

[54] **PHOTOGRAPHIC REFLEX PROCESS**

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[56] **References Cited**

UNITED STATES PATENTS

3,102,026	8/1963	Metcalf et al.	96/1
3,249,430	5/1966	Metcalf et al.	96/1.3
3,360,367	12/1967	Stricklin	96/1
3,380,823	4/1968	Gold	96/27
3,429,706	2/1969	Shepard et al.	96/64

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[57]

ABSTRACT

This disclosure relates to a method of making a reflex copy of a master by reflex exposing a photosensitive medium comprising a photoconductor sensitized to the reflex light but substantially not sensitive to the light which passes through the said medium from the external light source employed. The photoconductor is rendered chemically reducing when exposed to activating radiation, and is sensitized to the reflex light by uniformly exposing the photoconductor to bandgap light and allowing the activation to decay. Development of the medium after reflex exposure gives a negative image. To obtain a positive image, the developed reflex-exposed medium is used as a master and again reflex exposed using the same process to obtain a positive image.

9 Claims, No Drawings

PHOTOGRAPHIC REFLEX PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a reflex copying process and, more particularly, to a reflex copying process which employs a photosensitive medium which is sensitized to substantially only the reflex light and not to the initial light which passes through the medium from the external light source.

2. Description of the prior art

Reflex copying is a well-known process for obtaining an un-magnified duplicate of an original without using an optical system for projecting the original on to a photosensitive medium. Simply stated, reflex copying involves exposing to activating radiation a reflex system composed of a photosensitive medium superposed on the master copy. The exposing radiation passes through the photosensitive medium and is reflected by the non-image areas of the master to the photosensitive medium. The image areas of the master absorb the radiation and this leads to activation of the photosensitive medium to obtain a laterally reversed, i.e. wrong-reading, latent image which on development gives a negative of the master. A positive of the master is obtained by repeating the process using the negative as the master.

Photosensitive media comprising radiation-sensitive materials such as titanium dioxide are described in detail in U.S. Pat. No. 3,152,093; No. 3,052,541; French Pat. No. 345,206 and No. 1,245,215 and in British Pat. specification No. 1,043,250. In the aforementioned British Pat. specification, radiation-sensitive titanium dioxide functions as a photosensitive component of the media and exposure of said media to activating means such as radiant energy, electron beams or the like results in the storage of a reversible latent image pattern therein. The reversible latent image pattern exists for a finite time during which said pattern can be converted to an irreversible form and read out visually by contacting said pattern with a suitable image forming material, such as a chemical redox system. In the aforesaid U.S. and French patents, the radiation-sensitive material is combined with at least one component of an image-forming material prior to exposure to activating means. For example, U.S. Pat. No. 3,152,904 describes a photosensitive copy medium comprising photosensitive materials such as titanium dioxide in combination with a reducible metal ion such as silver nitrate. This copy medium is exposed to activating means to produce a visible image. On the other hand, U.S. Pat. No. 3,152,903 discloses a system wherein the photosensitive material is used in combination with both an oxidizing agent such as silver nitrate and a reducing agent such as hydroquinone. Upon exposure to suitable activating means, a visible image is formed.

One of the features of the above-mentioned data or image storage systems is that the photosensitive materials are often sensitive to a very narrow range of electromagnetic radiation. Therefore, it is often desirable to sensitize these photosensitive materials to additional ranges of electromagnetic radiation by uniformly exposing the photoconductor to bandgap light followed by decay of the resulting activation which then renders the decayed photoconductor sensitive to light of a different wavelength, usually light of a longer wavelength extending into the near visible, to the visible region and in some cases to the infrared region. Such sensitization of photoconductors is described in commonly assigned copending U.S. Pat. No. 3,554,749.

A bireflex xerographic system composed of two discrete layers of a photoconductor-containing medium one of which layers is dyesensitized to visible light is described in U.S. Pat. No. 3,165,405. In this patent, the layer which is not sensitive to visible light is the image-forming layer which because of the positive charge on the top surface thereof is developable with powder toners to a positive image. The dye-sensitized layer generates photo-injected charge carriers which cause the intensity difference which must be employed to yield an imagewise distribution of surface potential at the positively charged top surface of the non-sensitized layer.

SUMMARY OF THE INVENTION

It has now been unexpectedly discovered that acceptable reflex copies of a master can be produced utilizing a photosensitive medium comprising a photoconductor which is rendered chemically reducing by activating radiation, the photoconductor being sensitized to the reflex light and being substantially non-sensitive to the light from the external source which passes through the medium and is reflected by the master. For example, as hereinafter described, the medium is sensitized by uniform exposure to bandgap light so that it will not be activated to any appreciable extent by the light from the external light source but will be activated by the light reflected by the master to be copied by virtue of the frequency of reflections between the medium and the master. Since the photoconductor employed is activatable by light of specific wavelength, such light, i.e. actinic light, must be removed from the light used in this reflex process which should be non-actinic to the medium. This is readily accomplished by the use of suitable filters arranged between the original light source and the reflex copy system or by use of radiation which is devoid of such activating radiation. For photoconductors which are activated by ultraviolet light, light of a wavelength of 400 millimicrons or longer is used in this process.

For the purpose of this disclosure, the expression, light which is substantially non-actinic to the medium, refers to light which is substantially non-activating as incident light but activating as reflex light.

After reflex exposure of the photosensitive medium, the latent image is rendered visible by contact with image-producing agents to obtain a negative image of the master. The negative image can be converted to a positive image identical to the master by using this negative as the master and repeating the same process with a second photosensitive medium.

The image-producing agents include those commonly employed in photography and in xerography, as hereinafter described.

It is totally unexpected that a process such as herein-described is possible due to the fact that it was never recognized that a photoconductor of the type described could be made selectively sensitive to the "reflex light," i.e. the light reflected between the master and the photosensitive medium, and, at the same time, substantially insensitive to the light from the initial light source.

This invention provides a relatively simple, economical method of producing reflex copies from a master. of especial value is the aforementioned method of preparing positive copies from the first negative, which process can be repeated as often as desired to form multiple positive copies from the one negative, particularly in an automatic copying system.

DESCRIPTION OF PREFERRED EMBODIMENTS

The photoconductor or photocatalyst preferred in this invention are metal containing photoconductors. A preferred group of such photosensitive materials are the inorganic materials such as compounds of a metal and a non-metallic element of Group VIA of the periodic table, e.g. oxides, such as zinc oxide, titanium dioxide, zirconium dioxide, germanium dioxide, indium trioxide; metal sulfides such as cadmium sulfide (CdS), zinc sulfide (ZnS) and tin disulfide (SnS₂); and metal selenides such as cadmium selenide (CdSe). Metal oxides are especially preferred photoconductors of this group. Titanium dioxide is a preferred metal oxide because of its unexpectedly good results. Titanium dioxide having an average particle size less than about 250 millimicrons and which has been treated in a reducing atmosphere at a temperature between about 200° and 950° C for about 0.5 to about 30 hours and then rapidly quenched is especially preferred, and more especially that titanium dioxide produced by high temperature pyrolysis of titanium halide.

Also useful in this invention as photoconductors are certain fluorescent materials. Such materials include, for example, compounds such as silver activated zinc sulfide and zinc activated zinc oxide.

While the exact mechanism by which this invention works is not known, it is believed that exposure of the photoconductors or photocatalysts to the activating means causes an electron or electrons to be transferred from the valence band of the photoconductor or photocatalyst to the conductance band of the same or at least to some similar excited state whereby the electron is loosely held, thereby changing the photoconductor from an inactive form to an active form. If the active form of the photoconductor or photocatalyst is in the presence of an electron accepting compound a transfer of electrons will take place between the photoconductor and the electron accepting compound, thereby reducing the electron accepting compound. Therefore a simple test which may be used to determine whether or not materials have a photoconductometric or photocatalytic effect is to mix the material in question with an aqueous solution of silver nitrate. Little, if any, 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 control, the material is a photoconductor or photocatalyst.

It is evident that the gap between the valence and the conducting band of a compound determines the energy needed to make electron transitions and the light required to provide the needed energy is called "bandgap light," as employed herein. The higher energy needed, the higher the frequency to which the photoconductor will respond. It is known in the art that electrons may be present in secondary levels within the band gap due to impurities or defects in the structure of the photoconductor. With light of suitable energy, which in this case would be less than the band gap, electrons from these levels could be raised to the conduction band. A typical example of a secondary level due to a defect in the structure would be an F-center (electrons trapped at negative ion vacancies in an alkali halide crystal). The band gap of KCl is about 8.5 eV (1,460Å.), but the secondary levels due to F-centers are about 2.4 eV (5,400Å.) below the conduction band. Electrons could be raised to the conduction band with 5,400Å. light. An example of the effect of an impurity is ZnS doped with Cu. The band gap of ZnS is about 3.7 eV (3,350Å.), but by doping it with Cu one could introduce some secondary levels which would result in photoconduction due to 4,600Å. light.

As is generally known, the activation of photoconductors, i.e. transference of electrons from valence bands to conductance bands, is not permanent but rather the activation decays primarily as a function of time. The decay is apparently due to the loss of electrons in the conductance bands, the electrons reverting to lower energy levels, many reverting to the original valence band and others to energy levels intermediate between the respective bands, i.e. secondary levels, or traps. After decay of the activated photoconductor, the medium retains little, if any, ability to reduce silver ions, or similar metal ion, due to the fact that there are little, if any, electrons in the conductance band. When reference is made herein to a decayed sensitized medium it is intended that the photoconductor is in a state intermediate between the active and inactive states by virtue of the fact that electrons of the photoconductor are in the secondary levels, or traps.

When the decayed sensitized medium is exposed to an image pattern of light of wavelength longer than the bandgap light, the energy provided is sufficient to raise the electrons in the secondary levels to the conductance band, but not sufficient to raise electrons from the valence band to the conductance band. This results in a latent image on the medium corresponding to the pattern, and when the medium is brought into contact with an electron acceptor, electron transfer occurs. Accordingly, if the medium is contacted with a liquid redox system, reduction of the reducible component thereof occurs. If the reducible component, in the reduced form, is a particulate solid, the result obtained is a visible image corresponding to the pattern.

The foregoing theoretical explanation is offered to enable a better understanding of the present invention and is believed

to reasonably interpret the phenomenon of this invention. Of course, the applicants are not necessarily bound by this explanation.

For maximum sensitization of the photoconductor to light of longer wavelength, it is preferred to utilize high exposure energies of bandgap light. For example, the exposure energy should be about 10 millijoules/cm² or greater for best results, while energies ranging from 0.05 millijoule/cm² are found operable.

For decaying the photoconductor sensitized with bandgap light it is preferred to allow the medium to stand over a period of time usually of at least about 1 hour to ensure substantially complete decay. As mentioned hereinbefore, samples of the sensitized medium may be tested using, for example, aqueous silver salt solutions, to determine the time required for decay which will of course be dependent on the photoconductor, the exposure energy, and other factors known to those skilled in the art. After sensitization, the medium should be protected from exposure to activating light prior to exposure to a light pattern to form the latent image and subsequent to this step until the medium is developed. Techniques for avoiding unintended exposure are well known and need not be enumerated for those skilled in the art.

The sensitivity of the decayed, activated medium to the selected reflex light is determined by the initial activation by bandgap light. As pointed out in the aforementioned copending U. S. Pat. No. 3,554,749 the sensitivity to light of different wavelength from that of the bandgap light is a function of the intensity of the initial exposure to bandgap light as well as the time of exposure. For maximum sensitization, high intensities and long periods of exposure are used.

For best results, the decayed, sensitized medium should be activated by the reflex light and, at the same time, absorb little, if any of the light from the external source which passes through the medium. The decayed, sensitized medium should absorb not more than about 15 percent of the light which passes through the medium to obtain acceptable reflex prints. For best results, such absorption should not exceed 10 percent. For any given medium, the optimum extent of sensitization can readily be determined by testing various levels of sensitization and determining the optimum. This optimum will be determined to an appreciable extent by the time of exposure, the quality of reflex prints required and other factors recognized by those skilled in the art.

For the purpose of determining optimum conditions, the selected medium is pre-irradiated by the selected conditions, the activation allowed to decay and the medium is then exposed to the selected reflex light source, i.e. a source to provide visible light of wavelength longer than that to which the photoconductor is sensitive. The extent of absorption of light, i.e. activation, can be determined by treating the medium with a developing agent such as a solution of silver nitrate followed by a reducing agent for the silver ions, e.g. hydroquinone. The density of precipitated silver on the medium is indicative of the percentage absorption of the exposing light. As previously mentioned, the percentage should be less than 15 percent and preferably less than 10 percent. The comparison standard for this test is the same medium sensitized to visible light by irradiation with bandgap light as described in the aforesaid copending application and exposed to visible light of high intensity. A comparison of the respective densities of the test sample and the similarly exposed and developed standard will give a measure of the percentage absorption by the sensitized test sample.

The reflex light employed in the present process will be light of low intensity, as commonly used in reflex copying, which is substantially free of the bandgap light, e.g. ultraviolet light, of the photoconductor. Minor amounts of bandgap light can be tolerated but are preferably avoided by use of methods known in the art, e.g. by use of suitable filters.

Irradiation sources which are useful in the reflex exposure include any activating electromagnetic radiation which will provide the required light. One convenient source is a tung-

sten light source, e.g. as provided on a Verifax or similar machine.

The reflex exposure of the decayed sensitized photoconductor to the image pattern may be conducted using standard techniques. The light utilized is preferably visible light, of wavelength longer than the bandgap light of the photoconductor. Such wavelength preferably ranges from about 4,200 to about 7,000A. and may even include the near infrared. Certain ranges are more effective depending on the photoconductor, among other factors, and a minimum of testing will indicate the optimum range for the specific photoconductor. For example, a range from about 4,500 to about 6,000A. gives excellent results when titanium dioxide is the photoconductor. The time of exposure may be varied considerably, from fractions of a second to several minutes without appreciable variation in the results.

As should be obvious to those skilled in the art, the latent image at this state may be stored of course protected from unintentional light activation, but care should be taken to avoid substantial decay of the latent image for which reason long periods of storage should be avoided.

Image-forming materials which are useful in this invention are those such as described in U.S. Pat. No. 3,152,903 and in British Pat. specification No. 1,043,250. These image-forming materials include preferably an oxidizing agent and a reducing agent. Such image-forming materials are often referred to in the art as physical developers. The oxidizing agent is generally the image-forming component of the image-forming material. However, this is not necessarily true. Either organic or inorganic oxidizing agents may be employed as the oxidizing component of the image-forming material. Preferred oxidizing agents comprise of reducible metal ions having at least the oxidizing power of cupric ion and include such metal ions as Ag^+ , Hg^{+2} , Pb^{+4} , Au^{+3} , Pt^{+4} , Ni^{+2} , Sn^{+2} , Pb^{+2} , Cu^{+1} , and Cu^{+2} . Other suitable oxidizing agents useful in this invention as components of an image-forming material are permanganate (MnO_4^-) ion, various leuco dye materials such as disclosed in co-pending application Ser. No. 623,534 filed Mar. 19, 1967 in the name of L. Case, and the like. Organic oxidizing agents include tetrazolium salts, such as tetrazolium blue and red, and diphenyl carbazone, and genarcyl red 6B (methine dye).

The reducing agent component of the image-forming materials of this invention are compounds such as the oxalates, formates, substituted and unsubstituted hydroxylamine, and substituted and unsubstituted hydrazine, ascorbic acid, aminophenols, and the dihydric phenols. Also, polyvinylpyrrolidone, alkali and alkaline earth metal oxalates and formates are useful as reducing agents. Suitable reducing compounds include hydroquinone or derivatives thereof, o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenol glycine, o- and p-phenylene diamine, 1-phenyl-3-pyrazolidone.

The oxidizing agent and/or reducing agent may be present on the copy media prior to exposure so far as it does not substantially interfere with the exposing light.

Additionally, the image-forming materials or physical developers may contain organic acids which can react with metal ions to form complex metal anions. Further, the developers may contain other complexing agents and the like to improve image formation and other properties found to be desirable in this art.

Alternatively, the present media after reflex exposure, can be developed using toners commonly employed in electrostatic printing. After development of the visible image, the reflex copy is fixed, if desired, by heating, dark adapting or corona discharge to remove any sensitivity to visible light.

Optimum density difference between the visible image and the background of the medium is attainable by selection of light of specific wavelengths. The determination of the optimum wavelength is readily accomplished by a mere comparison of the spectral response of the photoconductor before and after bandgap light radiation. For example, the spectral response curve of normal titanium dioxide is determined by

plotting the activation versus the wavelength of light, the activation being measured by the ability of the light-activated photoconductor to reduce silver ions from solution as indicated by the density above fog on the thus-treated medium. If the density above fog is plotted against the wavelength of light, the resulting curve approaches zero density as the wavelength approaches that of visible light.

When the titanium dioxide is sensitized with bandgap light, decayed and exposed to light of longer wavelength than bandgap light at the same exposure energy, the corresponding curve does not approach zero in the visible light region of the curve.

The detailed procedure for the determination of optimum density difference is disclosed in the aforementioned copending U.S. Pat. No. 3,554,749 which is incorporated herein by reference.

In the initial sensitizing of the photoconductor, bandgap light is employed. Exemplary photoconductors with corresponding bandgap and absorption edges are listed in Table 1.

TABLE I

Photoconductor	Band Gap (ev.)	Absorption Edge
TiO_2	3.0	4100 A.
In_2O_3	3.5	3520 A.
SnO_2	4.3	2860 A.
PbO	2.3	5350 A.
Bi_2O_3	3.2	3850 A.
ZnO	3.2	3850 A.
TeO_2	1.5	8200 A.
Cu_2O	2.0	6150 A.

When used in the present process, the photoconductors are conveniently applied to a suitable light-transmissive backing which may be either porous or non-porous, such as of paper, plastic, glass and the like. The photoconductor which is suitably used in the form of finely divided particles, may simply be deposited on the surface of such a backing, or can be deposited on such a backing in a hydrophobic or, preferably, a hydrophilic binder known to those skilled in the art of making radiation sensitive papers. Suitable hydrophobic binders, for example, include the polyvinylacetate resin binders commonly used in the preparation of papers for electrostatic printing processes. Typical of the preferred hydrophilic binders having a limited water solubility are gelatin, polyvinyl alcohol, and ethyl cellulose, for example, though many other materials of both types could be mentioned. Particularly advantageous results are employed when the finely divided photoconductor is merely dispersed in the interstices of a fibrous backing such as paper, the fibers of the backing acting to lock in and to hold the photoconductor particles in the finished structure. For example, the photoconductor is easily incorporated in paper during its manufacture by methods known in the papermaking art.

As previously mentioned, a positive copy of the original master can be prepared using the present process which is readily adaptable to automated copying apparatus which will produce any desired number of positive prints. Such a copying apparatus comprises a number of stations at which the following steps would be carried out:

- Reflex exposure of the photosensitive medium to a master (as hereindescribed) provided with a suitable light source;
- Development of the reflex exposed medium provided with developing means and, if necessary, fixing means to remove the sensitivity of the medium to reflex light;
- Reflex exposure of a second photosensitive medium to the developed and fixed first medium provided with a similar light source;

d. Development of the second medium provided with developing and, if necessary, fixing means to remove the visible light sensitivity.

Such apparatus also includes conveying means for transporting the media to the various stations and can include timing devices controlling the conveying means as well as drying stations, supply roller means for the medium, cutting means, take up roller means and the like which are commonly employed in such apparatus.

The following examples are given to further illustrate the invention described herein.

EXAMPLE 1

A mixture of 4 parts by weight of titanium dioxide and one part by weight of an emulsion of an acrylate resin in water (50 percent solids) is used to coat paper sheets.

A sheet of the coated paper is exposed to light (ultraviolet) of wavelength 3,660A. for 5 minutes at an intensity of 50 microwatts/cm². The so-treated paper is allowed to decay by dark storage for 30 minutes.

The sheet is then reflex exposed to a master on a verifax machine for 3 seconds after which the exposed print is dipped into a saturated solution of silver nitrate in methanol and then in a solution of 5g. of phenidone and 40g. of citric acid monohydrate in one liter of methanol. A visible wrong-reading negative image of the original master is obtained.

The negative is then immersed for about 0.5 second in an aqueous fixing bath of sodium thiosulfate, water washed and air dried.

EXAMPLE 2

The developed and fixed negative of Example 1 is used as a master in the procedure of Example 1 to obtain a positive image corresponding to the original master. Additional positive prints of the master are obtained by repeating the procedure with the same negative as the master.

EXAMPLE 3

Zinc oxide is substituted for titanium dioxide in the procedure of Example 1 with similar results.

What is claimed is:

1. A method of making a reflex copy from a master comprising the steps of:
 - a. superposing a photosensitive medium adjacent to the surface of the master to be copied, said photosensitive medium comprising a photoconductor which is reversibly activatable by actinic radiation;
 - b. uniformly exposing the photosensitive medium to bandgap light to thereby activate said photoconductor;
 - c. decaying said photoconductor;
 - d. exposing said master through said decayed photosensitive medium to light which is substantially non-actinic to said medium, the photoconductor being rendered chemically reducing at areas exposed to the reflex light so produced; and,
 - e. developing the areas of said photosensitive medium rendered chemically reducing by reflex light by applying thereto image-forming materials.
2. A method of claim 1 wherein said photosensitive medium absorbs less than 10 percent of the exposing, non-actinic light.
3. A method of claim 2 wherein the photoconductor comprises an inorganic compound formed between a metal and a non-metallic element of Group VIA of the periodic table.
4. A method of claim 3 wherein said photoconductor comprises a metal oxide or sulfide.
5. A method of claim 4 wherein said photoconductor comprises titanium dioxide or zinc oxide.
6. A method of claim 5 wherein said image-forming materials comprise reducible metal ions having at least the oxidizing power of the cupric ion.
7. A method of claim 6 wherein said reducible metal ions comprise silver ions.
8. A method of claim 7 wherein said photoconductor is dispersed in a resin binder.
9. A method of claim 8 wherein said photoconductor and resin binder are coated on a paper substrate.

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