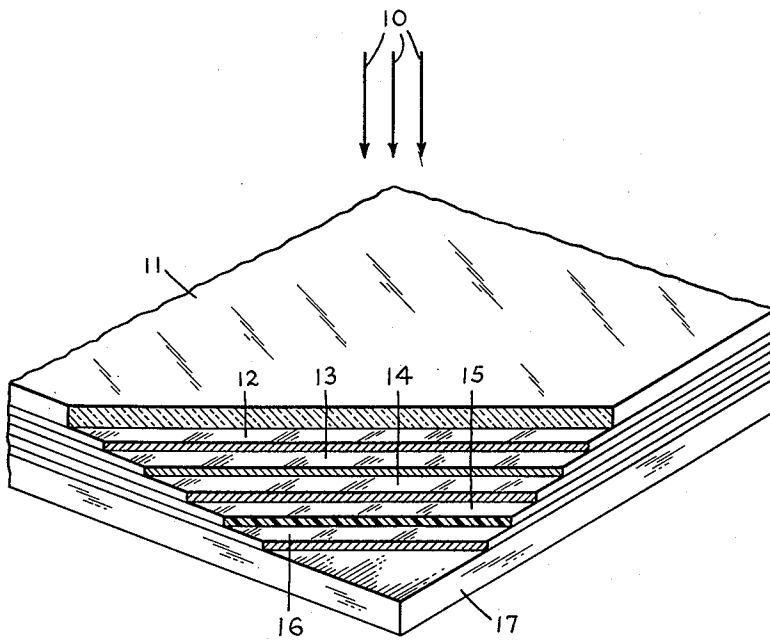


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ELECTROPHOTOGRAPHIC SYSTEM

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3,088,883

## ELECTROPHOTOGRAPHIC SYSTEM

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This invention relates generally to electrophotographic systems, and more particularly to an electrophotographic system which is characterized, among other advantages, by the capability of providing images using times of exposure on the order of microseconds.

In my copending United States patent application, Serial No. 658,918, filed May 3, 1957, now abandoned (which is a continuation-in-part of my copending application, Serial No. 570,259, filed March 8, 1956 now abandoned), there is disclosed, as an apparatus embodiment of the invention set forth therein, an electrophotographic sandwich structure consisting, in the order named, of a transparent foundation plate of glass, a coating of transparent, electrically-conducting material deposited on the glass plate, a very thin layer of photoconductive semiconductor material, an image receiving sheet impregnated with a material which will change in tone density in the presence of current conducted therethrough, and a metallic sheet or plate. The transparent electrically-conducting coating and the metallic sheet or plate form the two electrodes for the sandwich structure.

The mentioned sandwich structure operates in the following manner. The structure receives an image carried by electromagnetic radiation of infrared or of shorter wavelength. This radiation passes through the glass plate and transparent electrode to areally modulate the face-to-face resistance of the photoconductive layer in accordance with the image carried thereby. A pulse of voltage is then applied between the transparent electrode and the electrode formed of the metal plate or sheet to produce a flow of current through the photoconductive layer and the image-receiving sheet. This current will be areally modulated in density in accordance with the areal modulation of resistance of the photoconductive layer. The electrosensitive material with which the image receiving sheet is impregnated will change in tone density from point to point on the sheet in measure with the point-to-point density of the current passing therethrough. Hence, the image carried by the radiation will be reproduced on the sheet.

While the described sandwich structure is capable of producing pictures which have high resolution, and which are otherwise comparable with pictures obtained by conventional photography, the structure has the disadvantage that the formation of the image takes place primarily by the creation, through the flow of current, of an electrochemical reaction in the material of the image receiving sheet which undergoes the tone density change. By an electrochemical reaction is meant a reaction in which ions are produced by utilizing an electric current from an outside source to cause the atoms of one or more of the constituents of the image forming material to gain or lose electrons. The degree to which such electrochemical action takes place is a function of the number of coulombs of electricity (i.e., current multiplied by time of flow thereof) which are supplied to the situs of the reaction. All electrochemical reactions suitable for image formation have a lower limit of coulombs of electricity which are required to produce a noticeable change in tone density. Also, the density of current per square centimeter which can be used in an electrophotographic sandwich structure of the sort described has an upper limit. Hence, it has not been found possible, with electrophotographic processes dependent primarily on electrochemical reac-

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tions for image formation, to produce a satisfactory image with a time of exposure less than on the order of milliseconds, as, say, 20 milliseconds.

It is accordingly an object of this invention to provide an electrophotographic system wherein the shortest practical time of exposure is, at least theoretically, limited only by the time of response of the photoconductive layer.

Another object of the invention is to provide an electrophotographic system wherein a satisfactory image can be produced by a flow of current on the order of microamperes.

A further object of the invention is to provide an electrophotographic system wherein the image carrying radiation may be projected through the image receiving layer to the photoconductive layer.

A still further object of the invention is to provide an electrophotographic system which does not use an electrochemical reaction as the primary reaction causing the image formation.

For a better understanding of how these and other objects of the invention are realized, reference is made to the following description and to the accompanying drawing of a representative embodiment of apparatus according to the invention.

Referring now to the drawing, there is shown thereby a multilayer sandwich structure adapted to provide a permanent reproduction of an image transmitted by electromagnetic radiation which is represented by the arrows 10 in the drawing, and of which the upper limit for wavelength is the infrared wavelength region of the electromagnetic spectrum. Assuming that the incident radiation 10 is visible light, an electrophotographic structure according to the invention may take the form shown, in which one of the outside layers of the structure is a glass plate 11. Disposed beneath the plate 11 are, in the order named, a transparent conductive coating 12, a photoconductive semiconductor layer 13, a catalytic layer 14, a barrier layer 15 of polarizable dielectric material, an image receiving layer 16, and a metallic member 17 which may be a plate or a sheet as, say, a sheet of aluminum foil.

The enumerated elements of the sandwich structure will now be considered individually. The transparent conductive coating 12 may be a coating of what is known to the art as "NESA" glass or a coating of what is known to the art as "EC" glass. The coating 12 is used as one of the electrodes of the shown structure, the other electrode being the metallic member 17. Ordinarily, the coating 12 is deposited as a layer on the surface of the glass plate 11, although this glass plate may be dispensed with if suitable support is otherwise provided for the transparent conductive coating. The combination of the plate 11 and coating 12 is well known to the art, and is used in devices such as light amplifiers.

The photoconductive semiconductor layer 13 is constituted of semiconductor material as, say, cadmium arsenide, semiconductor germanium, semiconductor silicon, selenium, cadmium sulfide, antimony trisulfide, or cuprous oxide. The choice of the semiconductor material will depend on the desired spectral response and speed. When metallic germanium or silicon is used, these materials are rendered extrinsic semiconductors by the presence therein of a small percentage content of an appropriate doping agent. Ordinarily, the photoconductive layer 13 is in adhering relation with the electrode coating 12. The layer 13 may be prepared in various ways as, say, by chemical precipitation of the semiconductor material on the NESA glass (cadmium sulfide), by sintering particles of the semiconductor material which have been deposited on the NESA glass (cadmium sulfide, antimony trisulfide, cuprous oxide), or by deposition

of the semiconductor material from the vapor phase thereof in a high vacuum atmosphere. The latter mode of preparation may be in accordance with vacuum deposition methods disclosed in the text "Vacuum Deposition of Thin Films" by Holland (published in 1956 in London by Chapman & Hall Ltd.) or may, say, in the case of semiconductor germanium, for example, be in accordance with the technique for producing thin semiconductor films which is taught in my copending United States patent application, Serial No. 569,421, filed March 5, 1956, now abandoned.

As described in my mentioned copending application, Serial No. 656,918, the photoconductor layer should be very thin in order to minimize current spreading in the layer, and in order to minimize the voltage drop therein to thereby assure that a substantial fraction of the voltage applied between electrodes 12 and 17 will appear across the barrier layer 15. In the shown embodiment, suitable thickness values for the photoconductive layer are from less than 1 to 10 microns with preferred values being in the lower end of this range.

The image receiving layer 16 is constituted of a base or bulk forming material (as, say, paper or gelatin), a conductive salt to render the layer an electrical conductor from face to face thereof, and an amount of image forming material which is adapted, when properly activated, to undergo a change in visual appearance in the tone density scale from white to black or in some other tone density scale. As later described in further detail, the image forming material is activated to change in tone density by bringing into contact with the image forming material a very small quantity of a material which in itself undergoes no chemical change, but which causes the image forming material to undergo a chemical reaction resulting in the mentioned tone density change. This "catalyst" material, as it may be properly called, is the material constituting the catalytic layer 14. As shown in the drawing, the catalytic material in the layer 14 is ordinarily separated from the image forming material of the image receiving layer 16 by the barrier layer 15 of polarizable dielectric material. However, as later described in further detail, when a voltage pulse is applied to the electrode layers 12 and 17 of the multilayer sandwich structure, this voltage pulse establishes an electric field in the layer 15 of dielectric material. In the presence of this electric field a small amount of the catalytic material in layer 14 will be transported through the barrier layer 15 to the image-forming material of the layer 16.

The barrier layer 15 may be constituted of any dielectric material through which, in the presence of a suitable electric field in the dielectric, a transport of the catalytic material will take place from the layer 14 to the layer 16. Dielectric materials in which such transport will take place are characteristically crystalline and polarizable. Examples of such dielectric materials are silicon dioxide and titanium dioxide.

If the dielectric material is capable of being evaporated into a high vacuum atmosphere without the material dissociating at the temperature necessary for evaporation, the barrier layer 15 may be produced by depositing the dielectric material from a vacuum on the image receiving layer 16. As stated, methods for so depositing a thin layer on a substrate are disclosed in the mentioned text "Vacuum Deposition of Thin Films." A barrier layer 15 of silicon dioxide may be prepared by the vacuum deposition technique. In the event that the dielectric material to be utilized cannot be conveniently deposited from a vacuum (because the material will dissociate at the temperature required for the evaporation of the material into a high vacuum atmosphere), the barrier layer 15 may be formed by deposition of the dielectric material on the image receiving layer 15 by electrophoresis. To wit, very fine particles of the dielectric material are caused to be suspended in a liquid, an electric field is then developed in the liquid between two spaced elec-

trodes of which one is the image receiving layer 16, and the polarity of the electric field is made such that the dielectric material particles (which carry charges) will be attracted to the layer 16 to form a deposit thereon. The technique of the deposition of a thin film by the employment of the electrophoresis phenomenon is well known to the art. Titanium dioxide, for example, may be deposited by electrophoresis to form the barrier layer 15 on the image receiving layer 16.

Whatever the mode of preparation used for the barrier layer 15, the thickness of this layer should be of proper value to permit migration of an appropriate amount quantity of the catalytic material in layer 14 through layer 15 to layer 16 when an electric voltage pulse is applied to the electrode layers of the shown sandwich structure. It has been found in connection with the shown embodiment that a suitable thickness value for layer 15 is a thickness value of several hundred Angstrom units as say 500 Angstrom units.

The layer 14 of catalytic material is preferably prepared by depositing the last-named material from the vapor phase thereof in a high vacuum atmosphere onto the barrier layer 15 by methods for vacuum deposition which are well known to the art and which, as stated, are described, for example, in the mentioned text "Vacuum Deposition of Thin Films." Since only a minute amount of catalytic material need be transported through the dielectric layer 15, the catalytic layer 14 need not ordinarily have a thickness of more than a few microns as, say, 5 microns. An advantage of such small thickness is that, even when the catalytic material is electrically conductive, the layer 14 will have a high transverse resistance so that the layer will not act as a quasi-equipotential surface impairing the resolution obtainable in the image.

If the layers 14 and 15 are deposited on the layer 16 by vacuum deposition, the locales from which the materials of layers 14 and 15 are evaporated into the high vacuum atmosphere should be sufficiently removed from the locale of layer 16 in this atmosphere to prevent decomposition of the layer 16 from the high temperatures developed at the first-named locales for the purpose of causing the evaporation.

The preparation of the image-receiving layer 16 will be later described in further detail. As mentioned above, the base or bulk-forming material of the image receiving layer may be either a fibrous material as, say, paper, or may be gelatin. When gelatin is used, the image receiving layer will be transparent. An image receiving layer characterized by transparency is on occasion of substantial advantage. As an example, if the image receiving layer is transparent, the tone density image when developed thereon will be in the form of a transparency. Hence, assuming that the shown multilayer structure is composed of two separable parts consisting, respectively, of the layers 11, 12, 13 and the layers 14-17, and assuming further that the electrode layer 17 is transparent (as can readily be provided by using a glass plate and NESA glass coating in place of a metallic sheet for the layer 17), then further reproductions of the image on layer 16 can be made through conventional photographic methods in which the structural combination of layers 14-17 is used in place of a conventional photographic negative or positive transparency.

As another example of the desirability of having the bulk-forming material of the layer 16 a transparent material, when such material is transparent, a metallic sheet as, say, aluminum foil, can be substituted for the glass plate 11 and the NESA glass coating 12, to provide the electrode layer in contact with the other conductive layer 13, a transparent conductive coating of, say, NESA glass (suitably supported when necessary by a glass plate backing) can be substituted for the metallic member 17 to provide the electrode layer in contact with the image receiving layer 16, and the photoconductive layer 13 can

be areally modulated in face-to-face resistance in accordance with the image carried by radiation 10 by having this radiation pass (in the order named) through layer 17 (which is now transparent), layer 16 (which is transparent by the use of gelatin as the bulk-forming material), and layers 15 and 14 (which are transparent because of their extreme thinness) to the photoconductive layer 13. Certain conveniences of manufacture are afforded by an electrophotographic multilayer structure of this sort wherein the image-carrying radiation is projected through the image receiving layer to the photoconductive layer. As one such convenience, the aluminum foil (which, in the present discussion, is considered to replace the elements 11, 12 shown in the drawing) and the layers 13-16, inclusive, may be incorporated into a unitary and self-coherent multilayer structure. Such structure can be manufactured by utilizing the foil as a substrate, and by effecting successive vacuum depositions on the substrate of the semi-conductor material, the catalytic material, and the dielectric material to form the layers 13-15. The image receiving layer 16 is then deposited on the layer 15 in a conventional manner as, say, with a knife coater. The advantage of the multilayer structure just described is that the photoconductive layer is included within that part of the whole electrophotographic structure which is replaced each time a new image is to be obtained. By so including the photoconductive layer in the replaceable part of the electrophotographic structure, the problem of the wearing off of the photoconductive layer is avoided. The convenience of manufacture involved is that because of the relatively high temperature conditions which usually obtain when the photoconductive layer is deposited by vacuum deposition, it is substantially easier to deposit the photoconductive layer on the temperature resistant aluminum foil than onto a substrate including the image receiving layer which will tend to decompose under high temperature.

From the foregoing discussion, it will be appreciated that, in general, the whole electrophotographic structure shown in the drawing is ordinarily separable into two parts. One of these parts will be referred to herein as the replaceable part since a new such part is ordinarily used each time a new image is to be obtained. The other part is referred to herein as the permanent part since the part is not ordinarily replaced between one image reproduction and the next. Which layer or layers of the whole electrophotographic structure are in the replaceable part, and which in the permanent part, depends upon manufacturing considerations and upon the use to which the reproduced image is to be put. According to the present invention, however, there are a variety of ways in which the layers of the whole electrophotographic structure can be distributed between the replaceable part and the permanent part. As examples, the permanent part may be constituted of the layers 11 and 12, or, alternatively, of the layers 11-13, inclusive, or, alternatively, of the layers 11-14, inclusive, or, alternatively, of the layers 11-15 inclusive, while, of course, in each case the remaining layers or layers of the whole electrophotographic structure are located in the replaceable part.

The described electrophotographic structure is ordinarily operated in conjunction with an optical system which projects the image carrying radiation onto the mentioned structure. Such optical system may resemble a conventional camera and thus may, for example, be similar to the electrophotographic camera described in my mentioned copending United States application, Serial No. 656,918. A camera of this sort needs no shutter since the multilayer structure which reproduces the image is insensitive to received radiation until such time as an electric voltage pulse is applied to the electrode layers of the structure. Also, a camera of this sort is rechargeable in daylight with the replaceable part of the image reproducing structure.

The voltage pulse applied to the electrode layers of the

electrophotographic structure may be supplied from any conventional pulse generating circuit adapted to supply a voltage pulse of sufficient amplitude (as, say 400 volts) and of short duration (e.g., a duration on the order of 15 microseconds). One such type of pulse generating circuit is disclosed in my mentioned copending application, Serial No. 656,918. The voltage pulse must be applied to the mentioned electrode layers with proper polarity to cause ions of the material in the catalytic layer 14 to migrate through the barrier layer 15 to the image receiving layer 16. Thus, if the ions of catalytic material are positively charged (as, say, when the catalyst is copper) the voltage pulse should be applied with a polarity to make the layer 12 the positive electrode layer and the layer 17 the negative electrode layer. Conversely, if the ions derived from the catalytic material are negatively charged ions (as, say, when the catalyst ions are negatively charged iodine ions derived from dissociation of potassium iodide in the layer 14), then the voltage pulse should be applied with a polarity to make the layer 12 the negative electrode layer and the layer 17 the positive electrode layer.

A more detailed description will now be given of the phenomenon causing the formation of images on the layer 16. In chemistry, the quantitative relations between constituents of a chemical system can be expressed in terms of a situation in which one or more initial constituents of the system form one or more final constituents thereof by a forward chemical reaction, and in which, conversely, the one or more final constituents tend to reform the one or more original constituents by a reaction which is the reverse of the forward action. This situation is usually represented by the familiar chemical equation in which the one or more initial constituents appear on the left-hand side, the one or more final constituents appear on the right-hand side, and the left- and right-hand sides of the equation are separated by a forward reaction arrow pointing from left to right and a reverse arrow pointing from right to left.

Assume that a given chemical system at its beginning consists only of the one or more initial constituents. The said one or more constituents will start by the forward reaction to form the one or more final constituents. A state of equilibrium of the system is said to be reached when the rate at which the forward reaction proceeds is equal to the rate at which the reverse reaction proceeds. When once a state of equilibrium has been reached, the relative amounts of the one or more initial constituents and the one or more final constituents will remain unchanged so long as the system is not affected by some outside factor which changes its internal energy by changing, say, its temperature, pressure, or pH value.

From a starting condition wherein only the initial constituents are present, the ordinary chemical system reaches almost at once a state of stable equilibrium. By a state of stable equilibrium is meant the equilibrium state beyond which the chemical system by virtue of its own internal energy can proceed no further in increasing the amount of the one or more final constituents relative to the one or more initial constituents.

There are, however, some chemical systems which may be characterized by a state of unstable equilibrium. This unstable equilibrium state is a state which, from the starting condition where there is nothing but initial constituents, is reached before the final constituents increase in amount relative to the one or more initial constituents to the point corresponding to the stable equilibrium state for the system. A chemical system in unstable equilibrium can be induced, by disturbing its unstable state, to proceed to its state of stable equilibrium without any outside energy being added to the system.

In order, however, to induce a chemical system in unstable equilibrium to make the transition to stable equilibrium, it is necessary to change by a small amount the internal energy characterizing the system in its unstable state. This can be done by bringing into operational rela-

tion with the system some factor from outside the system which causes the necessary internal energy change to take place by, say, changing slightly the temperature, pressure or pH value of the system.

When once the required small amount of change in internal energy has been effected, the system proceeds almost instantaneously from its unstable equilibrium state to its stable equilibrium state, with the transition from the former to the latter state being accompanied by a change in internal energy which is substantially greater than the change of internal energy required to set off the transition in the first instance. Therefore, the outside factor which effects the initial change of small amount in the internal energy of the system while in unstable equilibrium can be considered as a "triggering" factor.

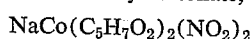
In the presently described embodiment, the image forming material in the layer 16 is a chemical complex which, before the image is produced, exists in a state of unstable equilibrium. Moreover, this chemical complex is adapted to undergo a change in tone density upon making the transition from its unstable to its stable equilibrium state. It is this transition which develops the image on the layer 16.

The transition of the image forming complex from unstable state to stable state is initiated by bringing into contact with the complex a catalyst material which, although small in amount, will effect a sufficient change in the internal energy of the complex to cause the complex to proceed from the unstable to the stable equilibrium state. A better understanding of how the catalyst is brought into contact with the image forming material will be derived from the following description of a specific example of an electrophotographic structure according to the invention, and of the composition, manufacture and operation of this exemplary structure.

In the specific example the layers 11, 12, 13 and 17 and the layers 14-16 constitute, respectively, the permanent part and the replaceable part of the whole electrophotographic structure shown in the drawing. As described in my mentioned copending application, Serial No. 656,918, the layers 11-13 and the layer 17 (which is in the form of a metal plate) may be components of a camera. The camera is loaded with the replaceable film pack (consisting of layers 14-16) by moving the plate 17 away from the photoconductive layer 13 (deposited on the coating 12 and the glass plate 11), inserting the said film pack in the space thus provided between the photoconductive layer and the plate 17, and moving the plate 17 back toward the photoconductive layer until the film pack is clamped with good pressure contact between the photoconductive layer and the plate.

When the image receiving layer 16 is separable from the electrode layer 17, it is convenient to use paper as a base or bulk-forming material for the image receiving layer. The image receiving layer is prepared by immersing the paper in a solution containing 100 grams of ammonium nitrate and 15 grams of mannitol or resorcinol for 100 cc. of water until the paper is well impregnated with the solution. After good impregnation has been attained, the paper is removed from the solution and dried. Upon drying, the mannitol or resorcinol (which, like ammonium nitrate are both soluble in water) recrystallizes in very intimate contact with the structure of the base material (i.e. the fibers of the paper) in the form of a solid solution of ammonium nitrate in mannitol or resorcinol. This recrystallization makes the base material electrically conductive, even in a dry state.

After the paper is completely dry, the paper is immersed for 10 minutes in an image forming solution of sodium di-nitrocobalt-di-acetylacetate,



and silver nitrate,  $\text{AgNO}_3$ . In order to prepare this solu-

tion of image-forming material, a solution is first made with the following composition:

|                                                               |       |
|---------------------------------------------------------------|-------|
| Acetylacetone $(\text{CH}_3\text{CO})_2\text{CH}_2$ -----gr-- | 8.00  |
| Sodium hydroxide $\text{NaOH}$ -----gr--                      | 3.20  |
| Water $\text{H}_2\text{O}$ -----ml--                          | 64.00 |

to this, a solution containing:

|                                                                        |       |
|------------------------------------------------------------------------|-------|
| Sodium cobaltionitride $\text{Na}_3\text{Co}(\text{NO}_2)_6$ -----gr-- | 15.00 |
| Water $\text{H}_2\text{O}$ -----ml--                                   | 36.00 |

is added.

The two solutions are mixed together and, after 10 minutes, the liquid is filtered. 50 gr. of a 10% solution of silver nitrate are then added and the pH is adjusted by a few drops of ammonium hydroxide to a value between 5 and 7.

After the paper has been immersed in the solution of image forming material for the stated 10 minute period, the paper is removed from the solution and is again dried. Next, several layers of material are deposited upon the paper base by vacuum deposition. The first deposition is a very thin film of silicon dioxide. A suitable thickness value for this film is a thickness of 500 Angstrom units or less. On top of the silicon dioxide film is deposited an extremely thin, essentially transparent film of copper. This latter film should also have an extremely small thickness dimension, suitable thickness values being 5 to 10 Angstrom units. The deposition of the copper film completes the preparation of the multilayer film pack. In this film pack, the impregnated paper, the silicon dioxide film and the copper film provide, respectively, the image receiving layer 16, the barrier layer 15 and the catalytic layer 14 which are shown in the drawing.

In the specific example being described, the photoconductive layer 13 is provided by a very thin film (less than 10 microns) of antimony trisulfide deposited by vacuum deposition on the substrate formed of the glass plate 11 and the NESA glass coating 12.

Assume now that the described film pack of paper based image receiving layer, silicon dioxide barrier layer and copper catalyst layer has been loaded in an electrophotographic camera so that there is assembled together a complete image-taking structure as shown in the drawing. Assume further that the image-carrying radiation 10 is directed on the structure in the manner shown. The radiation 10 passes through the plate 11 and the NESA glass coating 12 to areally modulate the face-to-face resistance of the photoconductive layer 13 inversely as the point-to-point distribution of intensity (in the plane of the photoconductive layer) of the radiation representing the image.

In the absence of a voltage pulse applied between the electrode layers (i.e. layers 12 and 17) of the image taking structure, the catalyst material (copper) in the layer 14 will be separated from the unstable image forming material (sodium di-nitrocobalt-di-acetylacetate and silver nitrate) in the image receiving layer 16 by the silicon dioxide barrier layer 15. Assume now, however, that there is applied between the electrode layers 12 and 17 a voltage pulse of suitable amplitude (e.g. 400 volts) and of such polarity that electrode layers 17 and 12 act, respectively, as positive and negative electrodes. This voltage pulse should have a very short duration, as, say, a duration of 15 microseconds.

Considering the electrophotographic structure as an electric circuit element, the structure can be thought of as being subdivided into a very large number of individual sections which each extend from the layer 12 to the layer 17, and which each are of incremental area in the cross-section thereof lying, say, in the plane of the layer 13. Each such section corresponds, electrically speaking, to the series combination of a variable resistance (photoconductive layer 13), a capacitor (barrier layer 15 of dielectric material) and another fixed resistance (image receiving layer 16). In each section the value of the resistance represented by the incremental area of photocon-

ductive layer in the section will vary inversely as the intensity of the radiation incident thereon. Hence, in each section, the voltage applied across the capacitor represented by the incremental volume of dielectric layer in the section will vary directly as the intensity of the radiation falling on the section. It follows that when the said voltage pulse is applied, the voltage developed by this pulse across the dielectric layer will be areally modulated from point-to-point in accordance with the areal distribution in intensity of the radiation which transmits the image.

The voltage developed across the dielectric layer will cause copper ions to migrate from the copper film 14 through the dielectric layer 15 and to the image-receiving layer 16. The quantity of copper which is so transported through the dielectric layer will vary from point-to-point thereover in accordance with the voltage value developed across the layer from point-to-point over its area. Upon reaching the image receiving layer, the transported copper acts as a catalyst which triggers off the dissociation of the unstable chemical complex constituting the image forming material. The susceptibility to dissociation of the image forming material is increased by the fact that the compounds constituting this material, being complexes, exhibit a rather strong dipole moment when in the presence of an electric field. This tends to increase the free energy of the reactants, and hence increases the instability of the complex formation.

The catalytic action of the migrated copper induces dissociation of the complexes to form free silver. It is the formation of this free silver which creates the image. The copper causes the dissociation reaction to occur, only upon contact, due to the fact that the copper is poisoned during the reaction and therefore is effective only a short time. Hence the reduction of the image forming material to free metal can be localized. Also with a suitably short voltage pulse, the density of the image developed by dissociation of the image forming material will vary with the total quantity of copper transported through the dielectric layer. When this functional relation exists between the amount of copper transported and the density of the image developed by dissociation, the image produced on the layer 16 will be a reproduction of the image transmitted by the radiation 10.

From the foregoing description of the operation of one form of electrophotographic structure according to the invention, it will be recognized that there are a number of distinctions between the invention disclosed herein and the invention disclosed in my mentioned copending application 656,918. Some of these distinctions are as follows. First, since the dielectric layer is essentially an insulator, the electrophotographic structure of the present invention is not a conductor of steady state D.C. electricity, i.e. is not analogous to a resistor. Second, while some current is needed to produce ions of the material used as the catalyst in order that this material will migrate through the dielectric barrier layer, the amount of catalyst involved in the image development is very small, and hence, the amount of current required to produce an image is also very small. The amount of current drawn may, thus, be, say, no more than a few microamperes. Third, while the production of the ions of the catalyst material may, in a sense, be considered an electrochemical reaction, since electric current from an outside source must be used to produce the ions, the energy involved in the ionization of the catalyst ions is very small compared to the energy involved in the dissociation reaction which develops the image. Hence, according to the present invention, the reaction which develops the image is not primarily an electrochemical reaction (which, to take place, must be supplied with electric energy from an outside source) but is, instead, primarily a reaction in which there is a transition from an unstable to a stable state of equilibrium. This latter type of reaction, when once started, requires no outside energy in order to continue. Fourth, the time required to develop a satisfactory image

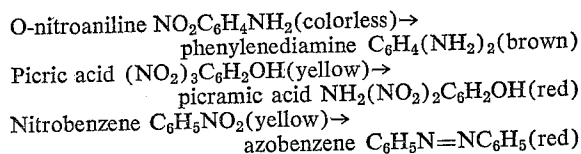
is extremely small and, with the choice of suitable materials for the various layers of the structure, can be reduced to close to the time required for the photoconductive layer to respond to the radiation incident thereon. Thus, as mentioned, it is easily practicable according to the present invention to reduce the time of exposure (as measured by the duration of the applied voltage pulse) to, say, 15 microseconds. Fifth, as a corollary to the extremely short time of exposure required, it has been found that an image with satisfactory contrast can be obtained irrespective of the average intensity of radiation incident on the electrophotographic structure so long as the average intensity is above a threshold value. This is so, since, because of the short duration of the applied voltage pulse, the number of current carriers produced in the photoconductive layer during the pulse will not vary appreciably with the average intensity of the received radiation. Sixth, the interposition of the dielectric layer between the photoconductive and image receiving layer serves to isolate the former from the possibly corrosive effect of the chemicals in the latter.

Other combinations of an image forming material and catalytic material will now be described. These combinations are as follows.

One such combination utilizes copper as the catalyst and cobaltisilvercyanide as the image forming material. This latter material is prepared by mixing 15.8 grams of cobalt  $\text{Co}(\text{CN})_2$  with a solution containing 100 ml. of water, 5 grams of nitric acid and 40 grams of silver cyanide. An insoluble precipitate results. As a preliminary to formation of layer 16, the particles of this precipitate are dispersed in an initially uncoagulated solution of gelatin and other substances to be later described. The dispersion is accomplished by adding the precipitate to the solution and by agitating the resulting mixture. The images obtained with this combination of catalyst and image forming material are characterized by a black and white tone density scale.

As another suitable combination, the material of the catalytic layer 14 may be potassium iodide. In this instance, the catalyst is iodine obtained by dissociation of the potassium iodide when a voltage pulse is applied to the electrophotographic structure. The image forming material is cryptoxanthin. The layer 16 is prepared, as later described, from an uncoagulated solution composed of 100 ml. of water, 5 grams of potassium hydroxide, 20 grams of cryptoxanthin, 40 grams of gelatin, and amounts of other substances which, as later described, are adapted to render the layer 16 electrically conductive. The cryptoxanthin dissociates to form the image.

The following reactions may also be used within a suitable catalyst:



In connection with the above combinations, the base material (to which the image forming material is added) may be prepared by mixing together 100 ml. of water, 100 grams of ammonium nitrate, 15 grams of mannitol and 40 grams of gelatin at a high enough temperature so that the gelatin does not coagulate until the solution has cooled somewhat. The image forming material is added to the uncoagulated gelatin solution. If the image forming material is likely to dissociate at the initial temperature used to dissolve the gelatin in the water, the addition of the image forming material to the gelatin solution should be delayed until it has cooled sufficiently so that dissociation of the image forming material will not take place. If the image forming material is soluble in water, the mentioned 100 ml. may be split into halves, one 50

ml. half being used to dissolve the gelatin, ammonium nitrate and mannitol, and the other 50 ml. half, the image forming material. The two solutions are thereafter added together. It is desirable, when the image forming material tends to dissociate at warmer temperatures, that the solution of image forming material be a cold solution. In this way, the solution of image forming material can be added to the gelatin solution without substantial dissociation of the image forming material taking place.

After the image forming material (or solution thereof) has been added to the solution of gelatin, ammonium nitrate and mannitol, the gelatin is permitted to coagulate, and the resulting gel is worked into the thin layer or coating which is used as the image receiving layer 16. This may be done by depositing the solidified mixture of gelatin and other substances on, say, a metallic foil sheet (used as electrode layer 17) with the help of a knife coater. The ammonium nitrate and mannitol perform the same role in the gelatin layer 16 as they do in the previously described paper layer 16, namely, to make the layer conductive to electricity.

Another specific example of an electrophotographic structure will now be given. In this example, the image receiving layer 16 is a gelatin coating deposited on a sheet of aluminum foil which provides the electrode layer 17 of the structure. The layer 16 is prepared in the following manner. An uncoagulated gelatin solution is formed by mixing together 50 ml. of water, 5 grams of sodium sulfate, 15 grams of mannitol and 40 grams of gelatin at a temperature above the coagulation temperature of the gelatin. At the same time there is prepared a cold solution consisting of 50 ml. of water, and 5.5 grams of hydroquinone,  $C_6H_4(OH)_2$ . In the example being considered, it is the hydroquinone which is the unstable material which will dissociate to form the image.

The cold hydroquinone solution is added to the uncoagulated gelatin solution when the latter is at a low enough temperature so that there is no danger of dissociation of the hydroquinone upon addition thereof to the gelatin. The gelatin is thereafter permitted to coagulate, and subsequently is spread as a coating on the aluminum foil.

Next, a silicon dioxide coating of a thickness of 500 Angstrom units or less is deposited by vacuum deposition on the gelatin coating. After the deposition of the silicon dioxide has been completed, a coating of nickel of an estimated thickness of 10 Angstrom units is deposited on top of the silicon dioxide. The film pack in the described example thus consists of a catalytic layer 14 of nickel, a barrier layer 15 of silicon dioxide, an image receiving layer 16 which employs gelatin as the bulk forming material and hydroquinone as the image forming material, and an electrode layer 17 of aluminum foil. In this film pack the nickel and the sodium sulfate act as co-catalysts for the dissociation of the hydroquinone. The sodium sulfate (in conjunction with the mannitol) also performs the additional function of rendering the gelatin conductive to electricity.

In the structure now under consideration, the photoconductive layer 13 is provided by a deposition of cadmium arsenide on a substrate provided by the glass plate 11 and the coating 12 of NESA glass. The cadmium arsenide layer has an estimated thickness of less than 10 microns.

The exemplary electrophotographic structure just described was operated (when assembled together as shown in the drawing) by the application to the electrode layers 12 and 17 of a D.C. voltage pulse having a voltage value of 400 volts and having a duration of about 15 microseconds. The pulse was applied with a polarity to render the layer 17 the negative electrode layer. The current drawn by the structure during the application of this pulse had a value of only a few microamperes. A picture obtained by such operation had a degree of

resolution and contrast which equaled the resolution and contrast obtainable in conventional photography.

It will be understood that the above-described embodiments of the invention are exemplary only, and that the invention comprehends embodiments differing in form and detail from the above-described embodiments. For example, the unstable chemical system comprising the image forming material may be induced to proceed to stable equilibrium to thereby develop an image by means other than by the introduction of a catalyst thereinto as, say, by bringing into operable relation with the system some other factor which effects a change in pressure, temperature or pH value to thereby alter slightly the internal energy of the system. Moreover, while in the described embodiment the photoconductive layer lies next to the layer of catalytic material, the order of occurrence of the catalytic layer, dielectric layer and image forming layer may be reversed so that the image forming layer is disposed between the photoconductive layer and the dielectric layer, and so that the catalytic layer is disposed between the dielectric layer and the electrode 17. With this reversed order of layer occurrence, a film pack may be prepared by successively depositing the catalytic and dielectric layers on a substrate of metallic foil providing the electrode 17, and by then topping the dielectric layer with an overlay of the image forming layer. Such mode of preparation avoids the problem of possibly subjecting the image forming layer to destructively high temperatures in the instance where one or both of the catalytic layers and dielectric layers are formed by heating the constituent material thereof to cause evaporation of the constituent material into an atmosphere under high vacuum, and by thereafter condensing the constituent material as a layer.

Accordingly, the invention is not to be considered as limited save as in consonant with the scope of the following claims.

I claim:

1. In an electrophotographic multilayer structure having electrodes on opposite sides thereof, with one of said electrodes being transparent to permit exposure of photoconductive material in said structure to light, the combination with said electrodes of a layer of photoconductive material in contact with an area of said transparent electrode, a thin film of copper in contact with said photoconductive layer, with said copper film being substantially uniform in thickness and being sufficiently thin to release copper ions therefrom when said structure is electrically energized, said photoconductive layer being adapted to areally modulate the flow of copper ions from said film, a barrier layer in contact with said copper film of a dielectric material selected from the group consisting of silicon dioxide and titanium dioxide, said barrier layer being sufficiently thin to allow copper ions to pass through the same when released from said copper film, and an image forming layer in contact with said barrier layer and with the other of said electrodes, said image forming layer being comprised of a bulk-forming material impregnated with ammonium nitrate, a polyhydroxy alcohol, and an organo-metallic compound selected from the group consisting of sodium di-nitrocobaltdi-acetylacetonate and cobaltisilver-cyanide, with said organo-metallic compound being adapted to change color when contacted by copper ions applied thereto through said barrier layer.

2. In an electrophotographic multilayer structure having electrodes on opposite sides thereof, with one of said electrodes being transparent, the combination with said electrodes of a photoconductive layer in contact with an area of said transparent electrode, said photoconductive layer being substantially uniform in thickness and having a thickness value less than about ten microns, a film of copper in contact with said photoconductive layer with said film being sufficiently thin to release copper

ions therefrom when said structure is electrically energized, and with said photoconductive layer being adapted to areally modulate the flow of such copper ions in accordance with the intensity distribution of light to which the photoconductor is exposed, a barrier layer of silicon dioxide material in contact with said copper film, said barrier layer being sufficiently thin to allow copper ions to pass through the same when released from said copper film, and an image forming layer in contact with said barrier layer and with the other of said electrodes, said image forming layer being comprised of a bulk-forming material impregnated with ammonium nitrate, silver nitrate, sodium di-nitrocobalt-di-acetylacetonate, and an alcohol material selected from the group consisting of mannitol and resorcinol, said barrier layer being adapted to conduct copper ions to said image forming layer to produce a visible record therein.

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