United States Patent

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[15] **3,658,540**

[45] **Apr. 25, 1972**

[54] **PRODUCTION OF PHOTOGRAPHIC MATERIALS WITH PHOTOSENSITIVE COMPOUNDS OTHER THAN SILVER HALIDES**

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[22] Filed: **Sept. 12, 1967**

[21] Appl. No.: **667,080**

[30] **Foreign Application Priority Data**

Dec. 31, 1966 Bulgaria.....................................1567

[52] **U.S. Cl.**...**96/88,** 96/48 PD

[51] **Int. Cl.**..**G03c 1/00**

[58] **Field of Search** 96/48, 67; 117/36, 8, 36.9; 250/65, 65.1

[56] **References Cited**

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[57] **ABSTRACT**

A method of making a photographic material in which a photosensitive semiconductor layer is applied to the substrate and a thin, radiation-permeable layer is deposited thereon to stabilize the image formed upon radiation of the material.

5 Claims, No Drawings

PRODUCTION OF PHOTOGRAPHIC MATERIALS WITH PHOTOSENSITIVE COMPOUNDS OTHER THAN SILVER HALIDES

The invention relates to a process for the production of photographic materials on the basis of photosensitive compounds other than a silver halide, which photographic material is capable of yielding on exposure to radiation a direct positive latent image capable of intensification by physical development.

Conventional methods make use of photographic emulsions of silver halides; a number of methods are also known for the preparation of light-sensitive materials based on optically homogeneous thin layers produced by the evaporation in vacuum of certain compounds, the layers of which decompose on exposure. Attempts have been made to prepare such photographic materials in the form of a layer of a silver halide, which forms on exposure either a negative or a positive latent image. However, these materials have very limited spectral sensitivity as determined by the absorption spectra of the silver halide used. The spectral sensitivity of such layers, when sensitized with suitable dyes, can be extended so as to cover the spectral photoresponse of conventional photographic emulsions, which spectra do not exceed 1.3 to 1.4 microns in the infrared region.

It is known that thin layers of photodecomposing compounds such as halides, sulphides, selenides, antimonides yield on exposure a visible image. The image obtained in such non-silver compounds, however, is not capable of being intensified by means of a developer, because the effective speed of these materials is very low. Until now the production of photographic materials using compounds nonsilver photosensitive compounds which form directly a positive latent image capable of intensification by development has not been achieved.

It is a common feature of photosensitive substances, that on exposure fundamental entities of the crystal lattice are brought into a state of excitation, corresponding to the generation of photoelectrons and electron holes. These entities however return quickly to their ground whereupon a complete restoration of the initial condition of the crystal takes place. It has been practically impossible until now to use such reversible or stable photoconductors for the production of photographic media inasmuch as the photographic process demands a finite irreversible decomposition of the photosensitive substance.

It is an object of the present invention to provide means for the realization of a detectable photodecomposition of photosensitive compounds and semiconductors intrinsically stable on exposure, thus making possible the use of such substance in the production of photographic materials.

It is therefore an object of the present invention to provide a method of producing photographic materials on the basis of photosensitive compounds other than a silver halide, thus making possible the use of photosensitive substances or combinations thereof, the intrinsic sensitivity of which lies in different regions of the spectrum, and more particularly in the far-infrared region beyond 1.3 microns.

It is, further, an object of the present invention to provide a method for the production of photographic materials which yield on exposure a direct positive developable latent image.

According to the present invention, there is provided a process for preparing photographic material capable of, yielding on imagewise exposure to radiation a direct positive developable image which comprises the steps of depositing onto a carrier base first a thin layer of one or of several photosensitive compounds other than silver halide or semiconductors and then depositing thereon in direct contact with said first layer, an additional extremely thin radiation-permeable layer of metal or other material capable of reacting with the photosensitive substance when the latter is actuated by radiation.

Usually the first layer of the material is built up of one or of several photosensitive substances other than silver halides, decomposing on exposure, or stable photoconductors, consisting of at least two elements, such as halides, oxides, selenides, sulfides and tellurides of Pb, of Tl and of metals of Group I or II of the Period Table of the Elements, or intermetallic compounds of the elements of Group III or Group V of the Periodic Table, and more particularly the halides of Cu, Pb, Tl, the oxides of Cd, Cu, Zn as well as GaAs, GaSb, CdTe, InSb, PbS; the layer is deposited to a thickness between 0.1 and 10 microns, and more particularly between 0.3 and 1 microns.

It is essential, that in the photographic material produced in accordance with this invention the two layers should be appropriately selected, so that the metal on top of the photosensitive substance is capable of reacting chemically with the primary product formed when electron holes are generated on exposure to radiation in said photosensitive layer, thereby permanently trapping these holes.

It has now been established, that when such a reaction occurs, the electron holes produced by photoexcilation are bound irreversibly to the metal, and their recombination with electrons is restricted. The equilibrium is disturbed and photodecomposition can proceed to a measurable extent even in compounds which generally are stable photoconductors. On account of this reaction the metal film deposited onto the photosensitive layer is correspondingly consumed in the exposed areas, and as a consequence a positive latent image of the object is directly obtained.

This entirely new and unexpected discovery provides a process for producing photographic materials from a large number of known photosensitive compounds, the intrinsic photosensitivity of which covers different regions of the spectrum from the ultraviolet to the far infrared.

Since as the present invention is concerned with photosensitive substances other than silver halides, conventional chemical developers cannot normally be used for processing these materials. Usual physical developers, however, some of them illustrated in the following examples can be successfully employed for the intensification of the invisible latent image produced on exposure.

Therefore it is preferred that metal used in the top (metal) layer is selected so as to catalyze the deposition onto it of silver from an unstable, slowly decomposing solution of a silver salt. In such case, the photographic material when processed in a conventional physical developer, without any prior exposure to actinic radiation, turns black.

Depending on the metal chosen, for example Ag, Bi, Cd, Cr, Cu, Fe, In, Pb, Se, Te and more particularly Ag, Bi, In and Pb, the amount of metal is adjusted between 10^{-8} and 10^{-5}g/cm^2 and more particularly about 10^{-7} g/cm^2, so that it can effectively initiate physical development and secure desired maximal density and contrast of the image obtained after exposure and development.

It is possible to make use of stable photosensitive semiconductors as the a method is provided for the production of photographic photosensitive substances. Such semiconductors consist of compounds of at least two elements and if they have a band gap not wider than 1 eV, a spectral sensitivity of the material in the far infrared spectrum beyond 1.3 microns is obtained. Such semiconductors include GaSb, InSb and PbS, the metal layer being of Ag, In, Bi, Pb or another metal corresponding to an electronegative component of the semiconductor.

The invention described makes replacement of possible to replace the silver halides in photographic materials by other much cheaper photosensitive substances.

Another advantage of the invention is the provision of different photosensitive compounds with specific intrinsic sensitivity in the different regions of the spectrum by avoiding the spectral sensitizing of photographic materials with dyes; for example layers of cadmium, copper and thallium halides are sensitive in the ultraviolet, lead halides are sensitive in the middle of the visible spectrum, gallium antimonide, indium antimonide, and lead sulphide are sensitive in the far infrared region. By the suitable combination of layers deposited one upon the other, or a mixture of appropriate compounds, the sensitivity of the photographic materials can cover an arbitrarily predetermined region of the spectrum.

The basic photosensitive layer, not containing silver halides, does not decompose to a measurable extent on illumination (irradiation), if an additional layer of metal has not been deposited upon it. Therefore the new photographic medium has also the advantage, not previously present, that the production of the basic layers of photosensitive substances (as well as any doping of them with suitable additives enhancing their sensitivity) can be performed in diffuse daylight. The treatment and storing of these layers in the dark becomes necessary only after the deposition onto them of the thin metal layer, which operation for some purposes can be done immediately prior to exposure.

It has now been established that after development the photoresponse of the material becomes negligible. Therefore the new material has still another advantage, not present previously, to the effect that the process of fixing is no longer necessary. In this way, if the starting photosensitive layer is thin and sufficiently transparent for visible radiation, which is usually the case, the image obtained after development is directly used for observation or projection.

The following examples are illustrations of the invention.

EXAMPLES

1. A layer of lead sulphide **0.1** to **1** microns thick is deposited onto a glass carrier. The said layer is further sensitized by heating in air at a temperature of about **500°** C, thus obtaining an enhanced photoconductivity in the infrared region of the spectrum. Though sensitized, the layer in its present state is completely stable when exposed to diffuse daylight and can be handled and stored by light. Now 10^{-7}g/cm^2 of lead or of silver is deposited on this sensitized layer. The resultant product is a photographic material yielding a positive latent image even when exposed to infrared radiation with wavelength up to **3** microns. For the development of the latent image a known physical developer is used, consisting for example, of the following ingredients.

Solution A		Solution B	
metal	8.3 g	Silver nitrate	30 g
citric acid	8.3 g	water to make	45 ml
acetic acid	42 g		
gelatin	6.7 g		
water to make	1 l		

Before use **50** ml of solution A is mixed with **1** ml of solution B.

2. A thin photosensitive layer of InSb about **1** micron thick is quite stable when exposed to diffuse daylight. The deposition of approximately 10^{-7}g/cm^2 of In upon this layer produces a photographic material sensitive to an infrared radiation with wavelength up to about **7** microns. On exposure a positive latent image is formed, which can be developed using the physical developer indicated in Example **1**.

3. A material sensitive to the visible region of the spectrum is produced on the deposition onto a glass carrier of a layer from **0.1** to **1** micron thick of PbI2 or TiI. These layers are completely stable by diffuse daylight. Either immediately or before use, 10^{-7}g/cm^2 of Ag is deposited upon each of them. Now the layers prepared in this way undergo on exposure a permanent change — a developable positive image being formed on them. For the development of photomaterials of thallium iodide the developer indicated in Example **1** may be used. With lead iodide better results are obtained with following developer.

Solution A		Solution B	
sodium sulphite, cryst.	180 g	sodium sulphite, cryst.	20 g
silver nitrate 10% p-p	75 ml	p-phenylendiamine	20 g
water to make	1 l	gelatine	4 g
		water to make	1 l

Before use mix **35** ml of solution A and **10** ml of solution B.

WHAT I CLAIM IS:

1. A method of making a photographic material, comprising the steps of depositing upon a carrier a layer of a normally stable and nonreactive photosensitive compound other than a silver halide; and depositing a radiation- permeable layer of a metal upon said compound and capable of reacting therewith upon photosensitization of said compound to stabilize an image formed by said compound.

2. The method defined in claim **1** wherein said compound is selected from the group which consists of the halides, oxides, selenides, sulphides, and tellurides of lead, tellurium metals of groups I and II of the periodic table, intermetallic compounds and the elements of group III and group V of the periodic table, said layer of said compound having a thickness between **0.1** and **10** microns.

3. The method defined in claim **2** wherein said metal is selected from the group which consists of silver, bismuth, cadmium, chromium, copper, iron, indium, lead, selenium and tellurium and is applied in a layer in an amount between 10^{-8} and 10^{-5} grams per cm^2.

4. The method defined in claim **3** wherein said layer of said compound is provided in a thickness between **0.3** and **1** micron and said layer of metal is provided in an amount of about 10^{-7} grams per cm^2.

5. The method defined in claim **1** wherein said compound consists of at least two elements with a band gap greater than **1** electron volt formed and selected from the group which consists of cadmium antimonide, indium antimonide and lead sulphides, said layer of metal being composed of silver, bismuth, indium or lead.

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