

1

3,700,449

PHYSICAL DEVELOPMENT OF A THIN REVERSIBLY ACTIVATABLE PHOTOCONDUCTOR ELEMENT HAVING A RESINOUS BARRIER LAYER

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19 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a photographic imaging medium comprising a substrate, a reversibly activatable photoconductor layer preferably having a thickness of less than about 2 microns, and a water or alcohol soluble, transparent barrier layer having a low permeability to oxygen over said radiation activatable photoconductor layer. The photographic imaging medium is characterized by the barrier layer which substantially prolongs decay time of a latent image stored in the photoconductor which latent image has been formed by exposure to a source of activating radiation. Prolonged decay time is believed to be due to the barrier layer preventing mass transport of oxygen from the atmosphere to the photoconductor.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a photographic imaging media comprising a reversibly activatable photoconductor, and more particularly, to a means for prolonging decay time of a latent image stored in said photoconductor.

(2) Description of the prior art

Image storage media comprising radiation activatable photoconductors such as titanium dioxide are described in British Pat. No. 1,043,250 and in commonly-assigned copending U.S. patent application Ser. No. 744,661 filed July 15, 1968, now abandoned. In the aforementioned application, a radiation activatable titanium dioxide layer functions as a photoconductive component of the media and exposure of said media to activating means such as radiant energy, electron beams of the like results in the storage of a reversible latent image pattern therein. Subsequent to exposure, the latent image begins to decay with the result that the reversible latent image pattern exists for finite but limited time during which said pattern can be converted to an irreversible form and read-out visually by contacting said latent image with a suitable image forming material such as a chemical redox system.

As noted above, it is known in the art that following exposure to a source of activating radiation, a latent image exists in a photoconductor for a finite time, but gradually fades through a process known as decay. The period that the latent image exists may vary from a few seconds to a few hours dependent upon various factors such as the composition and thickness of the photoconductor layer in which it is stored. The problem is particularly acute in thin layers—i.e., about 2 microns or less such as are provided in the preparation of lithographic plates.

Because of the decay of a photoconductor, it is desirable to develop the exposed photoconductive layer before substantial decay takes place and preferably, development should take place as soon as possible following exposure of the photographic imaging medium to the source of activating radiation in order to obtain a developed image of desired image density. Since it is not always pos-

2

sible, or from a processing standpoint, practical to immediately develop an exposed photographic imaging medium it is desirable to provide an imaging medium where the decay time is substantially prolonged. This is particularly desirable in the preparation of lithographic plates where a period in excess of two hours may pass between exposure and development.

SUMMARY OF THE INVENTION

It is believed that mass transport of oxygen from the atmosphere to a reversibly activatable photoconductor is a significant rate-controlling factor in the decay of a latent image stored in said photoconductor and prevention of mass transport of oxygen to said photoconductor substantially retards the decay time of the stored latent image. In accordance with a preferred embodiment of the invention a substantially transparent, water or alcohol soluble, barrier layer having a low permeability to oxygen is placed over the photoconductor layer to retard the rate of decay without affecting the photographic properties of the photographic imaging medium and which provides the additional advantages of decreased moisture sensitivity and improved processing characteristics. Accordingly, in one embodiment of the invention, a photographic imaging medium is provided comprising a substrate, a reversibly activatable photoconductor layer preferably having a thickness of less than about 2 microns, and a water soluble, oxygen impermeable, substantially transparent coating over said reversibly activatable photoconductor layer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The reversibly activatable photoconductors preferred in this invention are metal containing photoconductors. A preferred group of such photoconductors are inorganic materials such as the compounds of a metal and a non-metallic element of Group VI-A of the Periodic Table, e.g. oxides such as zinc oxide, titanium dioxide, zirconium dioxide, germanium dioxide, and indium trioxide; metal sulfides such as cadmium sulfide (CdS), zinc sulfide (ZnS), and tin disulfide (SnS); and metal selenides such as cadmium selenide (CdSe). Metal oxides are preferred photoconductors of this group; and titanium dioxide is a preferred metal oxide because of its sensitivity, availability, and color. Titanium dioxide which has an average particle size less than about 250 millimicrons and which has been treated in an oxidizing atmosphere at a temperature between about 200° C. and 950° C. for from about 0.5 hour to about 30 hours is especially preferred, and more especially that titanium dioxide produced by high temperature pyrolysis of a titanium halide.

The photoconductors present in the imaging media of this invention may be sensitized to visible and other wave lengths of light by foreign ion doping, addition of fluorescent materials, and/or by means of sensitizing dyes. Dyes useful for sensitizing the photoconductors of this invention include, for example, the cyanine dyes, the carbocyanine dyes, the carbocyanine dyes, and the hemicyanine dyes. Additional dyes which are useful for sensitizing the photosensitive medium of this invention are the cyanine dyes described on pp. 37-429 in "The Theory of Photographic Process," by C. E. Kenneth Mees, published by McMillan Company in 1952. Other useful dyes include those known to the art as triphenylmethane dyes, such as crystal violet and basic Fuchsin, diphenylmethane dyes such as Auromaine O, and Xanthene dyes such as Rhodamine B.

The photoconductors are usually dispersed as finely-divided particles in a binder which is preferably chosen to have a high index of refraction approaching that of the particles dispersed therein. Gelatin, the commercially available "Rhoplex" acrylates, acid-soluble acrylics, and

styrene-butadiene resins have all been employed in the art as binder materials. In these coatings the pigment to binder ratio may be between 1:4 and 16:1 and it is preferably between 2:1 and 12:1. In coatings containing a given weight of pigment, optimum transparency is observed, surprisingly, when the pigment: binder ratio is about 6:1 by weight. The addition of further binder, although "diluting" the pigment in the coating, increase the opacity of the coating. The particle size of the photosensitive semiconductor is preferably about 300 millimicrons or less in average diameter since films made using this particle size have much improved transparency.

In the preferred embodiments of this invention, the photoconductor layer has a maximum thickness of 2 microns as it is thin layers of this nature where decay time is a serious problem. These thin layers are frequently employed in the preparation of lithographic plates where, for formation of large plates, several exposures are required. Consequently, several hours may transpire between the first exposure and development thereby resulting in significant decay and poor image quality.

The photoconductor layer is preferably disposed over an inert carrier sheet or substrate which may be transparent or opaque. Any suitable backing of sufficient strength and durability to satisfactorily serve as a reproduction carrier may be used. The carrier sheet may be in any form such as, for example, sheets, ribbons, rolls and the like. This substrate may be made of any suitable material such as wood or rag content paper, or pulp paper; plastic such as for example, polyethylene terephthalate (Mylar) and cellulose acetate; cloth; metallic foil; and glass. The preferred form of the substrate is a thin opaque sheet which is flexible and durable and most preferably a metallic sheet is used where the formation of lithographic plates is desired.

The photoconductor layer of the photograph imaging medium is coated with a water or alcohol soluble, oxygen impermeable, substantially transparent barrier layer. The barrier layer should be water or alcohol permeable so that it will be readily permeated by an aqueous or alcoholic solution of developer or a water rinse during subsequent processing. This allows for contact of the developer with the latent image stored in the photoconductor layer, thus permitting formation of a visible image. The layer also desirably has a low permeability to oxygen as it is believed that the mass transport of oxygen from the atmosphere to the photoconductor is responsible for rapid decay of the latent image. Finally, the barrier should be optically transparent to permit imaging of the photographic medium by suitable activating radiation.

The thickness of the barrier layer is not critical to the present invention, but to obtain maximum transparency, the thickness of the barrier layer should be sufficient to completely cover any photoconductor particles and to thereby form a smooth surface on the copy medium. The barrier layer is not photosensitive and comprises photochemically inert materials which are not retained on an image bearing print and which are removed during the developing operation.

Typical materials that may be used as the barrier layer for the photographic imaging media include, for purposes of illustration, dextrine, water soluble salts of the group consisting of pectic acid and algenic acid, water soluble cellulose ether, water soluble salts of carboxy alkyl cellulose, water soluble salts of carboxy alkyl starch, water soluble caseinate, polyvinyl alcohol, polyvinylpyrrolidone, various polyacrylamides, water soluble salts of polyacrylic acid, starch, ethylene oxide polymers and the like. Other water soluble coating materials would of course be obvious to those skilled in the art. Polyvinyl alcohol is particularly preferred because of its high degree of oxygen impermeability as taught in "Water-Soluble Resins," 2nd edition, Reinhold Book Corp., 1962, p. 17, incorporated herein by reference.

A latent image is formed in the photographic imaging

media of the invention by exposure to a source of activating radiation such as actinic light. The period of exposure will depend upon the intensity of the light source, the particular imaging material, particular photoconductor, the type and amount of catalyst, if any, and like factors known to the art. In general, exposure may be from about 0.1 second to several minutes. Following exposure, the photographic imaging media may be developed or stored for a period of time such as two hours and frequently ten hours or longer dependent upon the particular barrier layer applied to the photoconductor layer. This is in sharp contrast to photographic imaging media of the prior art where development preferably is initiated immediately following exposure to the source of activating radiation.

Image forming materials or developers which are useful in this invention include those described in U.S. Pat. 3,152,903 incorporated herein by reference, and in the above noted copending application Ser. No. 744,661. 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 the reducible metal ions having at least the oxidizing power of cupric ion and include such metal 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. 3,623,865, filed in the name of L. Case, and the like.

The reducing agent component of the image forming materials of this invention include organic compounds such as the oxalates, formates, substituted and unsubstituted hydroxylamines, substituted and unsubstituted hydrazines, ascorbic acid, aminophenols, and the dihydric phenols. Additional reducing agents include polyvinylpyrrolidone and alkali and alkaline earth metal oxalates and formates. Suitable reducing compounds include, hydroquinone or derivatives thereof, o- and p-aminophenyl, p-methyl aminophenol sulphate, p-hydroxyphenyl glycine, o- and p-phenylene diamine, and 1-phenyl-3-pyrazolidone.

In addition to the above, as is known in the art, 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. Additional stabilizing and fixing steps such as known to the art may also be added to the process of the invention in order to increase the life and permanence of a final print.

A better understanding of the present invention and many of its advantages will be had by reference to the following examples given for purposes of illustration.

EXAMPLE 1

A substrate is provided comprising a number 1100 aluminum alloy 9 mils in thickness and mildly anodized in 3% ammonium tartrate at 6 volts and 12 volts. The substrate is roll-coated with a light sensitive layer comprising an aqueous mixture of a photoconductor and binder containing approximately 15% solids and having a pigment/binder ratio of 6:1. The photoconductor is a commercially available titanium dioxide having a mean diameter of 0.03 micron. The binder comprises polyvinyl alcohol. The layer applied has a thickness of about 0.1 mil. Additives which may optionally be present in the light sensitive layer include wetting agents and dispersants which aid in preventing agglomeration of the photoconductor particles.

5

The so prepared photographic imaging medium was coated with polyvinyl alcohol using a Gardiner coater and a 6" Bird applicator providing a wet film thickness of approximately 1.5 mils. A 12.6% solution of polyvinyl alcohol was used to form a coating, though considerably lower concentrations of polyvinyl alcohol are also effective. After coating, hot water is circulated beneath the coater base to speed up the film forming process.

The photographic imaging medium so prepared was exposed image-wise in a vacuum frame using a 650 watt G.E. Uniflood lamp at a distance of 30 inches. Exposure time ranged from approximately 15 to 45 seconds, several exposures being made on different portions of a single plate, so that various decay times could be compared under identical processing conditions.

Following exposure, the photographic imaging medium was allowed to stand for 12 hours and then immersed in a 0.1 N silver nitrate solution and agitated for about 150 seconds. Thereafter, the photographic imaging medium was immersed in a developer comprising 25 grams of Metol dissolved in one liter of water having pH adjusted to 2.0 by the addition of phosphoric acid. The medium was allowed to stand in the developer for about 2 minutes. Thereafter it was washed, wiped and left to dry. A heavy black image was formed on the photographic imaging medium which could not be removed by Scotch brand plastic tape.

It should be noted that though both the binder and barrier coating are polyvinyl alcohol, only the barrier is dissolved during processing as it is removed with agitation and rubbing. The binder is left substantially intact as it is not exposed to the developer for a time sufficient to cause solvation and is not rubbed from the substrate.

EXAMPLE 2

The procedure of Example 1 was twice repeated, but the polyvinyl alcohol over-coat was omitted. One sample was allowed to stand one minute in air and the second allowed to stand for twelve hours prior to development. No photographic image was obtained in either sample.

EXAMPLE 3

The procedure of Example 1 was repeated omitting the over-coat of polyvinyl alcohol and developing the exposed photographic imaging medium immediately after exposure. A heavy, black image was obtained.

EXAMPLE 4

The procedure of Example 1 was repeated using a developer comprising approximately 50 grams of citric acid monohydrate and about 55 grams of the trisodium salt of nitrilo-triacetic acid in one liter of water. The pH of the solution was adjusted to 3.4 with citric acid and 9 grams of Metol were added. A heavy black image was obtained.

The invention herein disclosed is especially useful for photographic imaging media having relatively thin layers of photoconductor. These imaging media typically have a metallic support layer and are useful as printing plates, name plates in the formation of printed circuits and the like. Such photographic imaging media are disclosed in co-pending U.S. application 744,631, filed July 15, 1968, now abandoned.

What is claimed is:

1. A photographic imaging medium comprising a substrate, a layer of a reversibly activatable photoconductor thereon, and a transparent, water or alcohol permeable resinous, barrier layer having a low permeability to oxygen disposed over said photoconductor layer and where the layer of photoconductor has a maximum thickness of about two microns.

2. A medium as in claim 1 where said photoconductor is a compound of a metal with an element of Group VI-A of the Periodic Table.

6

3. A medium as in claim 1 where said substrate is a conductive substrate.

4. A medium as in claim 1 where the substrate is aluminum.

5. A medium as in claim 1 where said photoconductor is zinc oxide or titanium dioxide.

6. A medium as in claim 1 where said photoconductor is dispersed in a binder.

7. A medium as in claim 6 where the ratio of photoconductor to binder by weight is about 6:1.

8. A medium as in claim 1 where said photoconductor is titanium dioxide on an opaque support.

9. A medium as in claim 8 where the support is aluminum.

10. A medium as in claim 1 where the barrier layer is polyvinyl alcohol.

11. In a photographic process comprising at least the steps of exposing to activating radiation a photographic medium comprising a substrate and a reversibly-activatable photoconductor layer thereon having a maximum thickness of about two microns, to thereby form a latent image, and subsequently contacting said medium with a solution containing reducible metal ions and a solution containing a reducing agent for said reducible metal ions, wherein said latent image is developed, and wherein the medium is exposed to an oxygen-containing atmosphere for a period of at least two hours subsequent to exposure but prior to contact with said solution of reducible metal ions, the improvement comprising:

disposing a layer of a water or alcohol permeable, transparent, resinous, barrier layer having a low permeability to oxygen over said photoconductor layer to thereby prolong the decay time of said latent image stored in said photographic imaging medium after exposure, and maintaining the solution containing reducible metal ions and the solution containing a reducing agent in contact with said medium for a time sufficient for penetration of said barrier layer.

12. An improvement of claim 11 wherein said photoconductor comprises a metal oxide.

13. An improvement of claim 12 wherein said photoconductor is dispersed in a resinous binder.

14. An improvement of claim 13 wherein said substrate is opaque.

15. An improvement of claim 14 wherein said substrate comprises aluminum.

16. An improvement of claim 15 wherein said photoconductor comprises titanium dioxide.

17. An improvement of claim 16 wherein said barrier layer comprises a water-soluble resin.

18. An improvement of claim 11 wherein said water-soluble resin comprises polyvinyl alcohol.

19. An improvement of claim 18 wherein said photoconductor comprises titanium dioxide.

References Cited

UNITED STATES PATENTS

3,140,174	7/1964	Clark	96—1.8
3,380,823	4/1968	Gold	96—67 X
3,494,766	2/1970	Iwai et al.	96—1.8
3,060,026	10/1962	Heiart	96—28

OTHER REFERENCES

"A Review of 'Electrofax' Behavior" by James A. Amick, in RCA Review, December 1959, pp. 757-58 and 760-61.

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