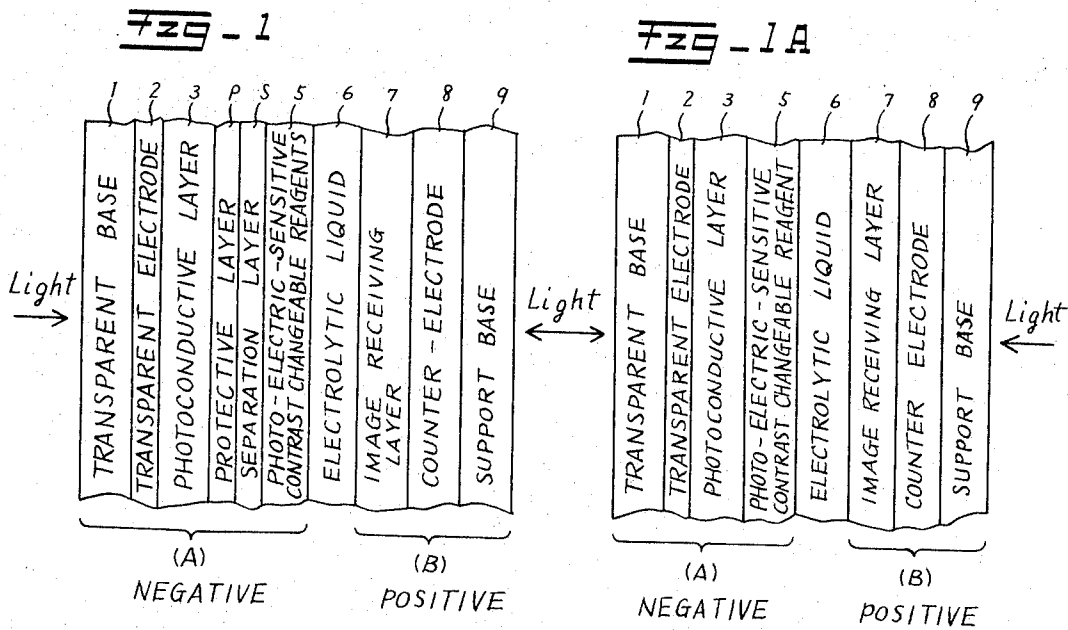
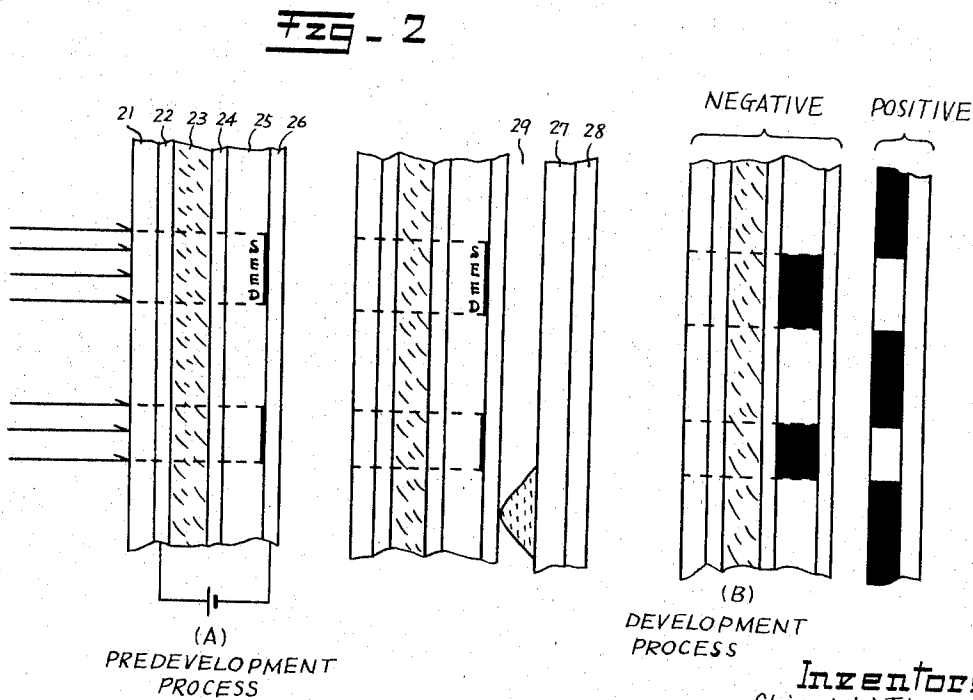


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SHIN-ICHI TOKUMOTO ETAL
ELECTROLYTIC PHOTOGRAPHIC PROCESS
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**ELECTROLYTIC PHOTOGRAPHIC PROCESS
AND ITS MATERIAL**

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10 Claims

ABSTRACT OF THE DISCLOSURE

A monochrome picture film and method of utilizing the same wherein a photoconductive layer controls the amount of electrolysis occurring in a reagent layer. The high sensitivity depends on the electrolytic formation of nuclei, which are produced by a very small quantity of electricity. The nuclei serve as centers for the chemical development reaction that produces the visible image. The process uses a photoconductive layer of, for example, cadmium sulfite and a reagent layer containing non-photo-sensitive metallic compounds such as sodium silver thio-sulfate, nickel salts, organic metal salts, etc.

The present invention relates to a photographic process wherein an image of a subject matter is formed by application of electric current to an image-forming film unit, and photographic material for use with said process.

This is a continuation-in-part of our application Ser. No. 134,794, filed June 30, 1961, now Patent 3,227,633 and is directed to photographic processes employing monochromatic light.

It is an object of the present invention to provide an electrolytic photographic process and photographic material for use with the process whereby application of a very small quantity of electricity makes it possible to obtain a picture of sufficient density. Thus, it is possible to use such electrolytic photographic material, which is highly sensitive, while it is being handled in light.

Another object of the present invention is to directly produce a contrasting picture in a single step without use of separation images.

A further object of the present invention is to produce a picture film making use of the transfer process.

The photographic process of the present invention is such that an electrolytic photographic process can be adapted for use in electrolytic photography wherein an image is formed by exposure to light and application of an electric current, or in an electric recording apparatus, such as telautograph, wherein an image record is made by application of electric current. Electric current in a quantity corresponding to the color and luminosity of each unit area of a subject matter is applied to each unit area of the image-forming film unit so as to produce or reduce in the image-forming film unit, the initiators which serve to accomplish or promote the chemical reaction necessary to form an image. The quantity of substance in each unit area of the image-forming film unit is differentiated according to the color and luminosity of each unit area of the subject, so as to differentiate in effect the extent of accomplishment or promotion of the chemical reaction necessary to form an image, at each unit area of the image-forming film unit. This manner of developing an image is characteristic of the electrolytic photographic process of the present invention. The characteristic of the electrolytic photographic material of the

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present invention is such that when electric current is applied to each unit area of the image-forming film unit, in a quantity corresponding to the color and luminosity of each unit area of the subject, the initiators, which serve accomplishment or promotion of the chemical reaction necessary to form an image, are brought into being at each unit area of the image-forming film unit in a quantity corresponding to the color and luminosity of each unit area of the subject. This accomplishment promotes the chemical reaction necessary to form an image to an extent in accordance with the quantity of initiators thus produced or reduced and the image of the subject can be developed.

The present invention is confined to monochrome photography. Thus, in the present invention, use of the term color and luminosity as used in the most broad sense, refers to a contrast ratio. The present invention is confined and relates only to monochrome photography, i.e., black and white and the various shades of gray, as contrasted to so-called "color" utilizing the three primary colors.

The instant invention has as its primary object, the provision of an electrolytic photography process wherein the amount of electric current flowing through the photo-conductor is proportional to the intensity of light, thus allowing the image to be reproduced by the electrolysis caused by the current and allowing further amplification by subsequent chemical development.

A further object of the present invention is the provision of an electrolytic photographic process and material whereby the electrolytic reaction requires only a very small amount of electricity to produce the amount of initiators, or seeds needed for the development centers, and sensitivity is gained by chemical means, through chemical or diffusion transfer development.

Other and further objects, features and advantages of the present invention will become more apparent to those skilled in the art from the following detailed disclosure thereof and the drawings attached hereto and made a part of the present invention.

On the drawings:

FIGURE 1 is an enlarged, cross-sectional view of a system embodying the electrolytic photographic process and its photographic materials of the present invention;

FIGURE 1a is an enlarged, cross-sectional view of the preferred embodiment of the present invention; and

FIGURE 2 is an enlarged, cross-sectional view of the pre-development process and development process embodying the electrolytic photographic process and its photographic material of the present invention.

In the present invention when reference is had to the application of electric current to each unit area of the image-forming film unit in a quantity corresponding to the color and luminosity of each unit area of the subject, such reference indicates that an electric current has passed through the image-forming film unit in such a manner that when a photo image of the subject is formed on the image-forming film unit, there flows through each unit area thereof, electric current in a quantity corresponding to the color and luminosity of each unit area of the subject. Since, therefore, this selective application of current, which means that different quantities of electricity are applied to each unit area of the image-forming film unit, does form an image of the subject, it must be closely related to the color and luminosity of each unit area of the subject. This selective application of current closely related to the color and luminosity of the subject may be controlled either by a photoconductive layer, photovoltaic layer, or photorectifying layer positioned in parallel with the image-forming film, or it may be controlled, as in the case with telautograph, by counter-positioned electrodes scanning over the surface of the image-forming film.

The above-mentioned photoconductive layer may be selected from the group consisting of photosensitive cadmium sulfide, zinc selenide, antimony tri-sulfide, or amorphous selenium. The photovoltaic layer or photo-rectifying layer is composed of such complexes as selenium and metal foil. Further, such complexes as photo-transistors, which are composed of heterogeneous semi-conductors acting as controllers, effect the same results.

Such complexes as mentioned above, function as a photovoltaic layer, or otherwise, being connected with an outside source of electricity in such a manner that when they are unexposed they resist the voltage of said source and check the flow of the current, but can release it only when exposed. Thus, they function as a photo-rectifying layer. A layer of such composite material is generally low in its horizontal or sheet-wise electrical resistance. In such a case, the material must be divided into a great number of points, electrically insulated one from the other, and arranged on the surface of a base.

The current to be applied to the image-forming film unit may be alternating current or direct current flowing in a definite direction. In the case of an alternating current, the current-caused reaction whereby the initiators, which serve to accomplish or promote the chemical reaction necessary to form an image, are produced or reduced in the image-forming film unit and need not be completely reversible. Examples of this reaction will be discussed in Example I, which will be described later.

The chemical reaction necessary to form an image is the one whereby it can be observed that substances are so colored, faded, changed in contrast ratio, or fixed as to form an image. The chemical reaction that may be employed in the formation of the image may involve any of such cases as, for example, a product of the reaction of a silver salt, copper salt, mercury salt, or lead salt with a developer having a color and luminosity different from those prior to the reaction; or a product wherein an inorganic or organic compound is converted into a product which has a solubility different from that prior to conversion.

Following are examples of the initiators that can be used to accomplish or promote the chemical reaction necessary to form an image.

If, for example, sodium silver thiosulfate or a like substance, which is comparatively irreducible is used alone, it undergoes little chemical reaction which is discernible to the naked eye when it contacts such liquid developers as are composed principally of hydroquinone. However, if silver sulfide, lead sulfide or other heavy-metal compounds coexist with the comparatively irreducible substance, even in a very small quantity, then the comparatively irreducible substance becomes reducible. For example, in the case of sodium silver thiosulfate, silver will be made free. If, in this case, there coexists an organic coupler with the sodium silver thiosulfate and a developer, the developer oxidizes upon reducing silver and couples with the coupler to produce a colored substance, although a non-reacted developer does not couple with such a coupler.

The above-mentioned sulfides or heavy-metal compounds are the substances that serve to accomplish or promote the chemical reaction necessary to form an image which could not proceed without them. In other words, they represent a catalyzer or an initiator for the image-forming reaction. Exemplified hereunder is the system to cause such initiators for image-forming reaction to be produced or reduced by application of electric current.

Example I

744 grams of sodium thiosulfate are dissolved in 3 liters of water, in which solution 376 grams of silver bromide are dissolved completely with stirring so as to give a solution of sodium silver thiosulfate. To this solution is added the same quantity of alcohol, so as to

precipitate the sodium silver thiosulfate therein. The precipitate thus obtained is washed with alcohol and dried into crystallized sodium silver thiosulfate. 60 grams of this crystal is added to 500 cc. of an aqueous solution of 10% gelatine. This liquid composition is spread, several microns or several tens of microns thick over a conductive base, such as NESA glass, which has a thin, transparent and semi-conductive layer principally made of tin oxide on a surface, or a layer of platinum, and is then dried. While this dry coated film is being made suitably wet, and a movable electrode of platinum is being moved with its end contacting the surface of the coated film, current variable according to the image pattern is sent with the movable electrode being made negative. In the present example, the maximum voltage between the electrodes is 7 volts, and the maximum quantity of electricity is 1 microampere second per square centimeter. The mere application of current causes no apparent change to the surface of the coated film that could be discernible with the naked eye. However, when electrolysis is conducted in an aqueous solution of sodium silver thiosulfate with a platinum electrode, or when, in the present example, the quantity of electricity is increased, silver sulfide is produced discernibly at the cathode. It is obvious, therefore, that in the above-mentioned example, silver sulfide is produced in such a slight quantity that it is indiscernible to the naked eye.

Over the said coated film is spread a developer comprising:

30	Water	-----cc----	60
	Sodium carboxymethyl cellulose	-----grams--	2.5
	Sodium sulfite	-----do----	2.6
	Sodium thiosulfate	-----do----	0.7
	Citric acid	-----do----	1.3
35	Sodium hydroxide	-----do----	2.5
	Hydroquinone	-----do----	1.7
	1-phenyl-3-pyrazolidone	-----do----	0.03

Several seconds after the developer has been spread, there appears a black image pattern corresponding to the quantities of electricity applied. In case the coated film used in the above example is utilized, especially together with a photoconductive layer, photovoltaic or photo-rectifying layer (which will be discussed later) to control the quantities of electricity to be applied, it is preferable for the application of the current that the developer be positioned between the coated film and such layer without contacting the air.

In order to preserve the image that is created on the image-forming film in the above-mentioned example, a preservable image can be obtained by washing away the unreacted or partially unreacted or excessive components used to form the image, including silver and dyes. The image obtained in any of the cases in the present example can be transferred to another image-receiving layer by the usual transfer process of photography.

In the above-discussed example, the initiators for the image-forming reaction are produced by application of electric current. The following example will discuss the case when such initiators are reduced by application of electric current.

Example II

A conductive NESA glass having a thin, transparent and semi-conductive layer principally composed of tin oxide on its surface or a layer of platinum, is coated, by evaporation very thinly and uniformly with silver, and this silver layer is covered with a protective layer of polyvinyl alcohol which is completely saponified making it insoluble in cold water. This layer unit is kept in contact with an aqueous solution of 20% sodium nitrate, and electric current is then applied in a manner similar to that described in Example I.

The layer unit is then adequately washed with water, and after washing, its protective layer is covered with a

gelatine film containing sodium silver thiosulfate such as described in Example I. To this gelatin film, the developer discussed in Example I is applied, and seconds later, the areas where current did not pass, turn black. The greater the quantity of electricity applied, the less the extent of blackening because silver, an initiator for image-forming reaction, is converted into silver nitrate and washed away. Thus, a desired image is obtained.

Unless transfer based upon this image is desired, unnecessary or excessive components other than those necessary for the formation of the image will be washed away from the layer unit. However, if desired, the image can be transferred to another image-receiving layer by means of the usual transfer process of photography.

Thus far, the present invention has been explained primarily around the system of producing or reducing initiators for image-forming reaction by application of electric current. Initiator agents of image-forming reactions are not limited to the above-mentioned silver salt, nor substances to initiate a reaction in the above-mentioned substances. A further example is: A product obtained through abrupt oxidation of a mixture of 100 grams of tin chloride, 1 gram of antimony chloride, 10 cc. of 35% hydrochloric acid, 1 gram of ammonium fluoride and 100 cc. of water being sprayed over a glass board heated above 600° C., which though electrically conductive, is ineffective as an initiator for the image-forming reaction. However, a product obtained by reducing the said product by electrolysis is a highly effective initiator for the image-forming reaction. As initiators or seeds for the image-forming reaction, organic compounds as well as inorganic compounds of metal can be used, particularly, for example, a metallic compound of pyrazole, triazole, imidazole, thiazole or thiazolidine, and derivatives of such compounds.

However, it is preferable that the initiators for the image-forming reaction be of a heavy metal or semi-conductive material per se, or else of heavy metal or semi-conductive material obtained through the application of electric current. Further, it is preferable to have the initiators in the form of a galaxy, as it is thereby made easier to form half tones, especially in the cases where the transfer process is employed in making a picture.

In the case of contrasting reaction by reduced silver as in Example I, in order to make it easier for the reduced silver, which is produced by the image-forming reaction, to grow into a size large enough to easily absorb visible rays, and in order to provide, beforehand, in the colloid enough room for the reduced silver to grow, it is desirable that the initiators or seeds of the image-forming reaction, such as the above-mentioned silver thiosulfate, be dispersed in the gel colloid in a crystal form of the desired size and that the said initiators be produced by application of current as a part of, or adjacent to, the space occupied by these crystals.

The pulverized sodium silver thiosulfate or the like initiator substance of the image-forming reaction attached to the silica aerogel discussed above, is dispersed in oil-soluble resin, such as polyvinylbutyral, so that it contains more than 10% of the initiator and is then spread in a thin film and dried. This thin film, being permeable to ions, is capable of having initiators for the image-forming reaction produced in the space occupied by the above-mentioned crystals. If, to the above-mentioned silica aerogel, or some such like substance, hydrophilic resin such as polyvinylpyrrolidone, polyvinylmethyl ether, or some such similar material, or hydrophilic colloid such as gelatine, sodium carboxymethyl cellulose, or similar material, is attached, better ion permeability can be obtained. In the above examples, again, the initiators of the image-forming reaction were contained beforehand in the image-forming film, but it goes without saying that they do not necessarily have to be counted in the image-forming film beforehand, but can be added

or applied thereto at any suitable time in the course of the image-forming process.

For convenience, in illustrating the accompanying drawing, the photoconductive layer, photovoltaic layer, or photorectifying layer will hereafter be inclusively called "photo-current-passable layer," and the initiators of the image-forming reaction will be called "contrast-changeable reagents."

Various systems of utilizing the photo-current-passable layer to control the quantities of electricity to be applied are illustrated hereunder with reference to the accompanying drawings:

In the accompanying drawings, FIGURE 1 and FIGURE 2 depict a system to obtain a mono-colored image. FIGURE 1a shows the preferred form of the invention wherein a protector layer P and separator layer S are not necessary. Other than these changes, the film shown and numbers used are identical to those discussed in conjunction with FIGURE 1.

FIGURES 1, 1a and 2 show, respectively, the photographic material of the present invention consisting of two blocks, block A comprising an image-forming film unit of layers 1 to 5 combined, and block B, a unit of layers 7 to 9 combined. The latter block B is shown in the figures merely to indicate the relative position to block A of a counter electrode 8, which is transparent or opaque, and may be utilized in application of electric current in the course of the image-forming process, and of an image-receiving layer 7 to be used in transferring the image. Layer 9 represents a base of paper, transparent cellulose derivatives or glass to support the electrode 8 and/or the image-receiving layer 7. Layer 6 represents the layer of electrolytic liquid or transferring liquid to be spread between said blocks A and B at the time of application of electric current or transferring. Layer 5 represents a layer containing photoelectric-sensitive contrast-changeable reagents such as sodium silver thiosulfate and couplers. Layers S and P (as shown in FIGURES 1 and 2) will be described later. Layer 3 represents the photo-current-passable layer. Layers 2 and 1 represent, respectively, the transparent or opaque electrode and the base.

In FIGURE 2, the image-forming light passes through the transparent base 21 and the transparent electrode 22, and forms an image on the photoconductive layer 23. A direct current voltage is then applied between the electrode 22 and the counter-electrode 26. During this application, current flows through the layers in proportion to the intensity of the light in the image, causing electrolysis in the reagent layer 25. Development centers or seeds are deposited on the face of the protector layer 24 or on the face of the cathodic counter-electrode that is in close contact with the reagent layer. Then, with the electric current open, the negative film (21-26) is placed over the image-receiving layer 27 and its base 28 with a transfer-developer 29 between. In the course of 10 to 45 seconds, development occurs in the negative film around the centers formed by the electrolysis, and the contrast reagents that have not reacted, diffuse into the image-receiving layer where a positive image is formed by development centers already present in that layer.

In FIGURE 1, the layer S represents a layer required with two or more contrast-changeable reagents, such as two types of contrast-changeable reagents as sodium silver thiosulfate and a coupler, mentioned above, used separately in the order of their performing the image-forming reaction, that is, for example, this layer S contains sodium silver thiosulfate, while the layer 5 contains the couplers.

Layer P, in FIGURE 1, represents a protector layer to protect the photo-current-passable layer 3 from the image-forming reaction. It is required that this layer be capable of passing electric current, and further that the passage of electric current be made easy layer-wise, or in a direction vertical to the layers and difficult sheet-wise, or horizontally. As shown in FIGURE 1, the layers are so divided that as the exposing light approaches the

layers from the side of the photo-current-passable layer, the said layer may be opaque. In this case, conductive paint containing carbon powder, silver powder and the like conductors for electricity, can be used. The vertical or layer-wise and horizontal or sheet-wise resistance of the layer can be controlled by adjusting the quantity of powder conductor contained in the paint and the thickness of the layer. Conductive paint having an ethoxy resin and containing 13% (in weight) carbon powder has, when formed in a 10-micron thick layer, a layer-wise resistance of 100 ohm per 1 square centimeter and a sheet-wise resistance of 100 megohm square, the embodiment of which has given satisfactory results.

However, as is shown in FIGURE 1, where it is so devised that the exposing light approaches the photo-current-passable layer from the side of the protector layer P, the layer must be transparent. The inventors of the present invention, intending to employ such protector layer, have invented the following transparent conductive paint and obtained very satisfactory results from employing it. Five grams of silica aerogel are dispersed in a mixture of 65 cc. of water and 50 cc. of alcohol, and then added thereto and mixed adequately therewith, is 35 cc. mixture of 100 grams of tin chloride, 1 gram of antimony chloride, 10 cc. of 35% hydrochloric acid, 1 gram of ammonium fluoride and 50 cc. of water. This mixture is sprayed into a gas flame and by this heat treatment a transparent powder is produced. This powder is piled 35 microns thick and spread lightly to have a vertical resistance of 80 ohms per square centimeter. Ten grams of this powder is dispersed in a toluene solution of 10 grams of methyl methacrylate and is so spread in a thin film, such that the film will be 5 microns thick upon drying. Then, after drying, the film is impregnated with paraffin at 60° C. The transparent and conductive protector thus obtained has a light-penetration rate of more than 90% and a layer-wise resistance of 80 ohms per square centimeter and a sheet-wise resistance of 100 megohms square.

As set forth below, the image-receiving layer is explained for the purpose of transferring the image.

In the present invention, when an image is to be transferred, the various known methods of transfer photography can be adopted. It is preferable that the previously mentioned color-changeable reagents remaining non-reacted within the image-forming film unit be made to pass through the transfer liquid layer 6 and be reacted on the image-receiving layer 7 to form a picture. If, for example, the reaction to reduce silver from a silver salt is utilized for the image-forming reaction and if the image-receiving layer has initiators for the image-forming reaction in it before the reduction reaction occurs, then the image-forming reaction will proceed immediately in those places where the color-changeable reagents are present. An example of the image-receiving for the purpose of transferring the image is:

Silica aerogel	-----grams--	15
Water solution of 2% sodium sulfide	-----cc--	140
Cadmium acetate	-----grams--	1.5
Lead acetate	-----do--	0.1
Zinc nitrate	-----do--	1.5

It is obvious, of course, that development on the image-receiving layer can be conducted independently, after the transfer of color-changeable reagents to the image-receiving layer has been completed.

Methods for the production of the photocurrent-passable layer are, by way of example, described in the following discussion.

A mixture consisting of a photo-conductive cadmium sulfide powder containing, in molar ratio, copper as an activator in quantities of one-ten thousandth of cadmium sulfide, the similar ethoxy resin as hereinbefore set forth in an amount of 4% by weight of the sulfide powder and a diacetone alcohol (solvent) of a suitable amount, which

mixture is then uniformly coated on the surface of an electrode, as for example, NESA glass to make a laminate having a thickness, as for example, of about 80 microns. When a potential of 100 volts is transversely or layer-wise imposed on this laminate, and the laminate is exposed to the light of about five-foot candles, a photocurrent of about 18 milliamperes per square centimeter develops. If the exposure is cut off, there is almost no flow of current. Further, in place of the above-mentioned photo-conductive cadmium sulfide, a photosensitive powder can be utilized which consists of, for example, two kinds of semi-conductive material which may be described as follows. A photosensitive powder is produced, for example, by precipitating a cuprous oxide (a semi-conductive material) from an aqueous solution of copper salt mixed with a reducing agent such as grape sugar on the surface of cadmium sulfide powder (another semiconductive material) containing, in molar ratio, fixe-ten thousandths of indium. Then by heat treating the thus obtained powder in an atmosphere of an inactive gas at a temperature of about 550° C. for a very short period of time, a suitable powder is obtained. The powder is then mixed with the resin in the same manner as that hereinbefore set forth and the resulting mixture is coated on the surface of an electrode to make a laminate having a thickness of about 40 microns. When a potential is imposed on this laminate under the same conditions as those described before, a photocurrent of about 7 milliamperes/cm.² develops under the irradiation of about five-foot candles, and if the irradiating rays are cut off, only a current of 3×10^{-4} of the current can be obtained.

Further, a photocurrent-passable layer of the following type may cause an available current to pass therethrough under a low potential. Such a photocurrent-passable layer can be produced in the following manner.

A nickel-plated electrode is applied to the surface of network glass plate which has a thickness of about 0.4 millimeter and has regularly been formed on the overall surface thereof with numerous perforations, these perforations being filled with selenium. The surface thereof is polished and the glass plate thus obtained is heated at a temperature of about 200° C. for 4 hours and then cooled slowly. Another network glass plate, which has the same size of perforations in the same position as that previously described, is used as a shadow mask, and cadmium and gold are thinly deposited on only the surfaces of the selenium particles insulated by the glass network, by a sputtering process and vapor deposition process, respectively, and thus, the desired photocurrent-passable layer is obtained.

The photosensitivity of the photocurrent-passable layer thus produced is shown as follows.

The gold portion of the above-mentioned photocurrent-passable layer is electrically connected to a copper electrode of an electric cell which comprises electrodes of copper and aluminum and an electrolyte solution of 5% aqueous sodium chloride solution, and the nickel portion of the photocurrent-passable layer is also connected to the aluminum electrode. When the layer is exposed to the light of 120-foot candles, photocurrent of 0.1 milliamperes/cm.² can be obtained, and when the exposure is cut off, the current substantially ceases to flow.

In place of the copper-sodium chloride solution-aluminum cell, a layer having an electric cell structure, in which metals having a different potential are placed on both sides of the color-changeable reagent layer in such a manner that the metals embrace the reagent layer between them, can be used in combination with the above-mentioned photocurrent-passable layer.

Of course, it will be understood that the above described process and materials, including the quantities thereof, arrangements of parts, etc., are given merely by way of example and not by way of limitation. Modifications and variations may be made in the above product and process without departing from the scope of the invention

herein described. Such technically comprehensible changes, as for example, wherein two or more types of color-changeable reagents are separately contained in the layers 5 and S as shown in FIGURE 1. Further, a protector layer or diffusion-controlling layer may be created to be positioned between 5 and S for the purpose of delaying the diffusion time of some of the color-changeable reagents so as to control the time and order of the color-changeable reagents reaction in the image-forming process.

By use of the term "photo-electric-sensitive contrast-changeable reagents" we mean a chemical which will not react to light or electricity alone to produce a different contrast ratio, but rather one that must have a substantially simultaneous application of electricity and light to produce a different contrast ratio. The term "color-changeable reagent" as used herein means substantially the same as photo-electric-sensitive contrast-changeable reagents.

Thus, it will be understood that modifications and variations may be effected without departing from the scope and spirit of the novel concepts of the present invention.

We claim as our invention:

1. In a black and white picture film for photosensitization with an energy source including a light source for monochromatic light, the combination consisting essentially of, (1) a layer containing photo-electric-sensitive contrast changeable reagents for at least two different contrast ratios and initiators for picture forming chemical reactions which are produced by the application of electric current, said initiators being selected from the group consisting of heavy metal salts, tin oxide, platinum and a product obtained through electrolysis-reduction of a mixture of tin chloride, antimony chloride, hydrochloric acid, ammonium fluoride and water, (2) a layer useable as an electrode for electric current corresponding to an objective image to be reproduced, and (3) means for providing said electric current.

2. A picture film as defined in claim 1 wherein said initiators are heavy metal salts obtainable by the application of electric current.

3. A picture film as defined in claim 1 wherein said initiators are semi-conductors obtainable by the application of electric current.

4. A picture film as defined in claim 1, wherein the initiator is tin oxide.

5. A picture film as defined in claim 1 wherein the initiator is lead sulfide.

6. A picture film as defined in claim 1, wherein the initiator is sodium silver thiosulfide.

7. In a black and white picture film for photosensitization with an energy source including a light source for monochromatic light, the combination consisting essentially of a layer of transparent support film, a second layer useable as an electrode for an electric current corresponding to an objective image to be reproduced, a third layer containing photo-electric-sensitive contrast changeable reagents and initiators therefore which are actuated to form a latent image by the combination of light and electric current, said initiators being selected from the group consisting of heavy metal salts, lead sulfide, sodium silver thiosulfide, tin oxide, platinum and a product obtained through electrolysis-reduction of a mixture of tin

chloride, antimony chloride, hydrochloric acid, ammonium fluoride and water, which product is sprayed on an inert substrate heated above 600° C., said third layer being upon the receiving layer which contains a counter-electrode with a support film, and a fourth layer of an electrolyte being inserted between said third and receiving layers.

8. In a photographic image-forming method consisting essentially of providing an actinic light source, a pair of electrodes lying in generally parallel planes, a photo-current-passable mosaic element lying in a generally parallel plane between the electrode planes and having a layer interposed between the mosaic element and one of said electrodes, said layer containing photo-electric-sensitive contrast changeable reagents which are coextensive and initiators therefore which are actuated to form a latent image by the combination of light and electric current, said initiators being selected from the group consisting of heavy metal salts, lead sulfide, sodium silver thiosulfide, tin oxide, platinum and a product obtained through electrolysis-reduction of a mixture of tin chloride, antimony chloride, hydrochloric acid, ammonium fluoride and water, means for creating electric potential across the electrodes, and selectively exposing portions of said mosaic to actinic light and an electric current to create a latent image thereon, subsequently developing said latent image to form a visible image.

9. In a black and white picture film for photosensitization with an energy source including a light source for monochromatic light, the combination consisting essentially of a layer containing photo-electric sensitive contrast changeable reagents for at least two different contrast ratios and heavy metal salt initiators for picture forming chemical reactions which are produced by the application of electric current, a layer useable as an electrode for electric current corresponding to an objective image to be reproduced, and means for providing said electric current.

10. In a black and white picture film for photosensitization with an energy source including a light source for monochromatic light, the combination consisting essentially of a layer containing photo-electric-sensitive contrast changeable reagents for at least two different contrast ratios and semi-conductor initiators obtained through electrolysis-reduction of a mixture of about 100 grams of tin chloride, about 1 gram of antimony chloride, about 10 cc. of 35% hydrochloric acid, about 1 gram of ammonium fluoride and about 100 cc. of water, which initiator is sprayed on a glass board heated above 600° C.

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