

- [54] **PHOTOGRAPHIC REFLEX PROCESS**
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Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 721,160, April 15, 1968, abandoned.
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[51] Int. Cl. **G03c 11/00**
[58] Field of Search **96/27 R, 47**

[56] **References Cited**

UNITED STATES PATENTS

- | | | | |
|-----------|---------|----------------------|---------|
| 3,663,225 | 5/1972 | McLeod | 96/27 R |
| 3,414,410 | 12/1968 | Bartlett et al. | 96/27 |
| 3,102,026 | 8/1963 | Metcalfe et al. | 96/47 X |

FOREIGN PATENTS OR APPLICATIONS

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| 1,043,250 | 9/1966 | Great Britain |
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529,041 11/1940 Great Britain 96/47

OTHER PUBLICATIONS

Van Der Grinten, *The Photographic Journal*, Sept. 1938, pp 579-582.

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[57] **ABSTRACT**

This disclosure relates to a method of making a reflex copy of a master by reflex exposing to visible light a slightly sensitized photoconductive medium comprising a reflective photoconductor not normally sensitive to visible light. The photoconductor is rendered chemically reducing by this exposure at areas corresponding to non-image areas in the master. To obtain a positive image, the developed reflex-exposed medium may be used as a master and again reflex exposed using the same process to obtain a positive image.

7 Claims, No Drawings

**PHOTOGRAPHIC REFLEX PROCESS
CROSS REFERENCE TO RELATED APPLI-
CATIONS**

This application is a continuation-in-part of Ser. No. 721,160, filed Apr. 15, 1968, now abandoned.

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 reflective photoconductive medium which is slightly sensitized to the visible exposing light.

2. Description of the Prior Art

Reflex copying is a well-known process for obtaining an unmagnified 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. A portion of 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 substantial quantities of the passed 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.

Reflex copying processes using photosensitive silver halide emulsions are described in detail in the following references, the teachings of which are incorporated by reference:

British Patent Specification 529,041; "A History of Reflex Copying — with Notes on the Retocce Process of Screen Reflectography" by L. van der Grinten, The Photographic Journal, pp 579-582, September, 1938; Light-Sensitive Systems by J. Kosar, pp 282-291, John Wiley & Sons, 1965. Additionally, an electrophotographic reflex copying process is described in Metcalfe et al., U.S. Pat. No. 3,102,026. As some of the above references indicate, attempts to use other photosensitive systems, such as diazotype in reflex copying processes, have been by and large unsuccessful because of the inherent characteristics of such systems.

Photosensitive media comprising radiation-sensitive materials such as titanium dioxide are described in detail in U.S. Pat. Nos. 3,152,093; 3,052,541; French Pat. Nos. 345,206 and 1,245,215 and in commonly-owned copending U.S. Pat. application Ser. No. 199,211, filed May 14, 1962 in the names of Berman et al. In the aforementioned U.S. Pat. application, 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 media com-

prising photosensitive materials such as titanium dioxide in combination with a reducible metal ion such as silver nitrate. This copy media 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 application of dyes. Such dyes are well known to the art and include, for example, cyanine dyes, dicarbocyanine dyes, the carbocyanine dyes, and the hemicyanine dyes. Such dye-sensitized systems are disclosed in copending application U.S. Ser. No. 432,887 filed Feb. 15, 1965, now abandoned, in the names of Berman et al., copending application U.S. Ser. No. 359,956 filed Apr. 15, 1964 U.S. Pat. No. 3,414,410 in the names of Bartlett et al., and copending application U.S. Ser. No. 633,689 filed Apr. 26, 1967 now U.S. Pat. No. 3,666,464, in the names of J. Keller and R. Sprague.

It had heretofore been assumed that a photoconductive media as described in the referenced patents would not operate successfully in reflex copying processes due to the inherent characteristics of such media. For example, these photoconductive media are known to have relatively low gammas, far below the gammas previously believed necessary for reflex copying media. Additionally, as pointed out in British Pat. Specification No. 529,041 and Kosar, it had previously been thought that the photosensitive layers should be as transparent as possible, while photoconductive media are normally highly reflective. Typical titanium dioxide layers as described in the patents mentioned above, for example, usually have percentage reflections of 95 percent and higher.

Additionally, Kosar and others teach that besides having a transparent photosensitive emulsion, it is desirable to have a highly reflective substrate. Many substrates used with photoconductive media are not highly reflective since the coating itself has high reflectance.

SUMMARY OF THE INVENTION

It has now been unexpectedly discovered that reflex copies of a master can be produced utilizing a photosensitive medium comprising a highly reflective photoconductor which is rendered chemically reducible by activating radiation, the photoconductor being only slightly sensitized to visible light, i.e., that light having wavelengths between 400 and 700 millimicrons. As hereinafter described, the medium is sensitized with a dye or by doping so that it will not be activated to the same extent by the light from the external light source as by the light which is transmitted through the photoconductive layer and reflected back and forth between the master to be copied and the photoconductive medium. Since the photoconductor itself may be 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 in the absence of dye sensitizers. 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, visible light with slight dye sensitization is used in this process.

After reflex exposure of the photoconductive medium, the latent image is rendered visible by contact with image-producing agents to obtain a negative image corresponding to the master. The negative image can be converted to a positive image by using this negative as the master and repeating the same process with a second photosensitive medium. Before using the negative as a master, it is preferable to remove any remaining sensitizer, i.e., foreign ions or dye, from the medium so that the medium will reflect rather than absorb the exposing radiation.

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

It is totally unexpected that a process such as herein described is possible due to the fact that it was previously believed that inherent properties of photoconductive media made them unsuitable for reflex copying. As described above, some of the properties are the relatively low gammas and the high reflectivities of these media. Also, slight dye sensitization, as described herein, was not suggested by other reflex processes heretofore known.

While not intending to be bound by this explanation, it is believed that the high reflectivity of the photoconductive media account for their unexpected success in reflex copying. Because of this, it is believed to be necessary to use photoconductive media having a percentage reflection of at least 80 percent, and preferably at least 95 percent, when exposed to visible light. The percent of exposing light reflected can be measured on standard reflecting densitometers, such as the MacBeth RD-100.

Thus, invention provides a relatively simple, economical method of producing reflex copies from a master. Of special 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 photoconductors or photocatalysts 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 such as 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); 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°C. and 950°C. for from about 0.5 hours to about 30 hours and then rapidly quenched is especially preferred for its photosensitivity and more especially that

titanium dioxide produced by high temperature pyrolysis of titanium halide. On the other hand, it may be desirable in some cases, to use titanium dioxide with a larger average particle size to increase reflectivity.

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 these photoconductors become capable of forming images is not known, it is believed that exposure of the photoconductors or photocatalysts to activating radiation causes an electron or electrons to be transferred from the valence band of the photoconductor or photocatalyst to the conduction 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 photographic 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 photoconductor 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 activating light, such as ultraviolet light. If the mixture darkens faster than the silver nitrate alone, the material is a photoconductor or photocatalyst for purposes of this invention.

It is evident that the gap between the valence and the conducting band of a compound determines the energy needed to make electron transitions. The more energy needed, the higher the frequency to which the photoconductor will respond. It is known to the art that it is possible to reduce the bandgap for these compounds by adding a foreign compound as an activator which either by virtue of its atomic dimensions or by possessing a particular electronic forbidden zone structure or through the presence of traps as donor levels in the intermediate zone between the valence and the conduction band stresses the electronic configuration of the photoconductive compound, thereby reducing its bandgap and thus increasing its ability to release electrons to its conduction band. Phosphors almost necessarily imply the presence of such activating substances. The effect of such impurities may be such as to confer photoconductivity upon a compound which intrinsically is non-photoconductive. The (Ca-Sr)S phosphors are believed to be an example of this group. On the other hand, excessive impurity content can interfere with a compound acting as a photoconductor, as above described.

Dyes useful for sensitizing the photosensitive copy medium of this invention include, for example, the cyanine dyes, the dicarbocyanine dyes, the carbocyanine dyes, and the hemicyanine dyes. Suitable cyanine dyes are the following: 3,3'-diethyl-4,5,4',5'-dibenzothiacyanine chloride; 3--carboxyethyl-1'-ethyl-6'-methoxy-5-phenyl-thia-2'-cyanine iodide; 3,3'-diethyl-4,5,4',5'-dibenzoxocyanine iodide; 3,3'-diethylthiazolinocarbocyanine iodide; 3,3'-diethyloxacar-

bocyanine iodide; and 3,3'-diethyl-9-methylloxaselenacarbocyanine iodide.

Suitable dicarbocyanine dyes are the following: 3,3'-di-hydroxyethylthiadicarbocyanine bromide; Anhydro-3,3'-di-carboxyethylthiadicarbocyanine hydroxide; 3,3'-diethylxathiadicarbocyanine iodide; 3,3'-diethyl-4,5,4', 5'-dibenzothiadicarbocyanine iodide; 3'-carboxymethyl-3-ethylxathiadicarbocyanine iodide; 3-carboxymethyl-3'-ethylxathiadicarbocyanine iodide; and 3,3'-di(carboxymethyl)oxathiadicarbocyanine bromide.

Suitable carbocyanine dyes are the following: 3,3'-diethyl-9-methyl-4,5,4',5'-dibenzothiadicarbocyanine chloride; Anhydro-3,3'-di-carboxyethyl-5,5'-dichloro-9-ethylthiadicarbocyanine hydroxide; Anhydro-3-carboxyethyl-5,5'-dichloro-9-ethyl-3'-sulfoethylthiadicarbocyanine hydroxide; 9-ethyl-3,3'-di-hydroxyethylthiadicarbocyanine iodide.

Suitable hemicyanine dyes are the following: 2-p-dimethylaminostyryl-4-methylthiazole methochloride; 2-[4-(p-dimethylaminophenyl)-1,3-butadienyl]-1,3,3-trimethylpseudoindolium chloride; 2-(p-dimethylaminostyryl) benzimidazole methochloride; 2-(p-dimethylaminostyryl)-6-ethoxy-quinoline methochloride; 6-dimethylamino-2-(p-dimethylaminostyryl)-quinoline methochloride; 2-p-dimethylaminophenyl-6-methylbenzothiazole methochloride (Thioflavine T); 3,3-dimethyl-2[6(p-dimethylamino-phenyl)-1,3,5-hexatrienyl]indolenine ethiodide; 2(p-dimethyl-aminostyryl)-3,5-dimethylthiadiazolium nitrate; 2-p-dimethylaminostyryl-4-methylthiazole- β -hydroxy-etho-chloride; and 2-p-dimethylaminostyryl-5-methyl-1,3,4-thiadiazole- β -hydroxy-ethochloride.

Aminostyryl hemicyanine dyes are an especially preferred class of dyes because of the improved photographic exposure speed and improved image densities for a given speed achieved with photosensitive copy media so sensitized. Mixtures of dyes can be employed, especially those which increase the photographic speed of the media.

Additional dyes which are useful for sensitizing the photosensitive medium of this invention are the cyanine dyes described on pages 371-429 in "The Theory of Photographic Process" by C. E. Kenneth Mees published by McMillan Company in 1952, the teachings of which are hereby incorporated by reference. Other useful dyes include those known to the art as triphenylmethane dyes such as crystal violet and basic Fuchsin, diphenyl-methane dyes such as Auramine O, and Xanthene dyes such as Rhodamine B.

The dyes useful in this invention may be used in solution to treat the photosensitive materials prior to their incorporation into a copy medium. These dyed photosensitive materials can then be deposited on a substrate, or incorporated into a substrate such as a fibrous web of paper. Alternatively, the dye can be combined with the photoconductive materials in the copy medium, as per example, by dispersion of the dye in the binder for the photosensitive material. In addition, it is possible to dip dye the photosensitive substrate by merely immersing a substrate containing the photosensitive material into a solution of the particular dye.

The amount of dye used in the present media is of prime importance and determines the ability of the sensitized medium to absorb, i.e., be activated by, the multiply reflecting reflex light, and at the same time, ab-

sorb little of the light from the external source which passes through the medium only once. The amount of dye present in the photosensitive medium of this invention should permit absorption of not more than about 15 percent of the light which passes through the medium to obtain acceptable reflex prints. For better results, the absorption by the sensitized medium should not exceed 10% of the light which passes through the medium to obtain good contrast reflex prints. With typical slightly dye-sensitized photosensitive titanium dioxide media, it has been found that about 95 percent of the exposing visible radiation is reflected; and it is believed that about 2 percent is absorbed, mostly by the substrate and binder, although a small portion of the 2 percent is absorbed by the dye-sensitized photoconductor; and therefore about 3 percent of the light passes the medium and is available for multiple reflections between non-image areas of the master and the highly reflecting photoconductive medium whereupon small amounts of the passed radiation are absorbed upon each reflection by the dye-sensitized photoconductor corresponding to non-image areas of the original.

The amount of dye required for the desired result is readily determined by testing various concentrations of the selected dye and determining the optimum concentration. This concentration will be determined to an appreciable extent by the time of exposure, the quality of reflex print required and other factors recognized by those skilled in the art. Also, comparisons between slightly dyed and undyed photoconductive media can be made on densitometers, such as a MacBeth RD-100 densitometer, to evaluate the increased absorption due to the dye present.

The normal use of dyes in sensitizing media comprising photoconductors to visible light, as described in the aforementioned copending U.S. application, preferably involves immersion of the medium in a solution of the selected dye. For example, the medium is immersed in a solution of the dye at a concentration of about 0.1 percent to 2.0 percent for a period of one to two minutes. The resulting dye-sensitized media absorb substantial amounts of visible light and are thus not suitable in the present reflex process since the whole medium would be activated. The present media can be similarly prepared by merely cutting short the time of immersion of the media at the same concentration of dye. For example, time periods of from about a few seconds up to ten seconds can be used. For the present media, however, it is preferred to use more dilute concentrations of the dye coupled with short periods of immersion. For example, concentrations of 0.01 percent dye in solvent for an immersion period of up to about 20 seconds gives media which provide excellent reflex prints. As previously stated, the optimum system for any given dye, or photoconductor, can be determined by routine testing at various levels of dye in the selected medium.

The results of such testing will show that, in general, the optimum concentration of dye in the present media is significantly lower than that required for direct image formation, i.e. for optimum sensitization of the medium to incident light. For example, some such dyes are normally employed at concentrations to yield an optical density over background of about 0.8 for direct image formation, but give optimum results in the present in-

vention at concentrations that yield an optical density above background of about 0.08.

For the purpose of the test, the medium is dye treated by the selected conditions and then exposed to visible light of wavelength longer than that to which the photoconductor is sensitive and preferably to light of wavelength range corresponding to the absorption of the dye. 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 a qualitative measurement of the percentage absorption of the exposing light.

While it has been known to use smaller quantities of dye sensitizers than normal in silver halide reflex processes, the reason is normally to lower speed of the silver halide emulsion so that longer exposures are required. Thus, better control can be achieved. On the other hand, the smaller than normal amounts of dye used in the photoconductive media described herein are used to preserve the high reflectivities of the media.

In general, it is preferred to use the best sensitizing dye available for the particular photoconductor, since very small quantities can be used to absorb the required amounts of radiation without destroying the good reflectivity of the medium.

Irradiation sources which are useful in this invention include any activating electromagnetic radiation which will provide the required light, i.e. visible light having a wavelength of from 400 to 700 millimicrons. One convenient source is a tungsten light source.

The inert carrier sheet upon which the photoconductor and dyes of this invention are deposited comprises any suitable light-transmissive backing of sufficient strength and durability to satisfactorily serve as a reproduction carrier. The carrier sheet may be in any form such as, for example, sheets, ribbons, rolls, etc. This sheet may be made of any suitable materials such as rag content paper, pulp paper, plastics such as, for example, polyethylene terephthalate (Mylar) and cellulose-acetate, cloth, metallic foil and glass. The preferred form of the carrier sheet is a thin sheet which is flexible and durable, and permits light to pass therethrough.

It is also useful to use a binder agent to bind the sensitizing dye useful in this invention and photosensitive materials to the carrier sheet. In general, these binders are translucent or transparent so as not to interfere with transmission of light therethrough. Preferred binder materials include gelatin or hydrophilic or hydrophobic organic materials such as resins. Examples of suitable resins are butadiene-styrene copolymer, poly(alkyl acrylates) such as poly-(methyl methacrylate), polyamides, polyvinyl acetate, polyvinyl alcohol and polyvinylpyrrolidone.

The photoconductive medium should be conditioned by storing it in the dark before exposure, or by other equivalent techniques. Such conditioning is generally conducted from one to twenty-four hours. After conditioning, the photoconductor is not exposed to light prior to its exposure to activating radiation for recording an image pattern.

The period of exposure will depend upon the intensity of the light source, particular photoconductor, the type and amount of catalyst, if any, and like factors known to the art. In general, however, the exposure may vary from about one second to several minutes. A

period of about 8-10 seconds with commercially available reflex sources is most desirable and can be easily attained by routine experimentation.

Image-forming materials which are useful in this invention are those such as described in U.S. Pat. No. 3,152,903 and in copending application Ser. No. 199,211. 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, now U.S. Pat. No. 3,623,865, filed March 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.

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 as the image-forming materials.

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:

a. Reflex exposure of the photosensitive medium to a master (as hereindescribed) provided with a suitable light source;

b. Development of the reflex exposed medium provided with developing means and, if necessary, fixing means to remove the sensitizing dye;

c. 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 sensitizing dye.

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 (containing about 50 percent solids) is used to coat paper sheets.

A sheet of the coated paper is sensitized by dipping into a solution of 2-(p-dimethylaminostyryl)-4-methylthiazole methochloride in methanol (0.01 mg./ml. concentration) for a total of ten seconds immersion and the paper is then dried. The medium is sensitive to light extending to 630 millimicrons.

The medium is then superposed on a master and light exposed to a source of visible light having substantially no ultraviolet light present through the medium on a Verifax machine for three seconds after which the exposed print is dipped into a saturated solution of silver nitrate in methanol and then in a solution 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 seconds in an aqueous fixing solution of sodium thiosulfate and potassium sulfite and finally washed in running water. The fixing solution is of the following composition:

K ₂ SO ₄	100-300 g.
Na ₂ S ₂ O ₃ ·5H ₂ O	80-200 g.
Dispersing agent	1 ml.
Water to one liter	

The negative is then air dried. The medium is substantially colorless.

EXAMPLE 2

The procedure of Example 1 is repeated with the exception that the dye is added directly to the titanium dioxide by suspending the water insoluble photoconductor in a dilute solution of the dye and the photosensitive medium is prepared from the dye-sensitized photoconductor. Similar results are obtained.

EXAMPLE 3

The procedure of Example 1 is repeated using a mixture of the Example 1 dye with 1',3-diethylthia-4'-carbocyanine chloride with similar results. The medium showed sensitization from 400 to 750 millimicrons.

EXAMPLE 4

The procedure of Example 1 is repeated using as the dye 2-(p-dimethylaminostyryl)-3,5-dimethylthiadiazolium nitrate with similar results.

EXAMPLE 5

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. Four additional positive prints of good contrast are obtained by repeating the procedure of Example 1 with the same negative print as the master.

EXAMPLE 6

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

The same effect can be obtained by using doping agents in lieu of the afore-mentioned dyes. The doping agents extend the spectral sensitivity of the photoconductor to light of longer wavelength as do the dyes and, when doping agents are employed, the same general considerations mentioned herein in connection with dye-sensitizing apply equally well to the use of doping agents, of which the preferred is chromium ions. The methods of incorporating the doping agent into the photoconductors are well-known to those skilled in the art and do not require extensive elaboration here.

EXAMPLE 8

The procedure of Example 1 is repeated with a medium comprising titanium dioxide doped with chromic ions in lieu of the dye mentioned therein.

After an exposure time of 60 seconds, a reflex print copy of a master is obtained.

What is claimed is:

1. A method of making a reflex copy from a master which comprises superposing a photosensitive medium adjacent to the surface of the master to be copied and exposing said master through said medium to visible light containing substantially no ultraviolet light, the photosensitive medium comprising a highly reflecting titanium dioxide photoconductor slightly dye sensitized to said visible light, the photoconductor being rendered chemically reducing upon appreciable absorption of visible light, the sensitization of said medium being insufficient to permit absorption of more than about 15% of said visible light by the medium as it passes from the light source through said medium, and thereafter contacting said medium with a physical developer.

2. A method of claim 1 wherein the medium comprises the photoconductor in a binder therefor.

3. A method of claim 2 wherein said dye is selected from the group consisting of cyanine dyes, dicarbocyanine dyes, carbocyanine dyes and hemicyanine dyes.

4. A method of claim 3 wherein said photoconductor has a diffuse reflectivity of at least about 80%.

5. A method of claim 4 wherein said physical developer contains a metallic ion which has at least the oxidizing power of cupric ion.

6. A process of claim 5 wherein said metallic ion comprises silver ion.

7. A method of claim 6 wherein said dye is a member selected from the group consisting of 2-(p-dimethylaminostyryl)-4-methylthiazole methochloride, 1',3-diethylthia-4'-carbocyanine chloride, 2-(p-dimethylaminostyryl)-3,5-dimethylthiadiazolium nitrate.

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