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ELECTROCATALYTIC PHOTOGRAPHY UTILIZING
PHOTODEACTIVATED CATALYSTS
Filed June 14, 1965

3,457,069

FIG. 1

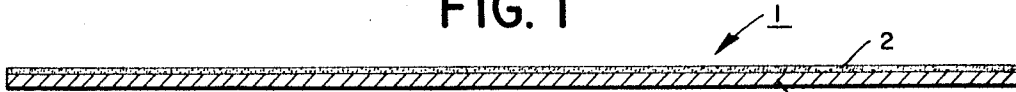
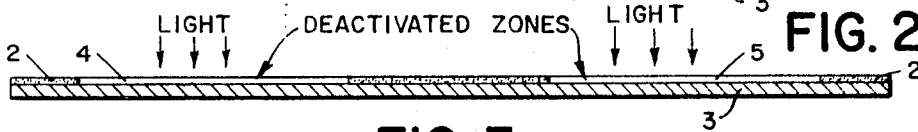


FIG. 3

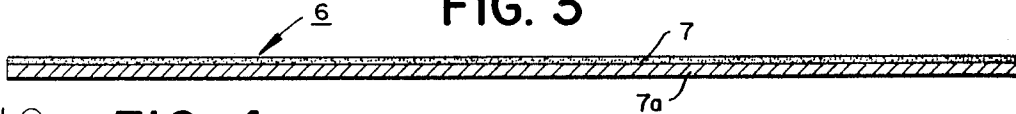
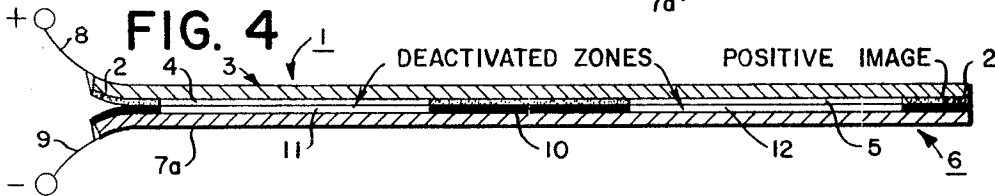
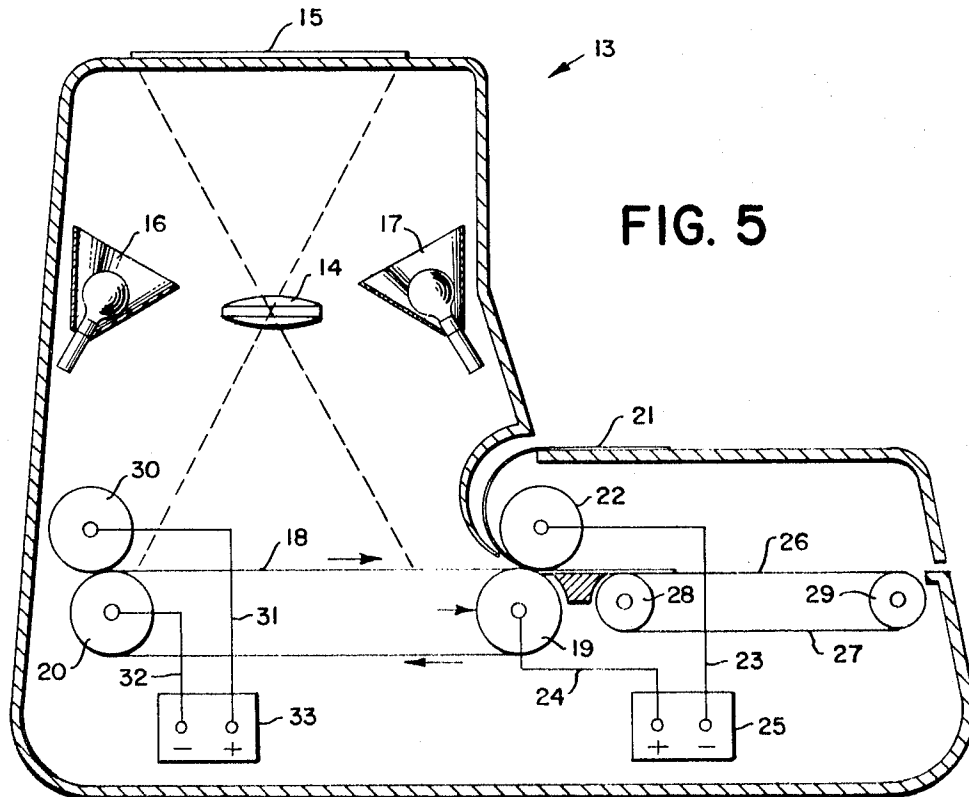


FIG. 5

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1

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ELECTROCATALYTIC PHOTOGRAPHY UTILIZING PHOTODEACTIVATED CATALYSTS

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15 Claims

ABSTRACT OF THE DISCLOSURE

A process of producing a substantially permanent visible photographic record is described which comprises exposing a radiation image to a catalytic surface adapted to be deactivated according to the intensity of the radiation striking the catalytic recording medium and contacting the surface of the catalytic medium with a semiconductor material containing recording medium and then impressing an electric field through the contacting surfaces to produce a permanent visible photographic record on the semiconductor recording medium. A photocatalytic recording medium for use in carrying out the reproduction process is also described.

The present invention relates to a positive-to-positive reproduction process involving the deactivation of a catalyst layer under the influence of light and the reduction of a semiconductor oxide.

In my copending U.S. patent application, Ser. No. 205,600, filed June 27, 1962 now U.S. Patent No. 3,355,290, 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 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

2

into the semiconductor layer triggers a change in the state of oxidation of the semiconductor, usually an oxide, and thereby provides a change in color. While the described structure 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.

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

Another object of the present invention is to provide an electrophotographic system wherein a two-step process is employed which produces a positive image of the original.

According to the invention, a dry 2-step process, with quite good speed (sensitivity) is provided in which a substantially permanent positive image is formed by having an image projected onto a catalytic material and placing the catalytic material in contact with a copy sheet comprising a semiconductor oxide and applying an electric field between the conductive base of the catalytic material and the conductive base of the copy sheet.

It is another object of the present invention to provide a process whereby a catalytic recording medium is first exposed to an image of the original, and as a result a latent image is formed by virtue of deactivated catalytic areas on the surface of the catalytic material.

It is also an object of the present invention to provide an electro-catalytic photographic process wherein catalytic ions, from the areas of a catalytic recording medium which has not been deactivated, are electrically injected in minute quantities into an image-forming material, thereby producing a positive image of the original.

It is another object of the present invention to provide an electrocatalytic photographic recording medium comprising a catalytic material which, upon exposure to an image, produces deactivated catalytic areas in those portions of catalytic material exposed to light.

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

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

FIGURE 2 is a diagrammatic illustration of the projection of an image on a catalytic record medium with the formation of deactivated catalytic areas according to the present invention;

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

FIGURE 4 is a diagrammatic illustration showing the placing of a catalytic recording medium with deactivated areas in contact with a semiconductor oxide under the application of an electric field so as to form a positive image of the original according to the present invention; and

FIGURE 5 is a schematic diagram of a photocopy apparatus according to the present invention.

Referring now to FIGURE 1, there is shown in recording medium 1 comprising a catalytic material 2 supported on a suitable conductive carrier 3. The conductive backing 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 ex-

posure of the catalytic material 2 and the semiconductor material 7 shown in FIGURE 3, to an electric field as will be explained later in reference to FIGURE 4.

The composition used for the catalytic material 2 can be a mixture of a metal thiocyanate with an oxide which is capable of being reduced to a lower state of oxidation. The preferred catalytic composition includes a mixture of cuprous thiocyanate with titanium dioxide or a mixture of cuprous thiocyanate with cerium oxide. These compositions are particularly suitable for coating on the conductive backing 3. Other suitable compositions for use as the catalytic material is a mixture of a metal halide such as silver chloride with a metal oxide such as cuprous oxide or cerium oxide. This latter class of catalytic compositions are deposited on the conductive backing 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.).

A catalytic composition for coating on the conductive backing may be prepared according to the following procedure.

A metal oxide and a metal halide are combined with a solution of an ionic salt such as ammonium nitrate in water which provides conductivity in the coating. There is also added a minor amount of a humectant such as glycerol, sorbitol or other glycols. This mix is ball-milled for about 24 hours. The resulting homogeneous mixture is slowly added with agitation to an organic binder in a suitable solvent. There is obtained a dispersion of low viscosity which is spread over the metal lamina of thin aluminum foil. The solvent is evaporated at elevated temperatures.

As suitable binders, non-hydrophilic binders are preferred, and systems such as polyvinyl alcohol, polyvinyl chloride, gelatin and starch should generally be avoided. Among the preferred binders are "Pliolite" (resinous copolymers of butadiene and styrene, manufactured by Goodyear Chemical), "Zytel" (resin composed of alcohol-soluble polyamides, manufactured by DuPont Chemical Company), and "Versalon" (polyamide resin, manufactured by General Mills).

Preferred solvents for preparing the catalytic recording composition are toluene, methyl ethyl ketone, and alkanols such as absolute ethanol. However, other conventional solvents of the class of aromatic and aliphatic ketones and alcohols may be employed within the scope of this invention. After the recording composition has been prepared with a desired binder as outlined above, it may be coated on a foil, or other, preferably conductive material. Any suitable coating process may be utilized. For example, a conventional knife coating machine may be used to coat the layer of the material onto a base. The coating can also be performed with other usual methods such as wiring rod, kiss-coating, air knife, etc. Laboratory samples and small quantity production may conveniently be coated with the wiring rod.

Specific illustrative but non-limiting examples of the catalytic composition useful in the process of this invention are as follows.

EXAMPLE 1

There is introduced into a ball mill 40 grams of titanium dioxide, 60 cc. water, 5 grams cuprous thiocyanate, 2 grams ammonium nitrate dissolved in 5 cc. water and 2 cc. of glycerol. This mixture is ball milled for 24 hours. The resulting mixture is slowly added with stirring to 100 cc. of "Zytel" (15% solution) in 100 cc. of ethyl alcohol. This results in a paste-like substance which is spread over the metal surface of a lamina of thin aluminum foil in a uniform layer and at a thickness of 1 mil. The solvent is evaporated at a moderately elevated temperature and the coating is allowed to dry.

EXAMPLE 2

The same procedure as in Example 1 was employed except that 35 grams cerium oxide and 10 grams cuprous thiocyanate were used for the catalytic composition.

EXAMPLE 3

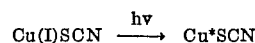
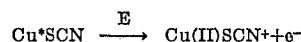
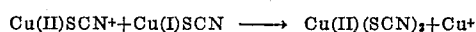
An evaporated layer was prepared under a high vacuum atmosphere employing 99.5% cuprous oxide and 0.5% silver chloride.

The catalytic recording medium 1 shown in FIGURE 1, is employed according to the present invention by exposure to the image of the original to be reproduced, and as a result of such exposure a latent image is formed on the catalytic recording medium by virtue of deactivated catalytic areas 4 and 5 on the surface of the catalytic material, as shown in FIGURE 2.

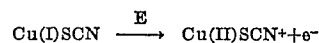
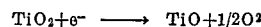
The bright areas of the image projected onto the catalytic material 2 correspond to the zones or areas 4 and 5 of deactivated catalytic material in the catalytic recording medium 1.

While it is not desired to be limited to any theories of operation, it is believed that the following proposed explanation of the formation of the deactivated zones in those areas of the catalytic recording medium exposed to light aid in an understanding and appreciation of the principles underlying the invention.

The deactivated catalyst areas in the catalytic recording medium result from a photolytic process whereby photoelectrons from the light source neutralize the metal ions. As a result, those areas exposed to light become deactivated and the metal ions cannot migrate into the semiconductor oxide layer upon the application of an electric field. Hence, those areas in the image forming layer corresponding to the deactivated catalyst areas remain unaffected by the application of an electric field. Taking a catalytic composition comprising a mixture of cuprous thiocyanate and titanium dioxide as an example, the photodeactivation in the regions exposed is believed to proceed as follows:



The regions which have been exposed to light contain only cupric thiocyanate which is not dissociable, but the regions which have not been exposed to light still contain cuprous thiocyanate which under an applied electric field will provide an electron according to the following general equations:



Upon the projection of the image on the catalytic recording medium in terms of deactivated catalytic areas, the catalytic recording medium is placed in contact with a semiconductor oxide or "so called" image forming material supported on a suitable conductive base to produce a positive image of the original upon the impression of an electric field throughout the surface of the catalytic recording medium and the semiconductor oxide, as will be more fully explained later.

Referring now to FIGURE 3, there is shown an image forming layer 6 comprising a semiconductor material 7. This semiconductor material is supported on a conductive base 7a which may comprise aluminum foil as an example. The conductive base may alternatively be a conductive layer on a reinforcing backing such as a plastic or paper.

The image forming layer 6 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 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 ₂ O -----	White, black.
TiO ₂ , TiO -----	do.
V ₂ O ₅ , V ₂ O ₄ -----	Yellow, blue.
Ta ₂ O ₅ (Ta ₂ O ₄ -----	White, black.
GeO ₂ , CeO -----	do.
Bi ₂ O ₃ , Bi ₂ O ₅ -----	Yellow, black.
Cr ₂ O ₃ , CrO -----	Green, black.
CoO, Co ₃ O ₄ -----	do.
MnO, Mn ₂ O ₃ -----	do.
NiO, Ni ₂ O ₃ -----	do.
TaO ₂ , TaO -----	White, black.
SnO ₂ , SnO -----	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 coating of titanium dioxide will be described in some detail. In the formulation of such coating commercially pure titanium dioxide (rutile) 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 coating 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 coating. Commercially pure titanium dioxide powder is ball milled for approximately one week to a grain size of about 0.1 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 be dried in a vacuum oven after the excess sodium hydroxide has been removed by washing the doped oxide.

In order that the titanium dioxide may be coated on a foil sheet, or other base, it is dispersed in a binder. The binder may be of aqueous or non-aqueous type.

As an example of a non-aqueous binder, Pliolite S-7 manufactured by Goodyear may be utilized and the powder mixed with commercial solution of Pliolite in a proportion of three parts powder to one part Pliolite. All proportions set forth herein are by weight unless otherwise specified.

The Pliolite-powder mixture is diluted with toluene to the proper viscosity for convenient coating (about the same viscosity as ordinary oil base house paint is convenient).

Rather than the non-aqueous binder described above, an aqueous binder may be utilized such as polyvinyl alco-

hol. A 10% solution of ammonium nitrate in water is used to dilute the polyvinyl alcohol. Ammonium nitrate solution rather than water provides conductivity in the coating. The original proportions of polyvinyl alcohol and the diluent may be 7% polyvinyl alcohol, 93% diluent. The binder is again mixed with powder in proportion of 1 part binder to 3 parts powder. The coating is thinned with 10% ammonium nitrate solution in water to obtain the desired viscosity for coating.

After the coating has been prepared with a desired binder as described above, it may be 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 semiconductor oxide composition onto a base. The thickness of the coating is not highly critical and may vary from 5 microns to as much as 2 mils in some instances. Generally a thin coating is desirable, particularly if very low potentials are to be utilized.

Another example of a formulation of semiconductor coating material according to the present invention is based upon the use of stannic oxide (SnO₂). The preparation of a stannic oxide coating is substantially similar to that previously described for titanium dioxide. The doping solution may be 5% sodium acetate solution, an aqueous binder may be utilized as previously described, and it may be found desirable to add to the binder a minute quantity of surfactant, for example "Igepal." The finely divided stannic oxide may be mixed with a binder in proportions of 50 grams of oxide per 100 cc. of binder.

The above described stannic oxide coating is characterized by very black recording on white background at a potential of approximately 10 volts.

As a further example a coating may be formed of CeO₂ by a process substantially as previously described for titanium dioxide. CeO₂ is doped by mixing the material with 10% solution of sodium hydroxide and agitating in this solution for a period of 6 hours.

The foregoing examples of formulation and preparation of semiconductor coatings used for the image forming material illustrated in FIGURE 2 are given by way of example only and are subject to considerable modification in accordance with the knowledge of the art. In particular, the doping of crystals with impurities is well known, for example, in the art of preparation of semiconductor materials, and these known techniques are applicable to the preparation of semiconductor coatings according to the present invention. For example, sodium acetate may be utilized as a medium for doping the titanium dioxide with sodium ions rather than sodium hydroxide, as previously described.

Referring now to FIGURE 4, a positive image of the original is obtained in the following manner. After the catalytic recording medium 1 supported on a conductive base, as shown in FIGURE 1, has been exposed to an image of the original to be reproduced, a latent image forms by virtue of deactivated catalytic areas as shown in FIGURE 2. The photodeactivated recording medium of FIGURE 2 is then transferred face to face onto a semiconductor material 7 supported on a conductive backing as shown in FIGURE 3. The electro-catalytic sandwich structure formed as a result of the face-to-face contact of the photodeactivated catalytic recording medium 1 and the image recording medium 6 will be explained with reference to FIGURE 4.

An electric field is applied by connecting conductive base 3 by lead 8 to an electrical source while lead 9 connects the electrical source to conductive base 7a. An electrical potential difference (e.g., 20 volts) is provided between the conductive base 3 as positive and the conductive base 7a as negative. The conductive base 3 on which the photodeactivated catalytic recording medium is supported is positive, so that the catalytic ions are transported from the catalytic layer 2 into the semiconductor layer 7 bringing about a

change in the state of oxidation of the semiconductor and thereby providing a color change which results in a positive image 10, as illustrated in FIGURE 4.

The current that will flow between the conductive base 3 and conductive base 7a, as the result of the application of an electric field, will be distributed according to the distribution of the catalytic layer. That is to say, photodeactivated areas 4 and 5 will not catalyze the reaction in the semiconductor layer 7, as shown by areas 11 and 12 in the semiconductor layer, which correspond to deactivated areas 4 and 5 in the photodeactivated catalytic layer. The areas of the catalytic layer 2 not deactivated will produce a darkening 10 of the semiconductor layer 7 as shown in FIGURE 4. In this manner a positive image of the original image is obtained.

The darkening of the semiconductor layer is due to the change in oxidation state of the oxide in the semiconductor layer resulting from the introduction of a small amount of active catalyst into the semiconductor layer. The source of the active catalyst is the photodeactivatable catalytic layer described in FIGURE 1.

The mechanism of the change in oxidation state due to the introduction of a small amount of catalyst in the semiconductor oxide material involves a consideration of 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.

It should be pointed out with respect to the mechanism of the semiconductor recording medium that it is necessary that the catalyst atoms or molecules in the catalytic layer be electrically charged in order that they may be transported with the electric current. The present invention provides that these catalytic atoms or molecules be ionized.

Another requirement for optimum operation of the semiconductor recording medium is that there be adequate transverse conductance in order that a low electrical potential will produce sufficient electric current to transport the small amount of catalyst required to form a positive visible image in the semiconductor layer.

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 dioxide a small amount of CeO is always present along with the predominant CeO₂. This small amount of CeO plays an important role in the initiation of further reduction. The introduction of copper ions into the existing CeO lattice will control the number of Ce³⁺ ions. The smaller charge of the Cu⁺ ions balances the excess charge of the Ce³⁺ 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 copper containing material shows a considerable increase in electrical conductivity of the p-type. The copper 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.

A condition apparently necessary for the mechanism involved in the present electrocatalytic photographic process is that the impurity cation should be of much the same size as the host cation. The principle is different from usual semiconductors in that it allows the creation of electrical defects without the creation of a corresponding number of vacancies in the lattice.

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 CeO₂ emulsion, where CeO ions are displaced from the lattice and are moved forward 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 O²⁻ 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 SnO₂, Ta₂O₅ and TeO₂.

The electro-catalytic recording medium of FIGURE 1 and the semiconductor oxide medium of FIGURE 3 are particularly useful in photocopy applications and may be utilized in an apparatus such as that illustrated in FIGURE 5, 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 catalytic belt 18, which is formed of a sheet as described in FIGURE 1. The catalytic belt 18 is driven by rollers 19 and 20.

The copy sheet 21 is contacted with the catalytic belt 18 under the pressure of rollers 19 and 22. These rollers 19 and 22 are electrically connected by leads 23 and 24 to a source of electrical potential 25 providing the necessary electrical field for the transfer of the latent image from the photo-deactivated catalytic belt 18 onto the copy sheet 21.

The positive reproduction 26 of the original image is transferred outside the machine by belt 27 driven by pulleys 28 and 29.

The latent image on the catalytic belt 18 can be erased by providing an electrical potential between rollers 20 and 30 which are connected by leads 31 and 32 to a source of electric potential 33. The image is erased due to the reactivation of the deactivated catalyst in the catalytic belt 18. The electric field applied between roller 30 and the base of the catalytic belt causes electrons to be accepted by the neutralized metal atoms and, therefore, reinstate the original ionic nature of the catalytic surface so that it can be used continuously.

The operation of the photocopy apparatus of FIGURE 5 is as follows. An image is projected by lens 14 onto a catalytic recording belt 18 for the exposure thereof. After the formation of the latent image by virtue of deactivated catalytic areas on the belt 18, the belt is contacted with copy sheet 21 under the pressure of rollers 19 and 22. An electrical field will flow through the area between the two rollers which will bring about the transfer of the latent image from the photo-deactivated catalytic belt 18 to the copy sheet 21, comprising a semiconductor oxide. In this manner a positive of the original is obtained which is transferred outside the photocopy machine by means of belt 27. The image formed on the catalytic belt is erased after a positive reproduction is obtained by providing an electrical field between conductive rollers 20 and 30, and the base of catalytic belt 18.

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: exposing to said image the catalytic surface of a catalytic recording medium adapted to be deactivated according to the intensity of the radiation striking the catalytic surface, contacting the surface of the catalytic recording medium with the surface of a semiconductor recording medium, said semiconductor recording medium comprising a semiconductor material having at least two oxidation states of contrasting color with the lower oxidation state being intensely colored, said semiconductor material being substantially in a higher oxidation state, impressing an electric field through the surfaces of the catalytic recording medium and the semiconductor medium, thereby producing a permanent visible photographic record of the original on said semiconductor recording medium.

2. A process according to claim 1 wherein the surface of the catalytic recording medium comprises a catalyst which is a mixture of metal oxide with a compound selected from the class consisting of a metal thiocyanate and a metal halide.

3. A process according to claim 2 wherein the catalyst is a mixture of titanium dioxide with cuprous thiocyanate.

4. A process according to claim 2 wherein the catalyst is a mixture of cerium dioxide with silver chloride.

5. A process according to claim 1 wherein said semi-

conductor recording medium is a copy sheet comprising said semiconductor material supported on an electrically conductive backing.

6. A process according to claim 5 wherein the semiconductor material is a semiconductor oxide.

7. A process according to claim 7 wherein the catalytic mixture contains an organic binder.

8. A process of producing a substantially permanent visible positive photographic record characteristic of a radiation image which comprises: projecting the image onto the surface of a catalytic recording medium, said recording medium comprising a catalytic layer deposited on an electrically conductive backing, said catalytic layer comprising a mixture of a metal oxide with a compound selected from the class consisting of a metal thiocyanate and a metal halide; forming deactivated areas on the surface of said catalytic recording medium in accordance with the intensity of the radiation striking said surface; contacting the surface of said catalytic recording medium with a copy sheet, said copy sheet comprising a semiconductor oxide supported on an electrically conductive backing, said oxide having at least two oxidation states of substantially contrasting color, said oxide being substantially in the higher state of oxidation; and impressing an electric field throughout said catalytic recording medium and said copy sheet to convert said semiconductor oxide to a lower oxidation state in selected areas thereby producing a permanent visible positive photographic record of the original on said copy sheet.

9. A process for the positive reproduction of a light image on a copy sheet which comprises: exposing to said light image the surface of a photocatalytic recording medium, said surface being deactivated in those areas exposed to the light of said image, said deactivation being in accordance with the intensity of the light striking said catalytic surface; contacting the catalytic surface of said photocatalytic recording medium with a copy sheet, said copy sheet comprising a semiconductor oxide supported on an electrically conductive backing, said oxide having at least two oxidation states of substantially contrasting color, said oxide being in a substantially higher state of oxidation; impressing an electric field throughout the copy sheet and photocatalytic recording medium to cause said semiconductor oxide to be converted to a lower state of oxidation in selected portions of said copy sheet which correspond to those areas of said photocatalytic surface of said photocatalytic recording medium which have not been deactivated, thereby producing a positive image of the original image on said copy sheet.

10. A process for the positive reproduction of a light image on a copy sheet which comprises: exposing to said light image the surface of a photocatalytic recording medium, said surface being deactivated in those areas exposed to the light of the image in accordance with the intensity of the light striking said surface, said photocatalytic recording medium comprising a catalytic layer supported on an electrically conductive backing, said catalytic surface comprising a mixture of a metal oxide with a compound selected for the class consisting of a metal thiocyanate and a metal halide; contacting the surface of said catalytic layer of said photocatalytic recording medium with a copy sheet, said copy sheet comprising a semiconductor oxide supported on an electrically conductive backing, said oxide having at least two oxidation states of substantially contrasting color, said oxide being in a substantially higher state of oxidation; impressing an electric field throughout said copy sheet and said photocatalytic recording medium to inject ions from the areas of said catalytic surface which have not been deactivated into said semiconductor oxide surface to convert said semiconductor oxide to a lower state of oxidation in selected portions of said copy sheet which correspond to those areas of said catalytic layer which have not been deactivated, thereby producing a positive image of the original image on said copy sheet.

11

11. A process according to claim 10 wherein the catalytic layer of the catalytic recording medium comprises a mixture of cuprous thiocyanate with titanium dioxide and an organic binder.

12. A process according to claim 10 wherein the semiconductor oxide is cerium oxide and the ions injected into said oxide cause said oxide to convert to a lower oxidation state in selected areas of said copy sheet.

13. A photocatalytic recording sheet comprising a catalytic material on an electrically conductive backing, said material comprising a mixture of a metal oxide with a compound selected from the class consisting of a metal thiocyanate and a metal halide.

14. A photocatalytic recording medium which comprises: a catalytic layer on an electrically conductive backing, said catalytic layer including a mixture of a metal oxide with a compound selected from the class consisting of a metal thiocyanate and a metal halide, a copy sheet comprising a semiconductor material having at least two oxidation states of contrasting color with the lower oxidation state being intensely colored, said semiconductor material being substantially in a higher oxidation state, said semiconductor material being supported on an electrically conductive backing and electrodes for impressing an electric field through said semiconductor material and said catalytic layer.

12

15. A recording medium according to claim 14 wherein the surface of said catalytic layer and said semiconductor material are substantially co-extensive with each other.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,457,069 Dated July 22, 1969

Inventor(s) J.J.A. ROBILLARD

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

┌ Column 2, line 59 change "in" to --a--.
 Column 5, line 14, Table I change "Ge" to --Ce--.
 Column 6, line 43, change "FIGGURE" to --FIGURE --.

SIGNED AND
SEALED

JUN 16 1970

(SEAL)

Attest:

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