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3,429,706

RADIATION-SENSITIVE SYSTEM

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ABSTRACT OF THE DISCLOSURE

The present invention relates to an embodiment of the invention disclosed in U.S. Patent No. 3,152,903 in which three separate solid phases of active ingredients, one phase being the photocatalyst phase, another phase being the oxidizing phase and another phase being the reducing phase, form a light-sensitive sheet material. In accordance with the present embodiment the above phases are characterized further by incorporating either an oxidizing agent or a reducing agent or both with a binding material which is incompatible or immiscible with it or with the other agent or with another binding material used to form separate reactive phases on the carrier sheet. Although the oxidizing agent and reducing agent are in separate solid phases and are present in substantially dry condition on the sheet, they at least partially react with each other upon light exposure in the presence of the photocatalyst.

This application is a continuation of our copending application SN 221,329, filed Sept. 4, 1962, now abandoned, which is a continuation-in-part of our prior application SN 809,927, filed Apr. 30, 1959, now U.S. Patent No. 3,152,903.

The present invention relates to a novel and useful radiation-sensitive system. In one aspect the invention relates to the permanent reproduction of images or patterns on a surface by irradiation. In another aspect the invention relates to a new light-sensitive composition and to a reproduction surface or sheet made from such composition. 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. If fixing is necessary or desirable, fixing 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 disadvantage of the silver halide process, however, is the rather involved developing procedure. On the other hand, the disadvantage of the electrophotographic process is the low sensitivity thereof to

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the reproduction of images. Most 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 light-sensitive composition or combination of components.

Another object of this invention is to provide a novel process for graphic reproduction 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 light-sensitive combination of components of increased sensitivity for the graphic reproduction of images and the like.

Still another object of this invention is to provide a dry process for graphic reproduction.

Still another object of this invention is to provide a process for directly reproducing transparencies.

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

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

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 radiation-sensitive system comprises an image-forming combination of components or composition and a separate radiation-sensitive catalyst or photocatalyst chemically different from the image-forming composition. The radiation-sensitive system is usually in a dry or even anhydrous form and is supported by or is a part of a suitable inert carrier or sheet. The carrier sheet containing the radiation-sensitive system is then exposed to an image source or light source, and the image or pattern to be copied is reproduced either immediately upon exposure or upon subsequent development. In some instances, fixing or inactivation of the radiation-sensitive 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 or reactive components of the system are in the form of an irreversible oxidation-reduction reaction combination which is capable of initiation into reaction or of catalyzation by electron transfer thereto from the photocatalyst. The oxidation-reduction reaction combination or composition comprises two solid phases; a separate solid phase comprising an oxidizing agent and another separate solid phase comprising a reducing agent. During exposure to radiation, the oxidizing agent reacts with the reducing agent whereby a reproduction of the image or pattern results, which reproduction may be latent (invisible) or visible. Any redox combination of an

oxidizing agent and a reducing agent having a negative-free energy under the exposure or development conditions suffices as the image-forming or reactive composition.

In one embodiment of the invention, the reaction of the oxidation-reduction combination upon exposure produces a product or products having a change in color or reflectance resulting in a visible reproduction. In another embodiment, the reaction product or products of the reaction of the oxidation-reduction combination upon exposure are not visible (latent image) but are made to react further with each other or with other materials in a subsequent development step to produce a visible reproduction by a change in color or reflectance. In both embodiments, the image-forming composition is substantially dry when exposed, and reaction is effected at least partially at the time of exposure under exposure conditions which are usually ambient conditions. Exposure may be effected at somewhat elevated temperatures, such as 50° C. Subsequent reactions, if necessary, are effected by heating above the exposure temperature or by wetting the exposed redox combination with water.

In addition to the image-forming combination or composition above-described, the radiation-sensitive system requires a third solid phase comprising, as a radiation-sensitive catalyst, a relatively nonreactive material which is not the same as the oxidizing agent or the reducing agent and can be activated into the transfer or release of electrons upon exposure to irradiation having a wave length below 5 microns, preferably below 1 micron, such as actinic light, X-rays or gamma rays. Electrons are transferred from the catalyst to the oxidation-reduction combination, usually to the oxidizing agent as the electron acceptor, which electrons initiate or catalyze the reaction.

The radiation-sensitive system may comprise an admixture of the above three separate solid phases or may comprise separate layers of each, or layers of a combination of any solid phases, in any order. The radiation-sensitive catalyst phase may be applied as a layer bonded to a suitable carrier or inert substrate. Upon the catalyst layer is affixed the image-forming combination in the form of a single layer comprising an admixture of components or in the form of two separate adjacent layers of each of the components. Any one or all of the components of the radiation-sensitive system may also comprise, or be impregnated in, the carrier. Any one of the reactive components may be included with the catalyst layer and the other reactive component included in a separated layer adjacent and in contact with the catalyst layer.

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 or 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 reproduction 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 such as by removing or complexing at least one of the unreacted components, by inactivating the photocatalyst, or by the use of a combination of these methods.

In order to maintain the oxidizing agent and the reducing agent as separate solid phases, at least one of these reactive components is admixed with a material or binder which is incompatible or immiscible with that component or with the other component or with a second material or binder used with the other component. In applying the present combination to an inert substrate, such as paper, the metal containing catalyst is applied or affixed to the surface, such as with an organic resin or binder. Then one of the components of the oxidation-reduction combination is admixed with an organic solvent or diluent containing

dissolved therein an organic resin as a binder, which admixture is applied as a continuous layer over the catalyst layer and dried to form a solid layer. Upon this layer is applied the other reactive component from a solution thereof, the solvent of which solution is substantially immiscible with, but bondable to, the organic layer containing the other reactive component. Since most of the oxidizing agents and reducing agents are water-soluble, this latter layer may be applied from an aqueous solution containing dissolved therein a water-soluble binder to form a continuous layer when dried. There are various techniques which will become obvious to those skilled in the art for maintaining the reactive components and catalyst in separate phases and in a nonreacted condition while in admixture or in contact with each other without departing from the scope of this invention.

The reactive components of the radiation-sensitive composition are in actual contact or in mutually inter-reactive relationship with each other, but are physically distinct from each other. The catalyst is similarly in such close relationship with the reactive components as to be capable of transferring electrons to at least one of the components when the catalyst is activated by radiation.

As previously stated, the image-forming combination 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 combination. The preferred oxidizing agents comprise the metal salts, either inorganic or organic. Suitable metal salts include the salts of silver, mercury, lead, gold, manganese (in the form of the permanganate), nickel, tin, chromium, platinum and copper. Examples of typical nonmetal salt oxidizing agents include the nonmetal organic salts and dyes comprising the tetrazolium salts, such as tetrazolium blue (3,3'-dianisole-bis-4,4'-(3,4 diphenyl) tetrazolium chloride) and red (triphenyl-tetrazolium chloride) and diphenyl carbazone, and Genacryl Red 6B, a methine dye (CI 48020).

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 the carbazide. Also, additives may be used in combination.

When the above metal salts are used as the oxidizing agent, an organic nonmetal complexing 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, additives may be used in combination with the oxidizing agent to change the character and tonal value of the image. Images often 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 a small amount of an organic complexing additive, such as an acid amide as, for example, formamide or acetamide, and phytic acid. Similarly, the density of a gold image is increased by use of acetamide.

The reducing agents of the image-forming composition which are chemically different from and physically separate from the oxidizing agents are organic reducing compounds, such as the oxalates, formates, substituted and nonsubstituted hydroxylamine and substituted and nonsubstituted hydrazine, ascorbic acid, aminophenols

and the mono and dihydric phenols. 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 (1,4-methyl-p-aminophenol) and Elon (N-methyl-p-aminophenol sulfate); an example of a substituted hydrazine is phenyl hydrazine. Suitable mono and dihydric phenols include Ionol (2,6-ditertiary-butyl-4-methylphenol), 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 in one aspect by the ability of either one or both of the compounds in their reacted form to show a change in light value (a change in color or reflectance), or to react with another compound resulting in a change in light value. 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 phase 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 a radiation wave length below 5 microns. Such photocatalysts comprise both inorganic photoconductors and nonphotoconductors. Among the inorganic photoconductors which may be used are zinc oxide, indium oxide, zinc sulfide, cadmium sulfide and selenium. Of the photoconductors, the N-type is preferred, such as zinc oxide. Inorganic nonphotoconductors which act as photocatalysts are the polyvalent metal oxides including titanium dioxide and antimony trioxide. Of both the photoconductors and nonphotoconductors above described, the white materials are preferred to assure a white background.

It has also been found that certain fluorescent or phosphorescent metal compounds are also useful as photocatalysts since they can transfer electrons when activated with actinic light or other types of irradiation. 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, calcium borate and zinc-8-hydroxyquinoline. Photochromic materials, such as the photochromic metal complexes having readily reducible anions, 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 readily reducible anions which may be used in place of those of the peroxydisulfate of the above complexes 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 exposed to light at the same time that a control sample of an aqueous solution of silver nitrate alone is exposed to light, such as ultraviolet light. If the mixture darkens faster than the silver nitrate alone, the material is a photocatalyst. If, however, a reaction does take place in the absence of light, the materials should be coated out separately on a flat surface using a suitable binder in accordance with the procedure described herein. A control sheet is also made for comparison. The test is carried out on the sheets as described above.

The irradiation source is an important feature of the present invention. Ultraviolet light is one of the best radiation 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, Seto Flavin-T, Thioflavin, uranine, erythrosin, phosphine R, orthochrome P, Vasoflavin and dicyanine A. Radiation by X-rays or gamma rays is also effective in exciting the photocatalyst to transfer electrons.

The binding agent used to bind the image-forming composition and the photocatalyst to the carrier medium is also 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 for the reactive components and catalyst are organic materials, such as solid polymers and resins. Suitable organic resins and copolymers include a copolymer of butadiene and styrene sold on the open market as Pliolite, polystyrene, chlorinated rubber, polyvinylchloride, nitrocellulose, rubber hydrochloride, polyvinylbutyral, polyethyleneglycol, carbowax, polyamide resin sold as Zytel-61, hydroxyethyl cellulose, methyl cellulose and polyvinylpyrrolidone. The polar-type binders which are water or alcohol-soluble are useful with one of the reactive components, such as binders including polyethyleneglycol, polyvinylbutyral, polyamide resin and carbowax and polyvinylpyrrolidone. These binders may be removed by dissolving the binder with water or alcohol and thus removing the oxidizing and/or reducing agent. This inactivates the carrier to further exposure to light as will be hereinafter discussed. The nonpolar binders or water or alcohol insoluble organic binders are useful with the other reactive component or both reactive components. These binders include polystyrene, chlorinated rubber, rubber hydrochloride, polyvinylchloride, nitrocellulose and Pliolite. Any of these binders may be used for the catalyst phase, but the nonpolar binders are preferred. The binders may also be admixed and used in admixture for layer formation.

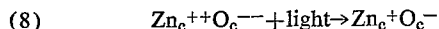
The carrier material or support upon which the photocatalyst and image-forming composition are deposited may be any suitable inert backing of sufficient strength and durability to satisfactorily serve as a reproduction. The carrier or support may be in the form of sheets, ribbon, roll or other suitable form for supporting the reproduction of the image. The carrier may comprise wood pulp paper, rag content paper, various synthetic plastics, such as cellulose acetate and polyethylene terephthalate (Mylar) in the form of film, cotton or wool cloth, metal foil and glass plate. 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

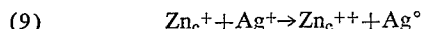
irradiation-sensitive system of this invention comprises zinc oxide as a photocatalyst, silver nitrate as the oxidizing agent and image-forming material, and sodium formate or sodium oxalate as the reducing agent, all of which which are bonded to the paper as a continuous uniform layer. A slurry is formed of these materials with an immiscible organic binder and diluent 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 (copolymer of butadiene and styrene) is useful as the binder since it securely adheres the components to the paper and to each other. Another method of construction is to apply an admixture of zinc oxide and silver nitrate to the paper first in about a 2-mil thickness with a suitable binder, such as Pliolite, followed by a separate layer of the reducing agent sodium formate in an aqueous solution of a suitable water-soluble binder such as carbowax.

A negative film or transparency (developed) as a master is applied to the surface of the above paper containing the image-forming composition and catalyst. The film is then exposed to actinic light (500 lumens) for about 1 to 15 seconds. The paper and film are then removed from the presence of actinic light, and the film removed from the paper. The paper contains a reproduced black image (Ag°) on the film, even though the paper has been dry throughout the procedure. When zinc oxide is omitted from the above process, no visible image is formed in 30 seconds of exposure. 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.

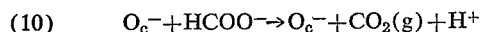
In the above typical system using zinc oxide, ultraviolet light has been theorized to raise the electrons of the zinc oxide to its conduction band in accordance with the following equation:



$\text{Zn}_c^{++}\text{O}_c^{--}$ 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 actually be 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, the electron 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 non-photoconductors, such as the fluorescent materials, the metal complexes and the nonphotoconductive metal oxides.

The probable theory for the action of the metal complexes as photocatalysts is that the metal ion can exist in more than one oxidation state, a nonionic 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 are usually 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 reactive components 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 inert carrier base or support, when in the form of a flexible sheet, is usually between about 5 and about 30 mils.

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.

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.

As previously stated, in one embodiment of this invention the image after exposure is latent under ambient and normal conditions. In other words, there is no visible image formed upon exposure which is effected at a temperature not higher than about 50°C. , usually at ambient conditions, even in the presence of the photocatalyst, although a reaction has taken place. In this embodiment, the exposed system is subsequently treated by heating above 50°C. or by wetting with water to cause further reaction. Upon further reaction, either the reducing agent or the oxidizing agent or some other reactive compound changes in light value so as to reproduce the image in those areas where the initial reaction has taken place; for example, where the initial reaction produces free metal in a small and invisible quantity which catalyzes the subsequent reaction to form the image.

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 1 to 24 hours is desirable in such instances. After conditioning, the catalyst is not exposed to light prior to its exposure for reproducing the image.

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 hydro-

quinone, silver saccharin and Metol or Elon, tetrazolium blue and sodium formate or sodium oxalate, silver behenate and Ionol, 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 image-forming combinations of this invention in dry condition are not normally considered light-sensitive in the absence of the photocatalyst. These reactive combinations, upon exposure to an ultraviolet light source such as a mercury arc lamp (2,000-4,000 lumens) for a period of time from 5 to 10 minutes, do not show any sensitivity to the light and are therefore considered normally latent under ambient conditions. Some sensitivity may be observed, darkening of the composition, upon prolonged exposure of several hours to an intense light source with certain combinations, such as with silver nitrate and a reducing agent. In other combinations, such as with silver saccharin and a reducing agent, no sensitivity is observed even upon prolonged exposure to light when no photocatalyst is present. These redox combinations are in no way similar in sensitivity to the silver halide emulsion type of light-sensitive compositions or those which are aqueous or moist (in solution).

In addition to the above, the redox combinations may be divided into two classes, one class in which the redox combination results in a reproduction of the image simultaneously with exposure (print out system), and the other class in which the visible reproduction is made after exposure by a separate developing step, such as by heating.

As previously stated, inactivation of the radiation-sensitive system is required where the reproduced image will be observed under the same or similar light conditions used during exposure or when the system does not require a subsequent development step, such as heating or wetting. However, where the light conditions of observation are not the same as under exposure, such as exposure to X-rays or gamma rays or where special development is required, 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 off the photocatalyst, such as zinc oxide, in a water-insoluble binder, such as Pliolite, and coating either the oxidizing agent or reducing agent on this surface with a water-soluble binder, such as polyethylene-glycol. After development of the image either at the time of exposure or in a subsequent step, the water-soluble film containing one of the reactive components 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 Bronsted 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 directly upon exposure to the image source. The metal salt oxidizing agent, the reducing agent and a basic additive are coated with suitable binders on top of a zinc oxide coated carrier. If separate layers are used for the reactive components, the layer containing the metal salt oxidizing agent will also preferably contain the basic additive. Since metals above oxygen in the electromotive series do not deposit in neutral media, the layer or layers forming the image-forming combination

are neutralized after light development of the image therein which stabilizes the metal ion of the metal salt oxidizing agent. This is accomplished by releasing an acid by a heat-sensitive reaction after exposure.

For example, the radiation-sensitive system is heated to a temperature of about 100° to 250° C. A suitable composition that will release hydrogen chloride and thus neutralize the basic material upon heating is an admixture of m-nitrobenzenesulfonyl chloride (acid-releasing compound) and phloroglucinol. This admixture is added to the layer containing the metal salt oxidizing agent of the photosensitive sheet. This method gives a dry reproduction, light-sensitive image system that does not require a development step and is heat-inactivated to give a permanent stable copy. Other acid-releasing compounds 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 or water-soluble polyamide binder. Included in this top layer, of course, is the metal salt of oxidizing agent composition. The lower layer of this system is a photo-catalyst dispersed in a nonwater-soluble binder, such as Pliolite. The reducing agent may be included in the lower layer or be in another separate intermediate layer using a nonwater-soluble binder, but cannot be included in the top layer if the binder is water-soluble. Upon wetting the top layer containing the water-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 layer containing the metal salt oxidizing agent and the acid former a compound that liberates water at low temperatures, which water will react with the acid former to liberate the acid. A diazonium fluoroborate as the acid former will release BF₃ upon heating to about 125° C. in the presence of a hydrate, 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 adjacent layer either above or below the layer containing the oxidizing agent. The chelating compound may also be admixed together with a single layer formation. In this method, the image reproduction system is exposed to develop the image and then heated at a temperature of about 120° to 250° C. to form the metal chelate with the unreacted metal ion of the oxidizing agent. The metal chelate formed must be nonlight-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° C. results in a black image on a stable white background which is no longer sensitive to light.

A simple test for determining whether the metal chelate is nonlight-sensitive is to expose the metal chelate to ultraviolet light. If the material does not darken after 5 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 sur-

face of the carrier. It has been found that pressure will desensitize the photocatalyst, such as zinc oxide, as a result of which it is 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 at least one of the reactive components 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 combination, 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 combination which is usually transparent may be coated upon a transparent backing or carrier, such as Mylar film. 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 inexpensive 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. When using zinc oxide as the photocatalyst, 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) photoconductive zinc oxide and (3 parts by weight) sodium oxalate (reducing agent) in a solution of (11 parts by weight) Pliolite, (23 parts by weight) acetone, (24 parts by weight) toluene was ball-milled for 12 hours. This dispersion was coated 4 mils thick on a transparent Mylar film as a flexible 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 (oxidizing agent), 20 parts by weight of water-soluble binder material carbowax (20-M), and 75 parts water was coated in the dark 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 to 15 seconds exposure to a mercury arc lamp (3,000 lumens). This sheet was fixed by washing away the unreacted silver nitrate along with the water-soluble binder. The image of reduced silver clings to the surface of zinc oxide in Pliolite and remains intact with a white background on the nonimage areas.

Substitution of a wood pulp paper as a support for the Mylar plastic film 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, hydroxyethyl cellulose and methyl cellulose, can be used in place of carbowax for the top layer containing the oxidizing agent. Other normally water insoluble or nonwater-soluble organic binders, such as polystyrene and polyvinylchloride, work equally well as binders for the photocatalytic layer containing the reducing agent in place of Pliolite.

EXAMPLE II

A dispersion of (42 parts by weight) zinc oxide in (11 parts by weight) Pliolite, (3 parts by weight) sodium oxalate, (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled for 12 hours. The zinc oxide and the sodium oxalate are immiscible with the Pliolite and the solvent. This dispersion was coated 4 mils thick on Mylar film as a flexible support and dried at room temperature with a subsequent dark-adapting period of 12 hours. An aqueous solution containing dissolved therein 4 parts by weight copper sulfate, 20 parts by weight of water-soluble binder carbowax (20-M), 1 part by weight of hexamethylenetetramine (basic media), and 75 parts water, was coated in the dark 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 (3,000 lumens). This sheet was fixed by washing away the top layer along with water-soluble binder and basic media. The image sheet was stabilized by washing away 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 and (3 parts by weight) sodium oxalate in (11 parts by weight) Pliolite, (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled for 12 hours. This dispersion was coated 4 mils thick on a Mylar film 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 in the dark as a top layer to 2 mils thick and air-dried in the dark. The dry sheet was exposed to a mercury arc lamp (3,000 lumens) for 20 seconds and then heated to 150° C. 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 (42 parts by weight) titanium dioxide and (3 parts by weight) sodium formate in (11 parts by weight) Pliolite, (23 parts by weight) acetone, (24 parts by weight) toluene and (2 parts by weight) p(N-acetyl-N-methyl amino) benzene diazonium fluoroborate was ball-milled 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 methanol-soluble polyamide resin and 85 parts by weight methanol was coated in the dark in a thickness of about 1 mil and allowed to air-dry in the dark. The dried sheet gave an image in 10 to 15 seconds exposure to a mercury arc lamp (3,000 lumens). 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 gave similar results.

EXAMPLE V

A dispersion of (42 parts by weight) zinc oxide and (3 parts by weight) sodium oxalate in (11 parts by weight) Pliolite (binder), (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled 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 in the dark to a thickness of 2 mils and allowed to air-dry in the dark. This sheet was exposed to a mercury arc lamp (3,000 lumens) for 20 seconds with no apparent development of image. The exposed sheet was 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. Substitution of titanium dioxide for zinc oxide in the above formulation gave substantially the same result.

EXAMPLE VI

A dispersion of (18 parts by weight) titanium dioxide and (27 parts by weight) silver behenate (oxidizing agent) in (18 parts by weight) Pliolite, (150 parts by weight) acetone, (150 parts by weight) toluene and (1 part by weight) 0.2% thioflavin in methanol was ball-milled for 24 hours. Prior to coating, (14 parts by weight) 25% Ionol (reducing agent) dispersed in acetone was added in the dark to the dispersion and then the dispersion was coated in the dark to a thickness of 4 mils on a transparent Mylar film support and dried at room temperature with a subsequent dark-adapting period of 12 hours. The dried sheet gave an image in 5 to 30 seconds exposure to a tungsten light source (500 lumens) with a subsequent heat development at 110° C. for 15 seconds. The stable copy had a blue-black image on an off-white background. In some cases the concentration of the dye was sufficient to color the sheet slightly.

EXAMPLE VII

A dispersion of (42 parts by weight) zinc oxide and (3 parts by weight) hydroquinone in (11 parts by weight) Pliolite, (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled 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 contain-

ing 1 part by weight gold chloride, 24 parts by weight polyvinylpyrrolidone and 75 parts by weight methanol was coated in the dark to a thickness of 3 mils and allowed to air-dry in the dark. This sheet was exposed to a mercury arc lamp (3,000 lumens) 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) zinc oxide and (3 parts by weight) sodium oxalate in (11 parts by weight) Pliolite, (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled 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 in the dark on the zinc oxide layer and allowed to air-dry in the dark. The dried sheet gave an image in 20 to 30 seconds exposure to a commercial sun lamp (1,000 lumens). This sheet was fixed by washing away all the top layer including 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 IX

A dispersion of (42 parts by weight) zinc oxide and (3 parts by weight) sodium oxalate in (11 parts by weight) Pliolite, (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled 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 in the dark to 3 mils thick and allowed to air-dry in the dark. This sheet was exposed to a mercury arc lamp (3,000 lumens) for 20 seconds with the formation of a latent image (reduction of small amount of gold chloride to gold). 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 was then washed to remove the unreacted image-forming material and water-soluble binder to give a stable sheet. A Mylar film support with the above system gave similar results.

EXAMPLE X

A suitable thin flexible and nonporous paper sheet was coated 3 mils wet with a suspension of (42 parts by weight) zinc oxide, (3 parts by weight) Metol (1,4-methyl-p-aminophenol) in a solution of (9 parts by weight) polystyrene resin binder in (75 parts by weight) methyl-ethyl ketone as a suitable volatile solvent, and the solvent was removed by evaporation. The sheet was then dark-adapted for 12 hours. There was produced a smooth uniform white coating, which in absence of light, was then uniformly further coated with a thin layer of 100 parts by weight of an aqueous solution containing 2 parts by weight nickel chloride and 2 parts by weight gelatin and air-dried in the dark. The coated paper was 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 was then rinsed with water, removing the remaining gelatin and nickel chloride, and leaving on the

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white zinc oxide coating a dark image corresponding to the radiation-exposed areas.

EXAMPLE XI

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

EXAMPLE XII

A dispersion of (42 parts by weight) zinc oxide, (5 parts by weight) silver nitrate and (3 parts by weight) sodium formate in (11 parts by weight) polystyrene resin and a (47 parts by weight) volatile organic solvent for the resin was prepared by ball-milling and was coated on a thin flexible organic film (Mylar) and dried, all under subdued illumination, to provide a light-sensitive sheet material which, when exposed to a light-image high in ultraviolet, was 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 produced on the coated sheet a positive copy. The resulting copy was fugitive, the white areas gradually darkening under further irradiation, but as initially formed, may be fixed by appropriate washing in water.

EXAMPLE XIII

A dispersion of (20 parts by weight) titanium dioxide and (3 parts by weight) 1,4-methyl paraminophenol sulfate (Elon) in a solution of (11 parts by weight) Pliolite, (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled for 12 hours. A slurry of (6 parts by weight) silver saccharin in (3 parts by weight) acetone

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EXAMPLE XIV

A dispersion of (20 parts by weight) titanium dioxide, (3 parts by weight) 1,4-methyl paraminophenol sulfate (Elon) and (2 parts by weight) sodium oxalate in a solution of (11 parts by weight) Pliolite, (23 parts by weight) acetone and (24 parts by weight) toluene was ball-milled for 12 hours. A slurry of (6 parts by weight) silver saccharin in (3 parts by weight) acetone was added to the ball-milled mixture and stirred. The final dispersion was coated 4 mils thick on a Mylar film 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 to 10 seconds to a tungsten lamp (500 lumens). The exposed sheet which had a latent (invisible) image was then placed in warm water for several seconds. A visible image appeared in the previously light-struck areas when the sheet was placed in warm water. This printed sheet was 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 to 10 seconds to a mercury arc lamp is also sufficient to cause a latent image that can be water-developed.

EXAMPLE XV

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 (500 lumens) was used as the light source. In Runs 1 through 4 and 7 of Table I, the paper compositions were prepared in accordance with the procedure of Example I with modifications as to the photocatalyst and omission of reducing agent as indicated. Runs 5 and 6 correspond to the paper compositions of Examples XIII and XIV. The tabulation of values in the columns below the time of exposure in seconds of Table I 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

		[Change in optical density=(O.D. Exposed—O.D. Unexposed)]							
Run	Compositions	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	.065	.08	.11	.18	.23
4.....	Titanium dioxide, silver nitrate, sodium oxalate.....	.035	.05	.07	.095	.12	.15	.25	.37
5.....	Titanium dioxide, silver sac- charin, Elon (heat-developed).....	.265	.32	.345	.37	.38	.395	.42	
6.....	Titanium dioxide, silver sac- charin, Elon (water-devel- oped).....	.15	.185	.22	.245	.27	.30	.37	
7.....	(No photocatalyst), silver nitrate, sodium oxalate.....								0.00

O.D. Unexposed=0.10.

was added to the ball-milled mixture and stirred. The final mixture was coated 4 mils thick on a Mylar film 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 to 10 seconds to a tungsten lamp (500 lumens). The exposed sheet which had a latent image was heated to 140° C. for a few seconds. The image appeared in the previously light-struck areas when the sheet was 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 to 10 seconds with a mercury arc lamp is also sufficient to cause a latent image that can later be heat-developed.

EXAMPLE XVI

A dispersion of (42 parts by weight) fluorescent zinc sulfide activated with silver and (3 parts by weight) sodium oxalate in (11 parts by weight) Pliolite and (23 parts by weight) acetone was ball-milled for 12 hours. This dispersion was coated 4 mils thick on a Mylar film 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 in the dark 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 to 20 seconds exposure to a mercury arc lamp (3,000 lumens). This sheet was fixed by washing away the un-

developed 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 as disclosed herein. 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 XVII

A dispersion of (80 parts by weight) photochromic

- (1) $[\text{Co}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]_2(\text{S}_2\text{O}_8)_3$

and (3 parts by weight) sodium oxalate in (11 parts by weight) Pliolite and (23 parts by weight) acetone was ball-milled for 12 hours. This dispersion was coated 4 mils thick on a Mylar film 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 water-soluble binder carbowax (20-M) and 75 parts water was coated in the dark 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 to 20 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 oxidizing agents, 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:

- (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) $[\text{Cr}(\text{C}_2\text{H}_4\text{N}_2\text{H}_4)_3]_2(\text{SO}_4)_2\text{S}_2\text{O}_8$

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. A dry radiation-sensitive combination which comprises three chemically different and separate solid phases, each phase being in contact with at least one of the other phases, said solid phases being a catalyst phase comprising a metal containing substance which is substantially nonreactive with the components of the combination and which is activated into the transfer of electrons to an electron acceptor by a radiation wave length below 5 microns, a reducible phase comprising an oxidizing agent which accepts electrons from said catalyst and an oxidizable phase comprising an organic reducing agent which is reactable with said oxidizing agent, said oxidizing agent and said reducing agent being in mutually inter-reactive contact and at least one of which being mixed with and bonded to the sheet with a material which is immiscible with that reactive component or with the other reactive component or with a second material used as a binder for the other reactive component, and said oxidizing agent and said reducing agent at least partially react upon irradiation in the presence of the metal containing catalyst.

2. A dry radiation-sensitive sheet which comprises an inert carrier sheet containing uniformly bonded thereover three chemically different and separate solid phases,

each phase being in contact with at least one of the other phases, said solid phases being a catalyst phase comprising a metal containing substance which is substantially non-reactive with the other components of the combination and which is activated into the reversible transfer of electrons to an electron acceptor by a radiation wave length below 5 microns, a reducible phase comprising an oxidizing agent which accepts electrons from said catalyst, and an oxidizable phase comprising an organic reducing agent which is reactable with said oxidizing agent, said oxidizing agent and said reducing agent being in mutually interreactive contact and at least one of which is mixed with and bonded to the sheet with a material which is immiscible with that reactive component or with the other reactive component or with a second material used as a binder for the other reactive component, and said oxidizing agent and said reducing agent at least partially react upon irradiation in the presence of the metal containing catalyst.

3. A dry radiation-sensitive sheet which comprises an inert carrier sheet containing bonded thereto three chemically different and separate solid phases, each phase being in contact with at least one of the other phases, said solid phases being a catalyst phase comprising a metal containing substance which is substantially nonreactive with the other components of the sheet and which is activated into the reversible transfer of electrons to an electron acceptor by a radiation wave length below 1 micron, a reducible phase comprising an oxidizing agent which accepts electrons from said catalyst, and an oxidizable phase comprising an organic reducing agent which is reactable with said oxidizing agent, said catalyst and at least one of said reactive components is admixed with and bonded to the sheet with a water insoluble organic resin which is immiscible with a water soluble organic binder for the other reactive component which is water soluble and is bonded to said sheet with said water soluble binder, and said oxidizing agent and said reducing agent at least partially react upon irradiation in the presence of the metal containing catalyst.

4. The radiation-sensitive sheet of claim 3 in which said catalyst is a fluorescent material.

5. The radiation-sensitive sheet of claim 3 in which said catalyst is a photochromic metal organic complex.

6. The radiation-sensitive sheet of claim 3 in which said catalyst is a photoconductor.

7. The radiation-sensitive sheet of claim 3 in which said catalyst is a nonphotoconductive metal oxide.

8. The radiation-sensitive sheet of claim 3 in which the organic reducing agent is an oxalate.

9. The radiation-sensitive sheet of claim 3 in which the organic reducing agent is a formate.

10. The radiation-sensitive sheet of claim 3 in which the organic reducing agent is an aminophenol.

11. The radiation-sensitive sheet of claim 3 in which the organic reducing agent is a hydric phenol.

12. The radiation-sensitive sheet of claim 3 in which the organic reducing agent is a hydroxyl amine.

13. The radiation-sensitive sheet of claim 3 in which said inert carrier is paper.

14. The radiation-sensitive sheet of claim 3 in which said inert carrier is plastic film.

15. The radiation-sensitive sheet of claim 3 which contains bonded to the surface thereof and in contact with one of the reactive components benzotriazole as an inactivator.

16. The radiation-sensitive sheet of claim 3 which contains bonded to the surface thereof and in contact with one of the reactive components salicylaldehyde as an inactivator.

17. The radiation-sensitive sheet of claim 3 which contains bonded to the surface thereof and in contact with one of the reactive components p(N-acetyl-N-methyl amino) benzene diazonium fluoroborate as an inactivator.

18. A method for making a reproduction of a light

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image which comprises at a temperature not higher than about 50° C. exposing to a light image a dry light-sensitive sheet which comprises an inert flexible carrier sheet containing bonded thereto three chemically different and separate solid phases, each phase being in contact with at least one of the other phases, said solid phases being a catalyst phase comprising a metal containing substance which is substantially nonreactive with the other components of the sheet and which is activated into the transfer of electrons to an electron acceptor by a radiation wave length below 1 micron, and a reducible phase comprising an oxidizing agent which accepts electrons from said catalyst, and an oxidizable phase comprising an organic reducing agent which is reactable with said oxidizing agent, said catalyst and at least one of said reactive components is admixed with and bonded to the sheet with a water insoluble organic resin which is immiscible with a water soluble organic binder for the other reactive component which is water soluble and is bonded to said sheet with said water soluble binder, and said oxidizing agent and said reducing agent at least partially react upon irradiation in the presence of the metal containing catalyst.

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19. An image reproduced on a sheet by the method of claim 18.

20. The method of claim 18 in which the exposed sheet containing a visible image is inactivated to further sensitivity to light by water-washing the sheet to remove the water-soluble reactive component.

21. The method of developing a latent image produced by the process of claim 18 which comprises heating the exposed sheet above 65° C.

22. The method of developing a latent image produced by the process of claim 18 which comprises wetting the exposed surface of the sheet with water.

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96—1, 27, 88, 95; 117—34; 252—461

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,429,706 Dated February 25, 1969

Inventor(s) JOSEPH W. SHEPARD and BENJAMIN L. SHELY

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

Column 3, line 47: "separated" should read -- separate --

Column 4, lines 53, 54: "the carbazide. Also, additives may be used in combination." should read -- zinc oxide as a photocatalyst on exposure to irradiation. --

Column 10, line 26: "of" second occurrence, should be deleted entirely

Column 10, line 54: after "admixed" and before "together" insert -- in a system where all of the components are mixed --

Column 18, line 69: "salicylaldorine" should read -- salicylaldoxine --

SIGNED AND
SEALED
JUN 23 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

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Commissioner of Patents