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REPRODUCTION SYSTEM

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The present invention relates to a novel and useful reproduction system. In one aspect the invention relates to the permanent reproduction of images or objects on a surface by irradiation. In another aspect the invention relates to a new reproduction surface or sheet material. In still another aspect the invention relates to a new and novel photographic process in which an image is reproduced directly without the conventional developing step.

Numerous processes are known for the light reproduction of images and for copying. One of the more common and typical of such processes is that known as the silver halide process. This process requires exposure of a sensitive film or paper to the light or image source followed by a separate step of wet developing of the image on the film or paper.

Another typical process is known as electrophotography, and this process depends upon the presence of a photoconductive material in the film or printing paper. As in the silver halide process, this process requires a separate step of developing of the image. However, the developing may be done by a dry process, such as by heat.

The silver halide process and similar processes are considered more sensitive than the electrophotographic process. The disadvantages of the silver halide process, however, is the rather involved developing procedure. On the other hand, the disadvantages of the electrophotographic process is the low sensitivity thereof to the reproduction of images. All of the processes require a separate step in addition to the developing step for the fixing of the image so that upon exposure to normal light conditions the image will not fade or the background will not darken. It is much to be desired, therefore, to provide a simpler process than the above with elimination of their disadvantages. It has been discovered that certain materials have a catalytic effect upon reactions when activated by irradiation. This photocatalytic effect is taken advantage of in accordance with the present invention.

An object of this invention is to provide a novel reproducing composition.

Another object of this invention is to provide a dry process for the reproduction of images or copying of printed matter and the like.

Another object of this invention is to provide a process which directly reproduces the image or directly copies upon exposure to the object to be reproduced and does not require a separate step of developing.

Still another object of this invention is to provide a more sensitive dry process for reproduction of images and the like.

Still another object of this invention is to provide a dry process which does not require either a developing step or a fixing step whereby the image is directly and permanently reproduced upon exposure.

Still another object of this invention is to provide a process for directly reproducing transparencies without a separate step of developing.

Yet another object of this invention is to provide a novel copy-paper or film.

Another object is to provide a new photographic transparency film.

Still another object of this invention is to provide a dry

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process which is receptive to a broader light spectrum than heretofore possible.

Another object of this invention is to provide a process for developing and an image-reproducing composition which can be developed and fixed in a single operation.

Yet another object is to provide an image-producing composition which upon exposure to light may be developed without a separate wet developing process or a separate electrostatic or heating process.

Still another object of this invention is to provide a new technique for permanently fixing or stabilizing a reproduced image.

Various other objects and advantages will become apparent to those skilled in the art from the accompanying description and disclosure.

According to this invention, the reproduction system comprises an image-forming composition and a separate light-sensitive catalyst or photocatalyst. The image reproduction system is supported by or part of a suitable receptive carrier or sheet. The carrier sheet or receptive material containing the image reproduction system is then exposed to the image source or light source and the image or material to be copied is reproduced directly upon exposure. In some instances, fixing or inactivation of the image reproduction system is required so that upon viewing the reproduction the image or reproduced matter will not fade or the background will not darken.

The image-forming composition of the image reproduction system is a normally latent, irreversible oxidation-reduction reaction composition which is capable of initiation by electron transfer. The oxidation-reduction reaction composition comprises a separate solid oxidizing agent and a separate solid reducing agent which can react with each other to produce the image. Any oxidation-reduction reaction composition having a negative-free energy under the exposure conditions and having at least one component thereof which can react to produce a change in light value suffices as the image-forming composition. The image-forming composition is dry and its initiation by electron transfer need not be effected in the liquid or aqueous condition.

In addition to the image-forming composition above described, the image reproduction system requires a separate light-sensitive catalyst comprising a normally latent material which can be activated into the transfer of electrons by exposure to irradiation having a wave length below 5 microns, preferably below 1 micron, such as actinic light, X-rays or gamma rays.

The image reproduction system may comprise an admixture of the above components described or may comprise layers of the components in any order. Preferably, the image-forming composition is applied as a layer over the light-sensitive catalyst layer bonded to a suitable carrier. However, any one or all of the components of the image reproduction system may comprise, or be impregnated in, the carrier. The initial reaction between the oxidizing agent and the reducing agent of the image-forming composition is initiated by the transfer of electrons from the light-sensitive catalyst upon exposure to irradiation and immediately produces an image which is permanent and irreversible. The image thus produced may be either latent or visible. If latent, a separate step is required to develop a visible image, such as by heating or wetting the latent image to cause a further reaction, and this separate step may be combined with the inactivation step, if used.

Although inactivation of the image reproduction system is not required in all instances, depending upon the components of the system or type of irradiation source used, in many instances an inactivation or fixing operation is desirable and necessary. Where the irradiation source is X-rays or gamma rays, visual observation of the image

will not be carried out in the presence of such rays; and, therefore, inactivation may not be necessary. On the other hand, where the type of irradiation source is actinic light and the visual image is to be observed in the presence of such light, inactivation is required in most instances. Inactivation is carried out by inactivating the image-forming composition, for example, by removing the unreacted composition or by inactivating the photocatalyst, or by both of these methods.

As previously stated, the solid image-forming composition includes both an oxidizing agent and a reducing agent. The oxidizing agent in this composition is usually the image former but not necessarily. Either organic or inorganic oxidizing agents may be employed as the oxidizing component of the image-forming composition. The preferred oxidizing agents comprise the inorganic and organic metal salts. The metals include silver, mercury, lead, gold and manganese (in the form of the permanganate), nickel, tin, chromium, platinum and copper. Organic oxidizing agents include tetrazolium salts, such as tetrazolium blue and red, and diphenyl carbazone, and genarcyl red 6B (methine dye).

When zinc oxide is used as a photocatalyst, as will hereinafter be discussed, molecules or ions with reduction potential below oxygen in the electromotive series are useful as the oxidizing agent in either neutral or acid media. Thus, the salts of the reducible metal ions, Ag^+ , Hg^{+2} , Pb^{+4} , Au^{+3} , Pt^{+4} , and MnO_4^- , can be used as the oxidizing agent with zinc oxide as the photocatalyst upon irradiation. In basic media, molecules or ions below zinc in the electromotive series can be used as the oxidizing agent when zinc oxide is used as the photocatalyst. Thus, the reducible metal ions, Ni^{+2} , Sn^{+2} , Pb^{+2} , and Cu^{+2} , are suitable in salt form as the oxidizing agent with zinc oxide as a photocatalyst on exposure to irradiation.

In addition to the above metal salts, an organic oxidizing agent may be used which will complex with the metal ion of the above metal salts. Thus, carbazone can be reduced to the carbazide and an image formed by complexing a metal ion with the carbazide.

Also, other additives may be used in combination with the oxidizing agent to change the character and tonal value of the image. Images assume a darker and more dense tone when the metal ion of the oxidizing agent is complexed with another material. For example, the density of a silver image is increased by the use of organic complexing additives, such as an imide as *o*-benzoic sulfimide, an acid amide as formamide or acetamide, and phytic acid. Similarly, the density of a gold image is increased by use of acetamide.

The solid reducing agents of the image-forming composition to be used separately from the oxidizing agents are organic compounds, such as the oxalates, formates, substituted and nonsubstituted hydroxylamine, and substituted and nonsubstituted hydrazine, ascorbic acid, aminophenols, and the dihydric phenols. Polyvinylpyrrolidone is also useful as the organic reducing agent. This latter material also has value as a binder for bonding the components to the carrier. The oxalates and formates are usually in the form of salts of the alkali earths and alkali metals, such as sodium, lithium and potassium. A preferred oxalate salt is sodium oxalate. A preferred formate is sodium formate. Examples of substituted hydroxylamines include phenyl hydroxylamine and benzyl hydroxylamine. An example of an aminophenol is Metol; an example of a substituted hydrazine is phenyl hydrazine. Suitable dihydric phenols include hydroquinone and catechol.

As previously stated, some of the oxidizing agents work best in acidic or basic media. Suitable acids which can be employed in admixture with the oxidizing agent and reducing agent as part of the image-forming composition include the carboxylic acids, such as oxalic acid and stearic acid. The basic media may be provided in the image-forming composition by the inclusion therein of

an organic or inorganic base, such as ammonium hydroxide or sodium acetate, or any salt of a strong base and weak acid.

The selection of the particular oxidizing agent to be used with a particular reducing agent is, of course, determined by the ability of either one or both of the compounds in their reacted form to show a change in light value, such as a change in color, or to react with another compound resulting in a light value change. The oxidation-reduction potential (E_0) for the reaction between the oxidizing agent (electron acceptor) and the reducing agent (electron donor) must be positive under the conditions of reaction. This can be calculated from the standard electrode potentials (E_0) for the half cells. Preferably, the oxidation-reduction potential (E_0) for the reaction is at least $+0.1$ volt.

As previously stated, the light-sensitive catalyst or photocatalyst is a separate solid which may be combined with the ingredients in the image-forming composition or may form a separate layer or impregnated in the carrier. The photocatalyst is a material which will transfer electrons when activated by radiation wave lengths below 5 microns. Such photocatalysts comprise both photoconductors and nonphotoconductors. Among the photoconductors which may be used are zinc oxide, cadmium sulfide and selenium. Metal oxide nonphotoconductors which act as photocatalysts are the metal oxides which include titanium dioxide, antimony trioxide, and aluminum oxide.

It has also been found that certain fluorescent materials are also useful as photocatalysts since they can transfer electrons when activated with actinic light or other irradiation source. Such compounds include silver activated zinc sulfide, zinc activated zinc oxide, manganese activated zinc phosphate, an admixture of copper sulfide, antimony sulfide and magnesium oxide, cadmium borate, and zinc-8-hydroxyquinoline. Photochromic materials, such as the photochromic metal organic complexes, are also useful as photocatalysts in accordance with the present invention. Such materials include the following photochromic complexes:

- (1) $[\text{Co}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]_2(\text{S}_2\text{O}_8)_3$
- (2) $[\text{Co}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]_2(\text{C}_2\text{O}_4)_3$
- (3) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_2\text{S}_2\text{O}_8$
- (4) $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3$
- (5) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
- (6) $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3]$
- (7) $[\text{Cr}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]_2(\text{SO}_4)_2\text{S}_2\text{O}_8$

In place of the ethylenediamine ($\text{C}_2\text{H}_4\text{N}_2\text{H}_4$) and ammonia of the above compounds, such coordinating groups as guanidine, azido and nitrito may be used. Other reducible anions which may be used in place of those of the above compounds include tetrathionate, selenate and perchlorate.

A simple test may be used to determine whether or not materials have a photocatalytic effect. The material in question is mixed with an aqueous solution of silver nitrate and no reaction should take place in the absence of light. The mixture is then subjected to light at the same time that a control sample of an aqueous solution of silver nitrate alone is subjected to light, such as ultraviolet light. If the mixture darkens faster than the silver nitrate alone, the material is a photocatalyst.

The irradiation source is an important feature of the present invention. Ultraviolet light is one of the best radiant sources, and all of the photocatalytic materials are sensitive thereto. Incandescent light is a fair source of ultraviolet light. Fluorescent light is a better source of ultraviolet light. The photocatalysts are not usually sensitive to the entire actinic light range but may be made so by the use of a dye sensitizer, such as eosin, uranine,

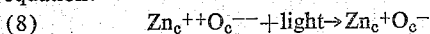
and erythrosin. Radiation by X-rays or gamma rays is also effective in exciting the photocatalyst.

The binding agent used to bind the image-forming composition and the photocatalyst to the carrier medium is an important feature of the present invention. In general, these binders should be translucent or transparent so as not to interfere with the transmission of light there-through. The preferred binders are the organic materials, such as resins. Suitable resins include a copolymer of butadiene and styrene sold on the open market as Pliolite, polyethyleneglycol, polyamide sold as Zytel-61, and polyvinylpyrrolidone. The polar-type binders which are water or alcohol soluble are most useful, such as polyethyleneglycol, polyamide, and polyvinylpyrrolidone, because these binders may be removed by dissolving the binder and releasing the oxidizing and/or reducing agent; thus, inactivating the carrier to further exposure to light as will be hereinafter discussed. Other binders include polystyrene chlorinated rubber, rubber hydrochloride, polyvinylchloride, nitrocellulose, and polyvinylbutyral. The binder polyvinylpyrrolidone is unique because it is also useful as a reducing agent or electron donor.

The carrier material upon which the photocatalyst and image-forming composition is deposited may be any suitable backing of sufficient strength and durability to satisfactorily serve as a reproduction. The carrier may be in the form of sheets, ribbon, roll or other suitable form for holding the image. The backing may comprise wood pulp paper, rag content paper, various plastics such as cellulose acetate and polyethylene terephthalate (Mylar), cloth, metallic foil and glass. The preferred form of the backing or carrier material is a thin sheet which is flexible and durable. An example of a suitable white paper containing the image-reproducing system of this invention comprises zinc oxide as a photocatalyst, silver nitrate as the oxidizing agent and image-forming material, and sodium formate or sodium oxalate as the reducing agent. A slurry is formed of these materials and coated on a wood pulp type paper in a thickness of about 4 mils. Approximately equal proportions of the components of the system are used. A resin, such as Pliolite, is applied to the coated paper in a conventional manner to securely bind the above composition to the carrier. Another method of construction is to apply the zinc oxide to the paper first in about a 2-mil thickness with a suitable binder followed by a top layer of the image-forming composition comprising the oxidizing agent and reducing agent in a suitable binder.

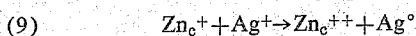
A negative film (developed) is applied to the surface of the paper containing the image-forming composition. The film is then exposed to actinic light for about 1 to 15 seconds. The paper and film are then removed from the presence of the actinic light, and the film removed from the paper. The paper contains a reproduced black image (Ag^0) on the film. When zinc oxide is omitted from the above process, no visible image is formed. If in the above system the reducing agent is omitted, the rate of image formation is considerably slower unless the backing or the binder itself contains a reducing agent or is in itself a reducing agent.

In the above system using zinc oxide, ultraviolet light has been theorized to raise the electronic of the zinc oxide into its conduction band in accordance with the following equation:



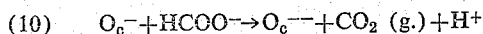
$\text{Zn}_c^{++} + \text{O}_c^{--}$ is zinc oxide crystal; Zn_c^{+} is the excited electron; O_c^- is the hole (absence of electron).

The silver ion of the oxidizing agent then apparently removes the electron from the zinc oxide conduction band in accordance with the following equation:



The hole created by the removal of the electron from the zinc oxide conduction band migrates to the surface and recombines with an electron from the organic reducing

agent (electron donor) in accordance with the following equation:



It may not be necessary that the electron raised to the conduction band by the light, such as in zinc oxide or other photoconductive materials. Irradiation may sufficiently activate the electron of the photocatalyst such that it is in an excited state and loosely held to the photocatalyst. In such a condition, it is easily transferred to the oxidizing agent (electron acceptor) of the oxidation-reduction system to initiate an irreversible reaction by electron transfer. This is the case with nonphotoconductors, such as the fluorescent materials, the metal organic complexes and metal oxides.

The probable theory for the action of the metal organic complexes as photocatalysts is that the metal ion can exist in more than one oxidation state, a non-ionic ligand and an oxidizable anion. The irradiation of the complexes involves excitation of electrons in the anions to higher energy levels by the adsorption of radiation wave lengths. The electrons thus excited become trapped in association with metal ions. The electrons, however, tend to return to their original state when irradiation ceases.

If an oxidizing agent, an easily reducible compound, is present, the electrons are available by transfer to the oxidizing agent and initiation of the irreversible oxidation-reduction reaction occurs.

Mixtures of the various components of the system may be used as well as the single components. Thus, mixtures of two or more photocatalysts may be used. Also, mixtures of two or more oxidizing agents or two or more reducing agents may be used without departing from the scope of this invention. Even mixtures of binders may be used.

The oxidizing agent and reducing agent may be used in substantially stoichiometric proportions. If desired, an excess of the oxidizing agent may be used without departing from the scope of this invention. The weight ratio of the image-forming composition; i.e. the combination of oxidizing agent and reducing agent, to photocatalyst is between about 10:1 and about 1:10; preferably, 2:1 to 1:2. The binder is used in a sufficient amount to effectively bind the various ingredients to the carrier surface. Generally, the weight ratio of binder to the material to be bound is between about 2:1 to about 1:5.

The thickness of the image-reproducing system on the carrier will vary between about 0.5 and about 8 mils. In case separate layers for the image-forming composition and the photocatalyst are used on the carrier base, the total thickness will be within the above range and the thickness of each layer will be about 0.5 mil to about 4 mils. The thickness of the carrier base when in the form of a flexible sheet is usually between about 5 and about 30 mils.

The image-reproducing system of this invention is latent under ambient and normal conditions. In other words, there is no reaction at temperatures up to about 125° F. under atmospheric conditions of humidity and pressure. The image-forming composition is also latent under irradiation in the absence of the photocatalyst. The photocatalyst is active when irradiated with wave lengths of less than 1 micron, but is latent in the dark. Upon reaction, either the reducing agent or the oxidizing agent changes in light value so as to reproduce an image. Normally, it is the oxidizing agent that reproduces the image. For example, a dark material may turn light upon reaction or a light material may turn dark. Also, a white material or colorless material may turn a color upon reaction or vice versa. Any change in the reflection of light from the surface as a result of the reaction between the reducing agent and the oxidizing agent constitutes a change in light value which causes a visual reproduction of the image, which reaction may be effected simultaneously with exposure or in a subsequent developing step.

The exposure time will vary to a considerable extent and will depend primarily upon the type and intensity of light or irradiation source, the sensitivity of the oxidation-reduction reaction, and upon the sensitivity of the photocatalyst. In general, the time of exposure will vary between about 0.001 of a second and about 10 minutes. Generally, the reproduction requires not more than about 15 seconds exposure.

Preferred image-forming compositions comprise (oxidizing agent and reducing agent): silver nitrate and sodium formate or oxalate, copper sulfate and sodium formate or sodium oxalate, silver saccharin and hydroquinone, silver saccharin and Metol or Elon, tetrazolium blue and sodium formate or sodium oxalate, diphenyl carbazone and sodium oxalate or sodium formate, silver nitrate or copper sulfate and sodium formate and benzene diazonium fluoroborate as a stabilizer, gold chloride and sodium oxalate or sodium formate, and gold chloride and hydroquinone.

The photocatalyst should be conditioned in the dark before exposure when the catalyst is sensitive to actinic light. Usually dark conditioning of the photocatalyst of one to twenty-four hours is desirable in such instances. After conditioning, the catalyst is not exposed to light prior to its exposure for reproducing the image.

As previously stated, inactivation of the image-reproducing system is required where the reproduced image will be observed under the same or similar light conditions used during exposure. However, where the light conditions of observation are not the same as under exposure, such as exposure to X-rays or gamma rays, no stabilization or inactivation of the image-reproducing system may be necessary.

One method of inactivation is washing off one of the components of the image-reproducing system after exposure. Washing may be effected with water or any suitable solvent, such as an alcohol or a ketone. For example, a permanent copy of a photographic negative may be obtained by coating out the photocatalyst, such as zinc oxide, in a water-insoluble binder, such as Pliolite, and coating the oxidizing agent or reducing agent or both on this surface with a water-soluble binder, such as polyethyleneglycol. After reduction of the image by exposure through the negative, the water-soluble film containing the image-forming composition can be washed off by holding under running tap water for several seconds. The reproduced image remains on the zinc oxide-Pliolite surface and is a permanent copy. By this method a permanent photographic print can be obtained in approximately 20 seconds, including all of the operations for making the print.

Another method for inactivation of the image reproduction system is by the use of heat in combination with the material capable of releasing an acid; i.e., either a Bronstad or Lewis classified acid, such as HCl, BF₃, HF, PCl₅, and p-toluene sulfonic acid. In accordance with this procedure, metal ions that are above oxygen in the electromotive series, such as copper, are used to deposit an image from a basic media. The metal ion, a reducing agent, and a basic additive are coated with a binder on top of a zinc oxide coated carrier medium. Since metals above oxygen in the electromotive series do not deposit in neutral media, the top layer forming the image-forming composition is neutralized after light development of the image therein which stabilizes the metal ion. This is accomplished by releasing an acid by a heat-sensitive reaction after exposure. For example, the image-reproducing system is heated to a temperature of about 125 to 250° F. A suitable composition that will release hydrogen chloride and thus neutralize the basic material upon heating is an admixture of m-nitrobenzene-sulfonyl chloride, and phloroglucinol. These components are added to the top layer of the photosensitive sheet. This method gives a dry reproduction, light-sensitive image system that is heat inactivated to give a permanent stable copy. Other

acid-releasing compositions include p-toluene sulfonic acid urea addition complex, p-acetamidobenzene diazonium fluoroborate, and m-chlorobenzene diazonium fluorophosphate.

Another method for releasing acids as a means of inactivation includes moistening of the system with water which results in the release of an acid in the system as above. This type of operation does not require heating. In this method of inactivation or fixing, diazonium fluoroborate is used alone and is combined on the top layer with a methanol-soluble polyamide binder. Included in this top layer, of course, is the image-forming composition. The lower layer of this system is a photocatalyst combined in a non-soluble binder, such as Pliolite. Upon wetting the top layer containing the methanol-soluble binder with water, the fluoroborate decomposes, releasing BF₃ or HF, thus neutralizing the basic media used in the image-forming composition and inactivating the composition to further sensitivity to light. No heating is required. A variation of the above two types of operations is the inclusion in the image-forming composition of a compound that liberates water at low temperatures, which water will react to liberate the acid. Using a diazonium fluoroborate will release BF₃ upon heating to about 125° F., resulting in an inactivation system stable to further light sensitivity.

Another method of inactivation of the image reproduction system constitutes the chelation of the oxidizing agent or reducible metal ion by forming a very stable metal chelate with any of the unreacted metal ions of the oxidizing agent. The chelating compound is combined in the binder or layer containing the oxidizing agent. The chelating compound may also be used as a separate layer either between the photocatalytic layer and the image-forming composition layer or as the top layer. The chelating compound may also be admixed in a system where all of the components are mixed together without layer formation. In this method, the image-reproduction system is exposed to develop the image and then heated at a temperature of about 125 to 250° F. to form the metal chelate with the unreacted metal ion of the oxidizing agent. The metal chelate formed must be non-light-sensitive. A suitable chelating agent which may be used when copper is the metal ion of the oxidizing agent is salicylaldehyde. The copper-salicylaldehyde chelate formed upon stabilization of the system is light colored and very stable. Another chelating agent is benzotriazole which may be used when silver is the metal ion of the oxidizing agent. Heating such a system to a temperature of about 150 to 200° F. produces a black image on a stable white background which is no longer sensitive to light. In this system, the original image after exposure for reproduction is latent, but the image is reproduced visually upon heating during the inactivation or fixing step.

A simple test for determining whether the metal chelate is non-light sensitive is to expose the metal chelate to ultraviolet light. If the material does not darken after five minutes exposure, the chelating agent is suitable as a means for inactivation of the system.

Inactivation of the image reproduction system may also be accomplished by the application of pressure to the surface of the carrier. It has been found that pressure will desensitize photocatalysts as a result of which they are no longer light sensitized. Thus, the sheet containing the image as a result of exposure may be passed through rolls which exert pressure upon the sheet. Another method is to pass a bar under pressure across the surface of the sheet containing the image. Generally, at least 500 pounds per square inch pressure must be applied to the surface to deactivate the photocatalyst. It has been found that with zinc oxide, for example, passing a pencil or rod across the image surface with exertion of heavy hand pressure will deactivate the zinc oxide to further sensitization by actinic light. This type of inactivation

is that which inactivates the photocatalyst rather than the image-forming composition.

Still another method of inactivation is to separately bind the photocatalyst and the image-forming composition on separate independent sheets. The sheets are then firmly pressed together and exposed to light. Thereafter, the sheets are separated and the image is formed on either the photocatalytic carrier or the image-forming carrier, depending upon the type of image-forming composition used. One method is to coat one sheet with a pressure-sensitive adhesive containing the image-forming composition, and the other sheet is coated with the catalyst and a conventional binder. The sheets are pressed together and form a sufficient bond such that electrons may transfer from one sheet to the other. After exposure, the sheets are separated by pulling them apart. The two-sheet method has been found to be quite distinctive in that a transparency or negative can be formed immediately upon exposure. For example, the image-forming composition which is usually transparent may be coated upon a transparent backing or carrier, such as Mylar. The second sheet is coated with a pressure-sensitive adhesive which contains a photosensitive catalyst in admixture therewith or which contains the photocatalyst dusted on the surface. The sheets are pressed together and the combined sheets are then exposed to an image source, such as through a negative. After exposure, the sheets are separated and a transparency is produced upon the Mylar film containing the image-forming composition. As a modification of the above, the image-forming compound, such as the oxidizing agent, is coated on the first sheet with a transparent binder. The second sheet is coated with an adhesive containing both the photocatalyst and the other component of the image-forming composition, such as the reducing agent. Various other combinations as will become apparent from the above are within the scope of this invention. The above methods of forming transparencies are simple and cheap and are particularly adapted to use by the amateur photographer.

The system of the present invention may be particularly adaptable to amateur photography. In accordance with the present invention, a composition of this invention is placed upon a paper backing in roll form and directly placed in the camera. The image is formed immediately upon exposure and the only remaining step in order to obtain a print is the inactivation of the composition. This may be done by the amateur photographer by removing the exposed print in the dark and washing with water as above described. Inactivation may also be achieved by using hand pressure with a pencil over the surface of the print. The camera itself can be constructed to have the film pass through small pressure rollers to desensitize the print. Other modifications or alterations are obvious for adaptation to conventional cameras.

The following examples are offered as a better understanding of the present invention and are not to be construed as unnecessarily limiting thereto. In the examples, the zinc oxide used was New Jersey Zinc Company's Zinc Oxide of the U.S.P.-12 or Red Seal #9 type and was prepared by the French Process of burning zinc metal in air, and the titanium dioxide was Merck's analytical reagent grade.

EXAMPLE I

A dispersion of (42 parts by weight) zinc oxide in (11 parts by weight) Pliolite, (23 parts by weight) acetone, (24 parts by weight) toluene and (3 parts by weight) sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer, containing 5 parts by weight silver nitrate, 20 parts by weight of water-soluble binder material Carbowax (20-M), and 75 parts

water, was coated on the white zinc oxide layer in a thickness of about 3 mils and allowed to air dry in the dark. The dried sheet gave an image in 10-15 seconds' exposure to a mercury arc lamp. This sheet was fixed by washing away the undeveloped image-forming layer along with the water-soluble binder. The image of reduced silver clings to surface of zinc oxide in Pliolite and remains intact with a white background on the non-image areas.

Substitution of a wood pulp paper support for the Mylar plastic support gave similar results to the above. Also, any commercial sun lamp will give a satisfactory source of ultraviolet light for exposure.

Other water-soluble binders, such as polyvinylpyrrolidone, o-hydroxycellulose, and methyl cellulose, can be used in place of Carbowax when fixing by removal of a component. Other non-water soluble polar binders, such as a polyamide resin, work equally well as binders for the photocatalytic layer.

EXAMPLE II

A dispersion of (42 parts by weight) zinc oxide in (11 parts by weight) Pliolite, (23 parts by weight) acetone, (24 parts by weight) toluene and (3 parts by weight) sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer containing 4 parts by weight copper sulfate, 20 parts by weight of water-soluble binder material Carbowax (20-M), 1 part by weight of hexamethylenetetramine (basic media), and 75 parts water, was coated on the zinc oxide layer to a thickness of about 2 mils and allowed to air dry in the dark. The dried sheet gave a permanent image in 30 seconds' exposure to a mercury arc lamp. This sheet was fixed by washing away the top layer along with water-soluble binder. The image sheet was stabilized by removing the basic media which was necessary for the oxidation-reduction reaction between the sodium oxalate and the copper sulfate.

EXAMPLE III

A dispersion of (42 parts by weight) zinc oxide in (11 parts by weight) Pliolite, (23 parts by weight) acetone, (24 parts by weight) toluene and (3 parts by weight) sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top coating solution which contained 3 parts by weight diphenylcarbazone, 5 parts by weight chromium chloride, 12 parts by weight polyvinylpyrrolidone, 50 parts by weight water, and 30 parts by weight methanol was coated as a top layer to 2 mils and air dried in the dark. The dry sheet was exposed to a mercury arc lamp for 20 seconds and then heated to 150° F. An image formed in the light-struck areas after heating. The light causes a reduction of the carbazone to carbazide which then complexes with chromium upon heating to give an image. This is stable at room temperature since the heat is needed to cause the complex formation reaction.

EXAMPLE IV

A dispersion of titanium dioxide (42 parts by weight) in 11 parts by weight of Pliolite, 23 parts by weight acetone, 24 parts by weight toluene, 3 parts by weight of sodium formate, and 2 parts by weight p(N-acetyl-N-methyl amino) benzene diazonium fluoroborate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer, containing 5 parts by weight silver nitrate, 10 parts by weight of polyamide resin, and 85 parts by weight methanol, was coated using a Pliolite binder on the zinc oxide layer in a thickness of about 1 mil and al-

lowed to air dry in the dark. The dried sheet gave an image in 10–15 seconds' exposure to a mercury arc lamp. This sheet was fixed by heating it to 130° C. When heated to this temperature, the fluoroborate decomposes to give boron trifluoride. The presence of BF₃ kills the sheet to any other sensitivity to light. This gives a permanent copy that heat stabilizes. Zinc oxide as the photocatalyst in the above system gives similar results.

EXAMPLE V

A dispersion of 42 parts by weight of zinc oxide in 11 parts by weight of Pliolite, 23 parts by weight of acetone, 24 parts by weight of toluene and 3 parts by weight of sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and air dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer containing 1 part by weight gold chloride, 24 parts by weight polyvinylpyrrolidone (binder), and 75 parts by weight methanol was coated to 2 mils and allowed to air dry in the dark. This sheet was exposed to a mercury arc lamp for 20 seconds with no apparent development of image. The exposed sheet is heated to 140–150° C. with immediate development of an image in the light-struck areas. This gives a stable sheet after development of the image and is no longer sensitive to light. This is an example of latent image formation by light and development and stabilization of the image by heat.

EXAMPLE VI

A dispersion of 42 parts by weight of titanium dioxide in 11 parts by weight of Pliolite, 23 parts by weight of acetone, 24 parts by weight of toluene and 3 parts by weight of sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer containing 1 part by weight gold chloride, 24 parts by weight polyvinylpyrrolidone (binder), and 75 parts by weight methanol was coated to 3 mils and allowed to air dry in the dark. This sheet was exposed to a mercury arc lamp for 20 seconds with no apparent development of image. The exposed sheet is heated to 140–150° C. with immediate development of an image in the light-struck areas. This gives a stable sheet after development of image and is no longer sensitive to light. This is an example of latent image formation by light and heat development and stabilization of the sheet.

EXAMPLE VII

A dispersion of 42 parts by weight zinc oxide in 11 parts by weight of Pliolite, 23 parts by weight of acetone, 24 parts by weight of toluene, and 3 parts by weight of hydroquinone was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. An image-forming layer containing 1 part by weight gold chloride, 24 parts by weight of polyvinylpyrrolidone, and 75 parts by weight of methanol was coated to 3 mils and allowed to air dry in the dark. This sheet was exposed to a mercury arc lamp for 10 seconds with no apparent development of image. The exposed sheet was dipped in water with an immediate development of an image in the light-struck areas. The image was deposited on the zinc oxide surface and the water-soluble binder and unexposed areas washed away. This is an example of a latent image formation by light with subsequent development and stabilization by water.

EXAMPLE VIII

A dispersion of (42 parts by weight) titanium dioxide in (11 parts by weight) Pliolite, (23 parts by weight) acetone and (24 parts by weight) toluene was ballmilled for 12 hours. This dispersion was coated 4-mils thick on

a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A solution of 5 parts by weight silver nitrate, 10 parts by weight of Zytel 61, a polyamide resin as a binder, and 85 parts by weight methyl alcohol was coated to 3 mils on the titanium dioxide layer and allowed to air dry in the dark. The dried sheet gave a brown image when exposed through a contact negative for 15 seconds. This sheet lasts for 24 hours before backgrounding makes the print unreadable. This gives a light-sensitive process for examining prints without fixing. The polyamide binder served as the reducing agent. Wood pulp or rag base paper can be substituted for the Mylar backing with similar results.

EXAMPLE IX

A dispersion of 42 parts by weight of zinc oxide in 11 parts by weight of Pliolite, 23 parts by weight of acetone, 24 parts by weight of toluene and 3 parts by weight of sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer containing 5 parts by weight tetrazolium blue (image former and oxidizing agent), 20 parts by weight of water-soluble binder material Carbowax (20-M), and 75 parts water, was coated on the zinc oxide layer and allowed to air dry in the dark. The dried sheet gave an image in 20–30 seconds' exposure to a commercial sun lamp. This sheet was fixed by washing away the undeveloped image-forming material along with the water-soluble binder. The image of insoluble formazan clings to the surface of zinc oxide in Pliolite and remains intact.

EXAMPLE X

A dispersion of 42 parts by weight of zinc oxide in 11 parts by weight of Pliolite, 23 parts by weight of acetone, 24 parts by weight of toluene and 3 parts by weight of sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. An image-forming layer containing 1 part by weight gold chloride, 24 parts by weight polyvinylpyrrolidone, and 75 parts by weight methanol was coated to 3 mils and allowed to air dry in the dark. This sheet was exposed to a mercury arc lamp for 20 seconds with the formation of a latent image. The exposed sheet was dipped in a solution of hydroquinone with an immediate visual development of the image in the light-struck areas. This is an example of latent image formation by light with subsequent visual development of the latent image by an external reducing agent. The sheet is then washed to remove the unreacted image-forming material and water-soluble binder to give a stable sheet. A Mylar support with the above system gives similar results.

EXAMPLE XI

A dispersion of 42 parts by weight of zinc oxide in 9 parts by weight of Zytel 61, a polyamide resin (reducing agent and binder), 23 parts by weight acetone, 24 parts by weight of toluene, and 5 parts by weight silver nitrate was ballmilled for 24 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature (dark conditions). The dried sheet was exposed to a mercury arc lamp for 10 seconds to develop a good image. The exposed sheet is light stabilized by leaching out the remaining silver nitrate for three minutes in a water bath. This gives a copy sheet that is light developed and water stabilized.

EXAMPLE XII

A suitable thin flexible and non-porous carrier sheet, e.g. paper, is coated with a suspension of zinc oxide, Metol (1,4-methyl-p-aminophenol) in a solution of polystyrene resin binder in a suitable volatile solvent, and the

solvent is removed by evaporation. There is produced a smooth uniform white coating, which in absence of light is then uniformly further coated with a thin layer of an aqueous solution of nickel chloride and gelatin, and dried. The coated paper is exposed to a light image formed by passing intense radiation, high in ultraviolet, through an appropriate stencil and onto the coating surface. The irradiated areas rapidly darken by an action which appears to involve deposition of metallic nickel. The sheet is then rinsed with water, removing the remaining gelatin and nickel chloride, and leaving on the white zinc oxide coating a dark image corresponding to the radiation-exposed areas.

EXAMPLE XIII

A zinc oxide coated base as employed in Example XII is further coated under dark conditions with a thin layer of silver nitrate applied from solution in water, and dried at room temperature. The coated sheet is exposed to a light image as in Example XII and is then washed in water, leaving a dark deposit on the light-struck areas. The image is permanent against further radiation. The dark image areas appear to be composed of metallic silver.

EXAMPLE XIV

A homogeneous mixture of zinc oxide, silver nitrate, sodium formate, and polystyrene resin in a volatile organic solvent for the resin is prepared by ballmilling and is coated on a thin flexible organic film and dried, all under subdued illumination, to provide a light-sensitive sheet material which when exposed to a light-image high in ultraviolet is found to darken rapidly at the light-struck areas while remaining at its original whiteness in areas not so irradiated. Thus, a light-image formed by passing the radiation through a photographic negative transparency produces on the coated sheet a positive copy. The resulting copy is fugitive, the white areas gradually darkening under further irradiation, but as initially formed may be fixed by appropriate washing in water.

EXAMPLE XV

A dispersion of (20 parts by weight) titanium dioxide in (11 parts by weight) Pliolite, (23 parts by weight) acetone, (24 parts by weight) toluene, and (3 parts by weight) 1,4-methyl paraminophenol sulfate (Elon) was ballmilled for 12 hours. A slurry of (6 parts by weight) silver saccharin in (3 parts by weight) acetone was added to the ballmilled mixture and stirred. The final mixture was coated 4-mills thick on a Mylar support and dried at room temperature. All procedures of making the film must be done in the dark. The dried sheet was exposed for 2-10 seconds to a tungsten lamp. The exposed sheet which has a latent image is heated to 140° C. for a few seconds. The image appears in the previously light-struck areas when the sheet is heated. This printed sheet is stable to normal room light provided it is not reheated. Reducing agents such as ascorbic acid, hydroquinone and catechol can be substituted for Elon. Zinc oxide can be substituted for titanium dioxide. An exposure of 1-10 seconds with a mercury arc lamp is sufficient to cause a latent image that can later be heat developed.

EXAMPLE XVI

A dispersion of (20 parts by weight) titanium dioxide in (11 parts by weight) Pliolite, (23 parts by weight) acetone, (24 parts by weight) toluene, (3 parts by weight) 1,4-methyl paraminophenol sulfate (Elon) and (2 parts by weight) sodium oxalate was ballmilled for 12 hours. A slurry of (6 parts by weight) silver saccharin in (3 parts by weight) acetone was added to the ballmilled mixture and stirred. The final mixture was coated 4-mills thick on a Mylar support and dried at room temperature, all procedures of making the film must be done in the dark. The dried sheet was exposed for 2-10 seconds to a tungsten lamp. The exposed sheet which has a latent image is placed in warm water for several seconds. The image

appears in the previously light-struck areas when the sheet is placed in warm water. This printed sheet is stable to normal room light. Reducing agents such as ascorbic acid, hydroquinone and catechol can be substituted for Elon. Zinc oxide can be substituted for titanium dioxide. An exposure of 1-10 seconds to a mercury arc lamp is sufficient to cause a latent image that can be water developed.

EXAMPLE XVII

The effect of the reducing agent in causing an increase in image density for a given exposure is exemplified by the following Table I. In the runs of the table a 150 watt projection lamp was used as the light source. In runs 1 through 4 of Table I, the paper compositions were prepared in accordance with the procedure of Example I with the modifications as the photocatalyst and omission of reducing agent as indicated. Runs 5 and 6 correspond to the paper compositions of Examples XV and XVI. The tabulation of values in the columns below the time of exposure in seconds is the change in optical density from unexposed to exposed, and the higher values are the most desirable.

Table I

CHANGE IN OPTICAL DENSITY FOR INDICATED EXPOSURES TO TUNGSTEN LAMP

$$[O.D. = (O.D._{\text{exposed}} - O.D._{\text{unexposed}})]$$

Exposure—Seconds.....	2.5	5	10	15	20	30	60	120
1. Zinc oxide—Silver Nitrate.....	.01	.02	.035	.055	.08	.13	.23	.275
2. Zinc oxide—Silver Nitrate—Sodium Oxalate.....	.055	.08	.115	.145	.165	.24	.355	.50
3. Titanium dioxide—Silver Nitrate.....	.025	.04	.05	.056	.08	.11	.18	.23
4. Titanium dioxide—Silver Nitrate—Sodium Oxalate.....	.085	.05	.07	.095	.12	.15	.25	.37
5. Titanium dioxide—Silver Saccharin Elon (Heat developed).....	.265	.32	.345	.37	.38	.395	.42	-----
6. Titanium dioxide—Silver Saccharin Elon (Water developed).....	.15	.185	.22	.245	.27	.30	.37	-----

$$O.D._{\text{unexposed}} = 0.10.$$

EXAMPLE XVIII

A dispersion of (42 parts by weight) fluorescent zinc sulfide activated with silver in (11 parts by weight) Pliolite, (23 parts by weight) acetone and (3 parts by weight) sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer, containing 5 parts by weight silver nitrate, 20 parts by weight of water-soluble binder Carbowax (20-M), and 75 parts water was coated on the fluorescent compound layer to a thickness of about 3 mils and allowed to air dry in the dark. The dried sheet gave an image in 10-120 seconds' exposure to a mercury arc lamp. This sheet was fixed by washing away the undeveloped image-forming layer along with the water-soluble binder. The image of reduced silver clings to the surface of the fluorescent compound in Pliolite. Other water-soluble binders as well as other image forming materials, such as tetrazolium salts and gold salts can be used in this example in place of silver nitrate. Reducing agents other than sodium oxalate can be used. Other fluorescent compounds which have been used and gave similar results are:

- (1) Zinc oxide-zinc
- (2) Zinc phosphate-manganese
- (3) Calcium borate
- (4) Zinc-8-hydroxyquinoline

EXAMPLE XIX

A dispersion of (80 parts by weight) photochromic $[Co(C_2H_4N_2H_4)_3]_2(S_2O_8)_3$ in (11 parts by weight) Plio-

lite, (23 parts by weight) acetone and (3 parts by weight) sodium oxalate was ballmilled for 12 hours. This dispersion was coated 4-mils thick on a Mylar support and dried at room temperature with a subsequent dark adapting period of 12 hours. A top layer, containing 5 parts by weight silver nitrate, 20 parts by weight of water-soluble binder Carbowax (20-M), and 75 parts water was coated on the fluorescent compound layer to a thickness of about 3 mils and allowed to air dry in the dark. The dried sheet gave an image in 10-120 seconds' exposure to a mercury arc lamp. This sheet was fixed by washing away the undeveloped image-forming layer along with the water-soluble binder. The image of reduced silver clings to the surface of the photochromic compound in Pliolite. Other water-soluble binders as well as other image-forming materials, such as tetrazolium salts and gold salts can be used in this example. Other photochromic compounds which have been used and gave similar results are:

- (1) $[\text{Co}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]_2(\text{C}_2\text{O}_4)_3$
- (2) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_2\text{S}_2\text{O}_8$
- (3) $[\text{Co}(\text{NH}_3)_6]_2(\text{C}_2\text{O}_4)_3$
- (4) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
- (5) $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3]$
- (6) $[\text{Cr}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]_2(\text{SO}_4)_2\text{S}_2\text{O}_8$

Various combinations of photocatalysts and oxidation-reduction reactions may be employed without departing from the scope of this invention. The application of the invention to various conventional cameras and other image-reproducing systems will also become apparent to those skilled in the art from the accompanying description and disclosure.

Having described our invention, we claim:

1. An image reproduction system comprising a catalyst which is activated into the transfer of electrons to an electron acceptor by at least one radiation wave length below five microns selected from at least one of the group consisting of photoconductors, non-photoconductive fluorescent materials, photochromic metal complexes, and the non-photoconductive metal oxides titanium dioxide, antimony trioxide and aluminum oxide, and an oxidation-reduction reaction composition having an oxidation-reduction potential of at least +0.1 volt, the reaction of which is initiated by electron transfer from said catalyst, comprising an oxidizing agent selected from at least one of the group consisting of the salts of silver, mercury, lead, gold, manganese, nickel, tin, chromium, platinum and copper, the tetrazolium salts, diphenol carbazone and methine dye, and a reducing agent selected from at least one of the group consisting of the alkali earth and alkali metal oxalates, alkali earth and alkali metal formates, hydroxyl amines, hydrazines, ascorbic acid, aminophenols, dihydric phenols and polyvinylpyrrolidone, said oxidizing agent and said reducing agent being present in substantially stoichiometric equivalent amounts, and the weight ratio of the oxidation-reduction composition to catalyst being between about 10:1 and about 1:10, and said catalyst, oxidizing agent and reducing agent being present in combination in separate solid phases and in substantially dry condition.

2. A radiation-sensitive sheet which comprises an inert carrier sheet containing uniformly bonded over the surface thereof a catalyst which is activated into the transfer of electrons to an electron acceptor by at least one radiation wave length below one micron selected from at least one of the group consisting of photoconductors, non-photoconductive fluorescent materials, photochromic metal complexes, and the non-photoconductive metal oxides titanium dioxide, antimony trioxide and aluminum oxide, and an oxidation-reduction reaction composition having an oxidation-reduction potential of at least +0.1 volt, the reaction of which is initiated by electron transfer

from said catalyst, comprising an oxidizing agent selected from at least one of the group consisting of the salts of silver, mercury, lead, gold, manganese, nickel, tin, chromium, platinum and copper, the tetrazolium salts, diphenol carbazone and methine dye, and a reducing agent selected from at least one of the group consisting of the alkali earth and alkali metal oxalates, alkali earth and alkali metal formates, hydroxyl amines, hydrazines, ascorbic acid, aminophenols, dihydric phenols and polyvinylpyrrolidone, said oxidizing agent and said reducing agent being present in substantially stoichiometric equivalent amounts, and the weight ratio of the oxidation-reduction composition to catalyst being between about 10:1 and about 1:10, and said catalyst, oxidizing agent and reducing agent being present in combination in separate solid phases and in substantially dry condition on said carrier sheet.

3. The radiation-sensitive sheet of claim 2 in which the oxidizing agent is a silver salt.

4. The radiation-sensitive sheet of claim 2 in which said reducing agent is an alkali metal oxalate.

5. The method for making the reproduction of a light image which comprises incorporating the oxidizing agent with the catalyst while in a non-excited state in the radiation-sensitive sheet of claim 2 and then exposing said sheet to a light image.

6. The method for making a reproduction of a light image which comprises incorporating the oxidizing agent with the catalyst while in a non-excited state in the radiation-sensitive sheet of claim 2, which contains a water soluble reactive component as at least one of the oxidizing agent and the reducing agent, then exposing said sheet to a light image, and thereafter water-washing the exposed sheet to remove a water-soluble reactive component whereby the sheet is inactivated to further sensitivity to light.

7. The method for making a reproduction of a light image which comprises incorporating the oxidizing agent with the catalyst while in a non-excited state in the radiation-sensitive sheet of claim 2, then exposing said sheet to a light image, and thereafter complexing one of the reactive components of said exposed sheet into a non-light-sensitive metal chelate whereby said sheet is inactivated to further sensitivity to light.

8. The method for making a reproduction of a light image which comprises incorporating the oxidizing agent with the catalyst while in a non-excited state in the radiation-sensitive sheet of claim 2, then exposing said sheet to a light image, and then changing the pH of the surface of said exposed sheet to a pH to which the reactive components will not react in the light whereby said sheet is inactivated to further sensitivity to light.

9. The method for making a reproduction of a light image which comprises incorporating the oxidizing agent with the catalyst while in a non-excited state in the radiation-sensitive sheet of claim 2, then exposing said sheet to a light image to produce a latent image thereon, thereafter heating the exposed sheet to produce a visible reproduction of the light image.

10. The method for making a reproduction of a light image which comprises incorporating the oxidizing agent with the catalyst while in a non-excited state in the radiation-sensitive sheet of claim 2, then exposing said sheet to a light image to produce a latent image thereon, thereafter wetting the exposed sheet with water to produce a visible reproduction of said light image.

11. A radiation-sensitive sheet which comprises an inert carrier sheet containing uniformly bonded over the surface thereof a photoconductor as a catalyst which is activated into the transfer of the electrons to an electron acceptor by at least one radiation wave length below one micron and an oxidation-reduction reaction composition having an oxidation-reduction reaction potential of at least +0.1 volt, the reaction of which is initiated by electron transfer from said catalyst, comprising an

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organic silver salt as an oxidizing agent and an alkali metal oxalate as a reducing agent, said oxidizing and said reducing agent being present in substantially stoichiometric equivalent amounts, and the weight ratio of the oxidation-reduction composition to catalyst being between about 10:1 and 1:10, and said catalyst, oxidizing agent and reducing agent being present in combination in separate solid phases and in substantially dry condition on said carrier sheet.

12. The radiation-sensitive sheet of claim 9 in which said organic silver salt is silver saccharin.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,152,903

October 13, 1964

Joseph W. Shepard et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 47, for "bentriazole" read --- benztriazole ---; column 14, Table I, under the heading "15" and opposite the third item, for ".056" read -- .065 --.

Signed and sealed this 23rd day of March 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents