March 14, 1967 J. J. A. ROBILLARD 3,309,198

POSITIVE TO POSITIVE REPRODUCTION PROCESS AND COPY SHEET FOR USE THEREIN

Filed Sept. 30, 1965 2 Sheets-Sheet 1

FIG 1

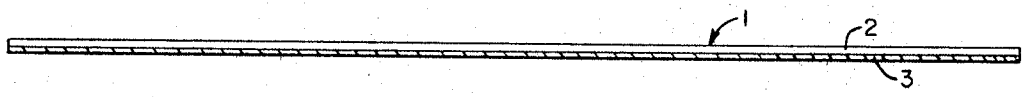


FIG. 2

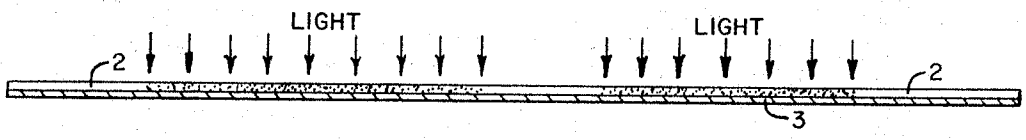


FIG. 3

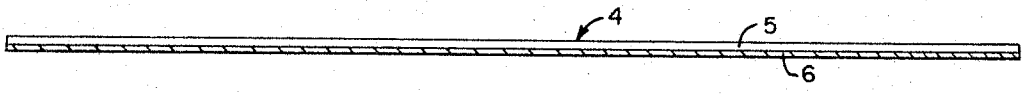


FIG. 4

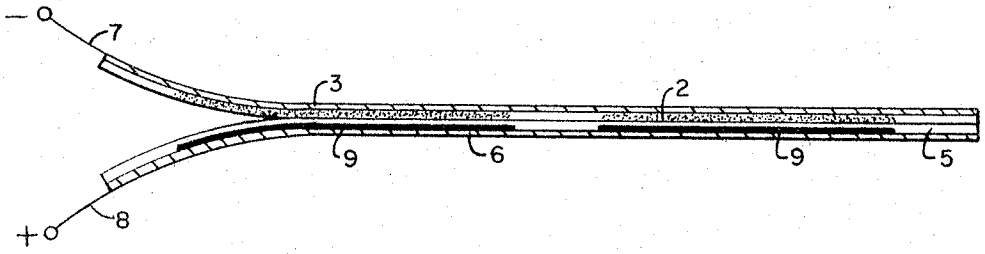
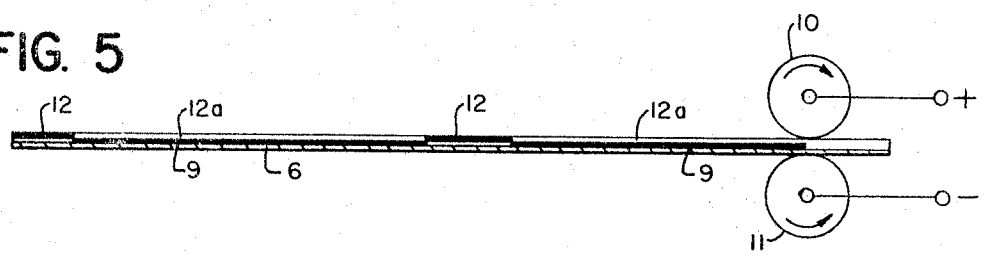


FIG. 5



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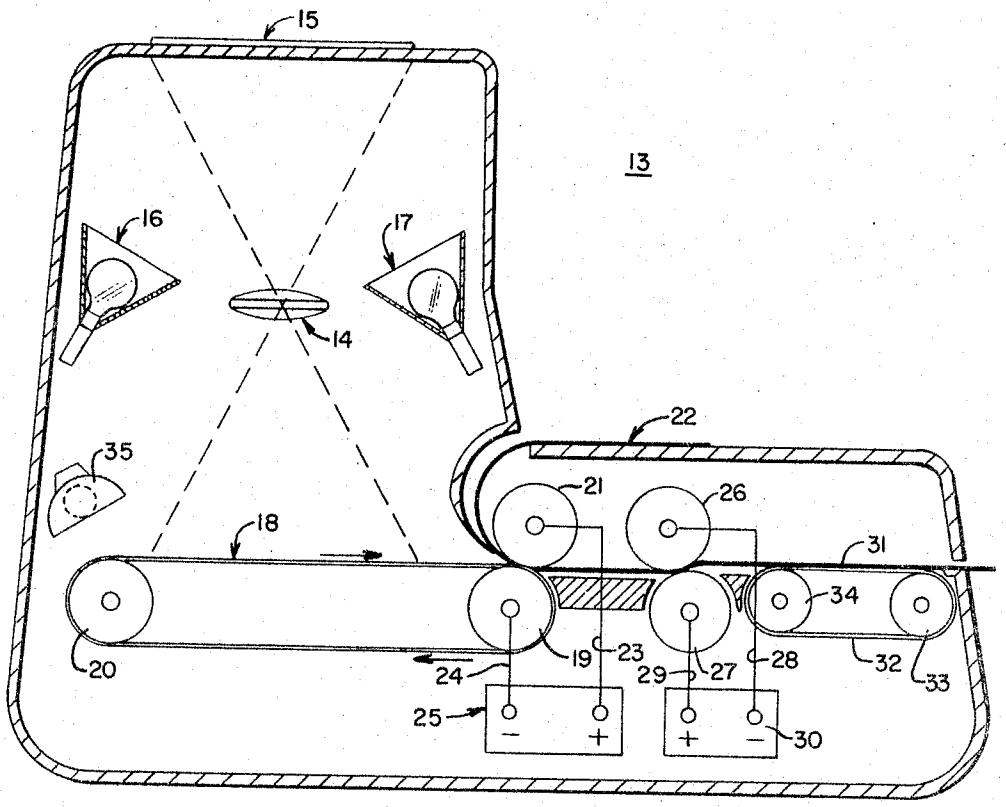
ATTORNEYS

March 14, 1967 J. J. A. ROBILLARD 3,309,198

POSITIVE TO POSITIVE REPRODUCTION PROCESS AND COPY SHEET FOR USE THEREIN

Filed Sept. 30, 1965 2 Sheets-Sheet 2

FIG. 6



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POSITIVE TO POSITIVE REPRODUCTION PROCESS AND COPY SHEET FOR USE THEREIN

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Filed Sept. 30, 1965, Ser. No. 491,786
17 Claims. (Cl. 96—1)

This application is a continuation-in-part of copending application Ser. No. 205,600, filed June 27, 1962, and copending application Ser. No. 182,864, filed Mar. 27, 1962, now abandoned, and refiled as application Ser. No. 567,684 on July 25, 1966.

The present invention relates to a positive to positive reproduction process involving the anodic oxidation of a metallic conductive base controlled by a photoconductive layer and the catalytic reduction of a semiconductor material.

In my copending U.S. patent application Ser. No. 205,600, filed June 27, 1962, there is disclosed a reproduction process in which the introduction of a small amount of catalyst into a semiconductor structure under the application of an electrical field provides a stable, high-contrast record of an original image projected onto the structure. There is disclosed, as an embodiment of the invention set forth therein, an electrophotographic sandwich structure consisting of, in the order named, an electrode which may be formed of conductive glass, a photoconductive layer which may be formed of cadmium selenide, zinc oxide, or antimony trisulfide, a catalyst layer which acts as a source of catalytic ions and may comprise, for example, a thin layer of silver or a silver compound, a recording layer comprising a semiconductor material and a second electrode which need not be transparent and may comprise aluminum foil as an example. The electrodes forming the top and bottom parts of the sandwich structure are connected to an electrical source.

The sandwich structure of my copending application operates in the following manner: When an image is projected onto the glass electrode, the transparent electrode transmits the radiation so that it falls on the photoconductive layer rendering those portions on which radiation falls relatively more conductive than the dark portions of the photoconductive layer. Thus, different conductivity paths will be produced in the photoconductive layer according to the distribution of the image brightness.

The current intensity will vary according to the conductivity of the photoconductive layer and hence according to the local brightness of the image. Catalytic ions from the catalytic layer will be transported into the semiconductor layer in numbers corresponding to the current flux in each area of the surface of the semiconductor layer (the polarity of electrodes is determined to transport the ion in the direction from the catalytic layer to the semiconductor layer). The transport of catalyst into the semiconductor layer triggers a change in state of oxidation of the semiconductor, usually an oxide, and thereby provides a change in color. While the described structure of my copending application is capable of producing good quality images, it is, however, not optimally suited for photocopy reproduction because of the negative image generally obtained from a positive original.

According to the present invention, a dry process, with quite good speed (sensitivity) is provided in which a substantially permanent positive image is formed by having an image projected onto a photoconductive layer which is then placed in contact with a copy sheet coated with a mixture of a semiconductor material and a dry electrolyte and applying an electric field between the conductive base of the photoconductive layer and the conductive base of the copy sheet and subsequently passing

the copy sheet under a roller or other electrode coated with a catalyst material and generating an electric field through the copy sheet to obtain a (preferably positive) reproduction of the original.

It is, accordingly, an object of this invention to provide a positive-to-positive electro-catalytic reproduction system.

It is another object of the present invention to provide a process whereby an oxide film is obtained on the conductive surface of a copy sheet upon the application of an electric field between the conductive base of a photoconductive layer placed in contact with the copy sheet and the conductive base of the copy sheet.

It is also an object of the present invention to provide a photographic process wherein catalytic ions are electrically injected in minute quantities into an electrosensitive coating on a copy sheet, the injection of such ions being controlled by an oxide image formed in selected areas of the copy sheet.

Still another object of the present invention is to provide a copy sheet comprising an electrosensitive material and a dry electrolyte, which upon contact with a photoconductive layer exposed to an image, will produce under the actuation of an electric field an oxide image in selected areas of the conductive base of the copy sheet.

Other objects and advantages of the present invention will be apparent from the consideration of the following description in conjunction with the appended drawings, in which:

FIGURE 1 is a diagrammatic illustration of a photoconductive recording medium according to the present invention;

FIGURE 2 is a diagrammatic illustration of a photoconductive recording medium of this invention exposed to the image of the original to be reproduced;

FIGURE 3 is a diagrammatic illustration of an electrosensitive recording medium according to the present invention;

FIGURE 4 is a diagrammatic illustration showing the contacting of the photoconductive recording medium exposed to the image of the original with the electrosensitive recording medium under the application of an electric field;

FIGURE 5 is a diagrammatic illustration of the passing of the electrosensitive recording medium between two conductive rollers, the upper roller being coated with a catalyst material, to obtain a positive reproduction of the original according to the present invention; and

FIGURE 6 is a schematic diagram of a photocopy apparatus according to the present invention.

Referring now to FIGURE 1, photoconductive recording medium **1** is shown comprising a photoconductive layer **2** deposited on a suitable conductive carrier **3**. The conductive carrier may be aluminum foil or the like. However, other metal foil or conductive material may be used. Metal conductors, such as aluminum, nickel, copper, etc. may also be deposited as a conductive material on a non-conductive plastic or the like to form the carrier. The purpose of the conductive backing is to facilitate exposure of the photoconductive recording medium **1** to an electric field.

The photoconductive layer **2** may be formed of well known photoconductors, including cadmium sulfide, cadmium telluride, zinc oxide, antimony sulfide, selenium, germanium, lead sulfide, zinc sulfide, etc. All of these materials show a change in conductivity or resistivity upon exposure to radiation.

The selected photoconductive material is coated on the conductive carrier as a dispersion in a binder. The binder holds the particles to the conductive backing and is believed to aid in insulating the particles from each other.

Suitable binders include "Pliolite" (resinous copolymers

of butadiene and styrene), "Zytel" (resin composed of alcohol-soluble polyamides), and "Versalon" (polyamide resin).

The photoconductive layer may be prepared by grinding in a ball mill a mixture of the photoconductive material with a binder and a solvent. The mixture is ground until a smooth dispersion is obtained. After the coating has been prepared, it is coated on foil or other conductive paper. Any suitable coating process may be utilized, for example, a knife coating machine may be used to coat a layer of the photoconductive material onto the carrier. The thickness of the coating might be optimized in a thickness range varying from 5 microns to as much as 2 mils. Generally a thin coating is desirable. The solvent is removed by evaporation and the coating is allowed to dry.

Preferred solvents for preparing the photoconductive coating are toluene, methyl ethyl ketone and alkanols such as absolute ethanol. However, other conventional solvents of the class of aromatic ad aliphatic ketones and alcohols may be employed within the scope of this invention.

A specific illustrative but nonlimiting example of a photoconductive coating will now be given. A mixture of 100 grams of zinc oxide, 8 cc. of Pliolite S–7 (30% solution), 1000 cc. toluene is ball milled for twenty-four hours. After ball milling, a 10 cc. of 0.1% solution of Rose Bengal (light sensitive dye) is added to the mixture. A smooth dispersion is obtained which is spread over the conductive carrier and the solvent removed by evaporation at room temperature.

The photoconductive recording medium is employed according to the present invention by exposure to the image of the original to be reproduced. This will result in a latent image being formed in terms of local variations of conductivity in the photoconductive layer as illustrated by FIGURE 2.

After the photoconductive layer **2** has been exposed to the image of the original, it is placed in contact, under the application of an electric field, with an electrosensitive recording medium which will be described hereinafter.

Referring to FIGURE 3, the electrosensitive recording medium **4** comprises an electrosensitive layer **5** containing a mixture of sensitive pigments, usually a semiconductor oxide, and a dry electrolyte deposited on a conductive carrier **6**. The conductive carrier may comprise aluminum foil or may be a conductive layer on a reinforcing backing such as plastic or paper.

The semiconductor material in the electrosensitive layer **5** comprises a semiconductor oxide which upon a change in the state of oxidation produces a change in color.

A list of different semiconductor oxides that are particularly suitable for the semiconductor material is given below, together with their reduced states and the change in color which accompanies the change in the oxidation state:

TABLE I

Materials		Color	
MoO_3	MoO_2	White	Gray.
PbO_2	Pb_2O	do	Black.
TiO_2	TiO	do	Do.
V_2O_5	V_2O_4	Yellow	Blue.
Ta_2O_5	Ta_2O_4	White	Black.
CeO_2	CeO	do	Do.
Bi_2O_3	Bi_2O_5	Yellow	Do.
Cr_2O_3	CrO	Green	Do.
CoO	Co_3O_4	do	Do.
MnO	Mn_2O_3	do	Do.
NiO	Ni_2O_3	do	Do.
TaO_2	TaO	White	Do.
SnO_2	SnO	do	Do.
WO_3	WO_2	Yellow	Brown.

In order to bring out the semiconductive properties of the semiconductor material it is necessary to "dope" this material. The doping material and procedure will vary somewhat with the oxide considered as will be understood by those skilled in the art. The doping material and procedure is determined from the semiconductor's energy band structure and other solid state properties.

By way of example the preparation of a doped titanium dioxide will be described in some detail. In this procedure commercially pure titanium dioxide may be used. This material is readily available and is utilized in the manufacture of paint, for example. Titanium dioxide of this grade will normally be found to have many crystal defects which is desirable for use in formulating a semiconductor oxide according to the present invention. If desired, an X-ray analysis of the titanium dioxide to be used may be made to assure that it has the desirable crystal defects.

The titanium dioxide is sensitized by doping to introduce impurities in minute quantities. A sodium hydroxide solution may be utilized for doping the titanium dioxide thus introducing sodium ions as impurities in the titanium dioxide crystals.

The following procedure may be followed to prepare the doped oxide. Commercially pure titanium dioxide powder is ball milled for approximately 24 hours to a grain size of about 1 micron.

The finely divided titanium dioxide powder is then agitated for several hours in a solution of sodium hydroxide (approximately 10%). This solution may be obtained by adding the appropriate amount of sodium hydroxide to the water in which the finely divided titanium dioxide was milled. The agitation in the sodium hydroxide solution results in the doping of the titanium dioxide which may thereafter be dried in a vacuum oven.

Another example of a doped semiconductor oxide material according to the present invention is based upon the use of stannic oxide (SnO_2). The preparation of a doped stannic oxide is substantially similar to that previously described for titanium dioxide. The doping solution may be 5% sodium acetate solution.

As a further example of a doped semiconductor oxide, CeO_2 is doped by a process substantially as previously described for titanium dioxide by mixing the material with 10% solution of sodium hydroxide and agitating this solution for a period of six hours.

The following procedure may be followed to prepare the electrosensitive coating comprising the semiconductor oxide and dry electrolyte. The doped semiconductor oxide is combined with water and ball milled for 24 hours. A homogeneous liquid is obtained. To this liquid there is added the following: a minor amount of a humectant, a solution of an ionic salt which provides conductivity in the coating and a compound which helps to form the oxide film on the conductive surface of the electrosensitive layer. This mixture, which is very viscous, is then added slowly with agitation to an organic binder in a suitable solvent. There is obtained a dispersion which is coated on a suitable conductive carrier. The thickness of the coating is not critical and may vary from 5 microns to as much as 2 mils in some instances. Generally a thin coating is desired.

The humectants useful in the electrosensitive composition include glycerol, sorbitol and other glycols. The ionic salt is preferably ammonium nitrate. Compounds suitable for use in the electrosensitive composition to bring about the formation of the oxide film in selected areas include phosphoric acid, chromic acid, ammonium tartrate, ammonium citrate, boric acid, oxalic acid, ammonium phosphate, ammonium pentaborate and tartaric acid.

The binders useful in the electrosensitive coating include "Zytel" (resin composed of alcohol-soluble polyamides), "Pliolite" (resinous copolymers of butadiene and styrene) and "Versalon" (polyamide resin).

Preferred solvents for preparing the electrosensitive

coating are toluene, methyl ethyl ketone, and alkanols such as absolute ethanol. However, other conventional solvents may be employed.

A specific illustration example of an electrosensitive composition will now be given. A mixture of 75 grams of doped tin oxide and 100 grams of water are ball milled for twenty-four hours. A homogeneous liquid is obtained. To 20 cc. of this liquid there is added 1 cc. of phosphoric acid, 2 cc. of glycerol, and 5 cc. of ammonium nitrate (25% solution). This mixture is added slowly with agitation to 20 cc. "Zytel" (15% solution) in 20 cc. ethyl alcohol. There is obtained a dispersion of low viscosity which is spread on a conductive carrier in a uniform layer at a thickness of 1 mil.

The foregoing example of the preparation of an electrosensitive coating used for the electrosensitive recording medium is given by way of example only and is subject to considerable modification in accordance with the knowledge of the art.

Referring to FIGURE 4, the photoconductive recording medium **1**, after exposure to the image of the original, is placed in contact with the electrosensitive recording medium **4** which is a copy sheet. An electric field is applied by connecting conductive base **3** and conductive base **6** by leads **7** and **8** respectively to an electrical source (electrical potential difference between about 10 volts and 100 volts), the copy sheet being positive with respect to the photoconductive recording medium **1**. A current will flow between the photoconductive layer **2** and the electrosensitive layer **5** at a rate proportional to the change in conductivity on the photoconductive layer according to the previous light exposure of the photoconductive recording medium, and a thin oxide film **9** will develop on the surface of the conductive layer of the copy sheet at the same rate. The oxide film is formed according to the well known process of anodic oxidation. The anodizing current is modulated by the photoconductive layer **1**.

Referring now to FIGURE 5, after the oxide film **9** has formed on the copy sheet, the sheet is fed between two rollers **10** and **11**, the one on the surface of the sheet being coated with a catalyst and maintained at a positive electrical potential, with respect to the lower roller (potential difference between about 10 volts and 100 volts). The current that will flow upon the application of the electric field will be modulated according to the distribution of the oxide film on the conductive carrier of the copy sheet, that is, the oxide film will offer high resistance to the passage of the current and a relatively small current will flow in these areas, while higher current density will exist in areas free of the oxide film.

As a result of this current flow, a variable amount of catalyst will be transferred from the catalyst coated roller **10** into the electrosensitive layer **5**, providing darkening proportional to the density of the current. As shown in FIGURE 5, the characteristic of the positive image **12** formed on the copy sheet will be such that to the areas covered by the oxide film **9** on the surface of the conductive carrier **6** will correspond white areas **12***a* on the surface of the copy sheet and to the areas free of the oxide film **9** will correspond the dark areas. In this manner a positive image of the original is obtained as shown at **12**.

The darkening of the copy sheet in those areas free from the oxide film is due to the change in oxidation state of the oxide in the electrosensitive coating resulting from the introduction of a small amount of active catalyst. It is necessary that the catalyst atoms or molecules be electrically charged in order that they may be transported into selected areas of the copy sheet with an electric current. In the present invention the catalyst atoms or molecules are ionized.

The catalyst layer deposited on roller **10** may comprise, for example, a thin layer of silver or a silver compound. The thin layer can be obtained by vacuum deposition according to the techniques well known in the art. Methods for so depositing a thin layer on a substrate are disclosed in the text "Vacuum Deposition of Thin Films" by Holland (published in 1956 in London by Chapman & Hall, ltd.).

The catalyst layer has a very high chemical activity for thicknesses lower than 0.1 micron and as a consequence, they are always oxidized. Furthermore, the bond between the oxygen atoms and the metal atoms is much weaker than in a bulk oxide or thick layer of oxide. This is due to the fact that the resultant of the forces exerted on a particular molecule of oxide in a direction perpendicular to the film does not balance the one exerted in a direction parallel to the film. As a result, if an electric field is applied perpendicular to the film, the oxide molecule will easily dissociate and provide a metal ion which is transportable by the electric current (Langevin theory).

While silver is an appropriate catalyst for use in connection with semiconductor oxides such as cerium oxide, titanium dioxide and stannic oxide, other catalysts may be preferred with other oxides. For example, tantalum oxide may be used with a copper or manganese catalyst, lead oxide may be used with a nickel catalyst. In addition, a thallium catalyst may be used with titatnium dioxide, cerium oxide or germanium dioxide as an alternative to the silver catalyst.

The mechanism of the change in oxidation state due to the introduction of a small amount of catalyst in the semiconductor oxide material in the electrosensitive layer involves a consideration of the two categories;

In the first category only the formation of activation centers proportional to the number of catalyst atoms introduced into the system is involved. These activation centers are invisible and form a latent image similar in these respects to the one obtained with silver halide photography. This latent image can be developed by further exposure to a radiation of short wave length such as ultraviolet light.

In the second and preferred category, the change in oxidation state, accompanied by the change in color, takes place spontaneously upon the introduction of the catalyst under influence of an electric field. This involves a chain reaction in which the number of oxide molecules affected is far greater than the number of atoms of catalyst introduced into the system.

It will be apparent that the second category process, which does not involve further exposure to radiation to develop the latent image, is somewhat preferable. However, the requirement for exposure to further radiation is usually met simply by exposure to daylight, fluorescent light, or other low level illumination with some ultraviolet component.

To present a better understanding of the catalytic reduction involved in the positive image forming process, the mechanism of the action will be explained with reference to a specific example, cerium oxide.

The catalytic reduction of the oxide in the semiconductor layer involved in the positive image forming process is based on the control of the number of ions of deviating valency in an ionic crystal by incorporation of impurity ions of a certain type into the lattice.

In the original cerium oxide a small amount of CeO is always present along with the predominant CeO_2. This small amount of CeO plays an important role in the initiation of further reduction. The introduction of catalyst ions such as silver ions into the existing CeO lattice will control the number of Ce^{3+} ions. The smaller charge of the Ag^{+} ions balances the excess charge of the Ce^{3+} ions without the simultaneous introduction of vacancies in the cation lattice.

The defect center may be described as an impurity cation of lower relative charge on a cation site plus a positive hole bound on a neighboring host cation. In contrast to stoichiometric CeO the silver containing material shows a considerable increase in electrical conductivity of the p-type. The silver catalyzed cerium oxide has much the same properties as CeO prepared under slightly reducing conditions, but in the latter material, there is no way of estimating or controlling the concentration of

defects. The incorporation of a cation site of an impurity cation of higher charge than the host cation can stabilize a lower valence state of the host cation.

In the first category of oxides previously discussed (those requiring "development" by exposure to further radiation such as ultraviolet light) the existence of electrical defects in the crystal lattice will provide trapping levels in the energy diagram at different depths under the conduction band. The position of these levels in the energy diagram is such that the absorption of a quantum of light in the ultraviolet band will create free electrons which will be trapped at the existing trapping centers. As a result, the trapping center will provide a local concentration of negative charges. In addition to this electron trapping, an ionic process takes place in the CeO_2 emulsion, where CeO ions are displaced from the lattice and are moved foward to the negative trapping centers where they discharge themselves.

The motion of the ions is of two kinds: direct motion from one interstitial position in the lattice to another, and the filling up of the vacated sites by several ions in the lattice producing new vacant sites so that "positive holes" migrate. As the development proceeds, more electrons are provided to the trapping levels by the absorbed UV light and the reduced state of oxide is built up accordingly. The oxygen atoms released are diffused to the surface or remain interstitially.

In the second category of materials, the development of the image takes place immediately upon the introduction of the catalyst into the oxide layer without absorption of UV light for the development. The mechanism is as follows: The trapping of an electron by the trapping centers as mentioned previously, tends to hasten the diffusion of O^{2-} ions away from their original sites and leave an equivalent number of cations adjacent to the reduced ion. These cations with anion vacancies are added to the reduced ion neutralizing the trapped electron, and so on. This represents the autocatalytic phase of the reaction which is responsible for amplification and self-development of the image.

A study of the reduction mechanism of different oxides, together with their band structure and semiconductive properties will determine whether an autocatalytic image forming reaction is possible. When this possibility exists, emulsions can be made which will not require UV exposure for development.

Examples of oxides which do not require any ultraviolet development are SnO_2, Ta_2O_5 and TeO_2.

The photoconductive recording medium of FIGURE 1 and the electrosensitive recording medium of FIGURE 3 are particularly useful in photocopy applications and may be utilized in an apparatus such as that illustrated in FIGURE 6, for example.

Photocopy apparatus **13** comprises a lens **14** for focusing an image of a document **15** or other subjects to be reproduced. The image of a document is focused by lens **14** under illumination from light sources **16** and **17** onto a photoconductive belt **18** which is formed of a sheet as described in FIGURE 1. The photoconductive belt **18** is driven by rollers **19** and **20**. A copy sheet **22**, which is a sheet as described in FIGURE 3, is contacted with the photoconductive belt **18** under the pressure of rollers **19** and **21**. These rollers **19** and **21** are electrically connected by leads **23** and **24** to a source of electrical potential **25** providing the necessary electrical field for the formation of an oxide film in selected areas on the surface of the conductive base of copy sheet **22**.

After passing between rollers **19** and **21**, copy sheet **22** is passed between rollers **26** and **27** which are electrically connected by leads **28** and **29** to a source of electrical potential **30** providing the necessary current for the formation of the positive image **31** of the original on copy sheet **22**. The conductive roller **27** is coated with a solid catalyst which migrates into the copy sheet **22** upon the application of an electric field.

The positive reproduction **31** of the original **15** is transferred outside the machine by belt **32** driven by pulleys **33** and **34**.

The latent photoconductive image provided on belt **18** after exposure to the image can be erased by exposure to infrared lamp **35** and the belt is then ready for a new exposure. The absorption of the infrared light by the belt **18** provides enough energy to release the electrons from the trapping centers through vibration of the lattice. The absorption of light by the belt **18** upon exposure to the image promotes the trapping of electrons and the infrared light releases these electrons.

The operation of the photocopy apparatus of FIGURE 6 is as follows. An image is projected by lens **14** onto a photoconductive belt **18** for the exposure thereof. After the formation of a latent image in terms of local variations of conductivity in the belt **18**, the belt is contacted with copy sheet **22** under the pressure of rollers **19** and **21** and an electric field is applied between the copy sheet **22** and the belt **18**, the copy sheet being positive with respect to the belt. The flow of a current between belt **18** and copy sheet **22** will result in the formation of an oxide film in selected areas on the surface of the conductive base of the copy sheet. The copy sheet is then fed between conductive rollers **26** and **27**, roller **27** being coated with a solid catalyst which will migrate into selected areas of the copy sheet upon the application of an electric field between rollers **26** and **27**, thereby providing a positive image of the original on the copy sheet. The image formed on belt **18** is erased by exposure to infrared lamp **35**.

The theoretical explanations of the processes involved in the present invention have been explained as they are presently understood and are believed correct. However the advantages, operability or scope of the invention is not predicated on the accuracy of such explanations but upon the actual operation of the disclosed devices, apparatus and processes.

Other variations and embodiments will be apparent to those of skill in the art and it is accordingly desired that the scope of the invention not be limited to those embodiments particularly illustrated or suggested, but that the scope of the invention be defined by reference to the appended claims.

What is claimed is:

1. A process of producing a substantially permanent visible photographic record characteristic of a radiation image which comprises (a) exposing to said image the surface of a photoconductive recording medium supported on an electrically conductive backing, said photoconductive recording medium comprising a layer of photoconductive material which exhibits a change in conductivity in those areas of said photoconductive recording medium exposed to said radiation image and forming as a result of exposure of said photoconductive recording medium to said image a latent image in terms of local variations of conductivity in said photoconductive recording medium, (b) contacting the surface of said photoconductive recording medium with the surface of an electrosensitive medium comprising an electrolyte and an oxidizable metallic electrically conductive backing, (c) impressing an electric field through said photoconductive recording medium and said electrosensitive medium to obtain a thin highly resistive oxide film in selected areas on the surface of the electrically conductive backing of said electrosensitive medium, said current flow between said photoconductive recording medium and said electrosensitive oxidizable medium being substantially proportional to the change in conductivity in said photoconductive recording medium according to the previous exposure of said medium to said radiation image, (d) placing a solid metal catalyst source in contact with the surface of a semiconductor material layer having at least two oxidation states of substantially contrasting color with the lower oxidation state being intensely colored, said semiconductor material being substantially in a higher oxidation state and said semiconductor material being doped with a donor impurity compatible with the energy band of said semiconductor ma-

terial, said semiconductor material layer being also in contact with said oxide film on said electrically conductive backing and (e) impressing an electric field through said solid metal catalyst source, said semiconductor material layer and said electrically conductive backing on which said oxide film is formed to inject metal ions of said catalyst into said semiconductor material layer, said current that flows upon the impression of said electric field being modulated according to the distribution of said oxide film on the surface of said electrically conductive backing, said oxide film offering a higher resistance to the passage of current and said metal ions into said semiconductor material layer than those areas on the surface of said electrically conductive backing free of said oxide film, whereby the injection of said metal ions into said semiconductor material layer causes said semiconductor material to convert into a lower oxidation state in selected areas of said layer thereby producing a photographc record of the image.

2. A process according to claim 1 wherein the photoconductive material is selected from the group consisting of cadmium sulfide, cadmium telluride, zinc oxide, antimony sulphide, zinc sulphide, lead sulphide, selenium, and germanium.

3. A process according to claim 1 wherein said dry electrolyte comprises an ionic salt, a humectant and a compound selected from the class consisting of phosphoric acid, chromic acid, ammonium tartrate, ammonium citrate, boric acid, oxalic acid, ammonium phosphate, ammonium pentaborate and tartaric acid.

4. A process according to claim 1, wherein the ions of solid metal catalyst are selected from the group consisting of silver, copper, manganese and thallium.

5. A process according to claim 4 wherein the catalyst comprises silver.

6. A process according to claim 1, wherein the semiconductor material is a semiconductor oxide.

7. A process according to claim 6 wherein said semiconductor oxide is titanium dioxide and said solid metal catalyst is silver.

8. A process according to claim 1, which includes the additional step of exposing said semiconductor material layer and the metal ions therein to a light source rich in ultraviolet.

9. A process for the positive reproduction of a light image on a copy sheet which comprises: (a) exposing to said image the surface of a photoconductive recording medium supported on an electrically conductive backing, said photoconductive recording medium comprising a layer of photoconductive material which exhibits a change in conductivity in those areas of said photoconductive recording medium exposed to said light image and forming as a result of exposure of said photoconductive recording medium to said image a latent image in terms of local variations of conductivity in said photoconductive recording medium, (b) contacting the surface of said photoconductive recording medium with the surface of a copy sheet comprising a semiconductor oxide having at least two oxidation states of substantially contrasting color with the lower oxidation state being intensely colored, an electrolyte and an oxidizable electrically conductive backing, said semiconductor oxide being substantially in a higher oxidation state and said semiconductor oxide being doped a donor impurity compatible with the energy band of said semiconductor oxide, (c) impressing an electric field through said photoconductive recording medium and said copy sheet to obtain a thin highly resistive oxide film in selected areas on the surface of the electrically conductive backing of said copy sheet, said current flow between said photoconductive recording medium and said copy sheet being substantially proportional to the change in conductivity in said photoconductive recording medium according to the previous exposure of said medium to said light image, (d) placing a solid metal catalyst source in contact with the surface of said copy sheet, and (e) impressing an electric field through said catalyst source and said copy sheet to inject metal ions of said catalyst into said semiconductor oxide in said copy sheet, said metal ions being selected from the class consisting of silver, copper, manganese and thallium, said current that flows upon the impression of said electric field being modulated according to the distribution of said oxide film on the surface of said electrically conductive backing, said oxide film offering a higher resistance to the passage of current and said metal ions into said semiconductor oxide than those areas on the surface of said electrically conductive backing free of said oxide film, whereby the injection of said metal ions into said semiconductor oxide causes said semiconductor oxide to convert to a lower oxidation state in selected areas of said copy sheet thereby producing a positive image of the original on said copy sheet.

10. An electrosensitive coating comprising a semiconductor oxide having two oxidation states of different color, said oxide being substantially in the higher state of oxidation and doped with an impurity in a quantity to render the coating sensitive to the introduction of a relatively small number of ions of a solid catalyst upon the application of an electric field to change said oxide by catalytic action from the higher to a lower state of oxidation, and a dry electrolyte mixed with said semiconductor oxide and dispersed in an organic binder.

11. A coating according to claim 10 wherein the oxide comprises titanium dioxide.

12. A coating according to claim 10 wherein the oxide comprises cerium dioxide.

13. A copy sheet comprising a mixture of a semiconductor oxide and a dry electrolyte, said oxide having two oxidation states of different color, said oxide being substantially in the higher state of oxidation and doped with an impurity in a quantity to render the coating sensitive to the introduction of a relatively small number of ions of a solid catalyst upon the application of an electric field to change said oxide by catalytic action from the higher state of oxidation to a lower state of oxidation, said semiconductor oxide and dry electrolyte being supported on an electrically conductive backing containing a material capable of undergoing anodic oxidation.

14. An electrosensitive recording medium comprising a semiconductor oxide doped with a donor impurity, an electrolyte, an organic binder and a oxidizable electrically conductive backing, said semiconductor oxide having at least two oxidation states of substantially contrasting color with the lower oxidation state being intensely colored, and said oxide being substantially in the higher oxidation state and said electrolyte comprising an ionic salt, a humectant and a compound selected from the class consisting of phosphoric acid, chromic acid, boric acid, oxalic acid, tartaric acid, ammonium phosphate, ammonium citrate, ammonium tartrate and ammonium pentaborate.

15. A recording medium according to claim 14 wherein the semiconductor oxide is selected from the group consisting of TiO_2, SnO_2 and CeO_2.

16. A recording medium according to claim 14 wherein said donor impurity are sodium ions.

17. A copy sheet comprising an electrosensitive layer on a contiguous oxidizable electrically conductive backing, said electrosensitive layer comprising: (1) a semiconductor oxide doped with a donor impurity in a quantity sufficient to render said oxide sensitive to the introduction of a relatively small quantity of metal ions of a solid metal catalyst upon the application of an electric field, said oxide having at least two oxidation states of substantially contrasting color with the lower oxidation state being intensely colored and said oxide being substantially in the higher oxidation state, (2) an organic binder, (3) a dry electrolyte comprising an ionic salt, a humectant and a compound selected from the class consisting of a phosphoric acid, chromic acid, boric acid, oxalic acid, tartaric acid, am-

monium phosphate, ammonium citrate, ammonium tartrate and ammonium pentaborate.

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