaction with corresponding areas of said recording member to record a physically distinguishable image pattern.

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