

United States Patent

Bredoux et al.

[15] 3,661,574

[45] May 9, 1972

[54] **PHOTOGRAPHIC PROCESS WITH AN AMINE METAVANADATE**

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[22] Filed: **Aug. 18, 1969**

[21] Appl. No.: **851,101**

[30] **Foreign Application Priority Data**

Dec. 18, 1968 France.....178794

[52] U.S. Cl.....**96/35, 96/88**

[51] Int. Cl.....**G03c 5/00**

[58] Field of Search96/88, 33, 67

[56] **References Cited**

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[57] **ABSTRACT**

There is described photosensitive elements which employ as the photosensitive component organic amine metavanadates and processes of producing photographic images and reliefs with these photosensitive elements.

12 Claims, No Drawings

A PHOTOGRAPHIC PROCESS WITH AN AMINE METAVANADATE

The present invention relates to photographic reproduction. In a particular aspect it relates to new photographic elements utilizing the photosensitivity of non-silver compounds, as well as to the use of these elements for producing photographic images.

Many non-silver photosensitive substances are known, and by exposing certain of these substances to lights of suitable wavelengths it has been possible to obtain photographic images. Processes of the electrophotographic type or processes based on the use of a photocrosslinkable polymer can be cited as examples. However, in order to be able to take advantage of the photosensitivity of a substance in a photographic process, it is desirable that it be possible, in certain cases, to intensify and to fix the image obtained. These problems, to the extent that they have not been solved, have reduced interest in many photosensitive substances, the photosensitivity of which, consequently, has remained a laboratory curiosity.

Among the chemical substances, the photosensitivity of which has been recognized but which have never found practical utility in photography, there can be mentioned vanadates of certain organic bases, especially vanadates of certain amines. Some of these compounds have been known for a long time. For example, according to Ditte, [Comptes Rendus 102, 1019 (1886)], by evaporating under vacuum a solution of vanadic anhydride, V_2O_5 , in an excess of methylamine, a colorless compound is obtained which spontaneously turns brown when cold. A combination of vanadic anhydride with ethylamine, which compound also displays this phenomenon of turning brown, can be prepared in like manner. Such compounds, however, have not found use in any practicable photographic applications.

It is an object of this invention to provide novel photosensitive elements with which direct-print images and relief images can be prepared.

It is a further object of this invention to provide a novel process for obtaining direct-print photographic images, and for intensifying and stabilizing photographic images obtained by this process.

It is another object of this invention to provide a novel process for the preparation of positive reliefs of hydrophilic colloids.

The above and other objects of this invention will become apparent from the further description of this invention which follows.

The photographic elements of this invention comprise a support coated with at least one photographic binder containing as the photosensitive compound, a metavanadate of an organic amine.

One process embodiment of this invention, for preparing direct-print images, comprises exposing a photographic element of the aforesaid type to ultraviolet radiation through a negative, and intensifying the image obtained by heating it, or by physically developing the image by contacting the element with a reducible salt, such as a silver salt, possibly with heating.

A second process embodiment of this invention, for forming positive relief images, comprises exposing to ultraviolet radiation through a negative, a photographic element of the aforesaid type, the photosensitive layer of which contains a hydrophilic colloid as the binding agent and a heterocyclic amine metavanadate as the photosensitive substance, and removing the exposed areas of the layer by washing the element with warm water, the unexposed areas adhering to the support.

The organic amine metavanadates that are used in the present invention result from the combination of vanadic anhydride with aliphatic amines, including cycloaliphatic amines, such as ethylenediamine, hexamethylenediamine, cyclohexylamine, etc., or with heterocyclic amines generally having 5 to 6 atoms in the nucleus, such as pyrrolidine,

piperidine, pyridine, morpholine, triethylenediamine, piperazine, N-methylamino-4-piperidine, etc. The metavanadates correspond to a general empirical formula $MNHVO_3$, wherein M represents the atoms necessary to complete an amine of the above-indicated type.

Metavanadates can be prepared only from amines having a pK_a greater than about 8. An amine such as acridine, the pK_a of which is 5.6, is not basic enough, and its combination with vanadic anhydride yields higher condensation products, which are much less photosensitive.

The following outline is given, as an example, for the preparation of piperidine metavanadate, $C_4H_{11}N \cdot HVO_3$, described by O. Baudisch and F. L. Gates in "Journal of the American Chemical Society", 56, 373, (1934). This procedure is equally applicable for preparation of other amine metavanadates. One gram of amorphous vanadium pentoxide (vanadic anhydride) is added to a hot solution of 5 grams of piperidine in 15 milliliters of water, and this mixture is kept boiling and under agitation until the oxide is completely dissolved. A greenish residue is separated by filtration, and a clear solution that is pale yellow in color is collected. The series of operations must be effected, if not in darkness, at least under artificial light, and in all cases protected from sunlight. By adding six volumes of acetone to the above solution a substance is precipitated that is allowed to stand for 1 or 2 hours, is filtered and is washed with acetone. In this way 2 grams (98percent) of pure piperidine metavanadate is collected, which is in the form of a white powder composed of colorless platelets. The product can be further purified, if desired, by dissolved in it in water and then re-precipitating it in acetone.

When kept in darkness and at ordinary temperature, the product is stable, but as soon as it is exposed directly to sunlight, it immediately turns brown and in a few seconds becomes completely black. Other photosensitive, amine metavanadates used in the invention also occur in the form of powders and behave in a like manner. The mechanism of this photochemical reaction is not understood fully. It is believed that it involves the photoreduction of pentavalent vanadium by radiation of wavelengths below 400 nm. However, we do not wish to be bound to any theoretical explanation as to the mechanism by which an image is formed.

According to the process of the invention for obtaining direct-print images, a photosensitive element is prepared by coating on a support a thin layer of a binder in which an amine metavanadate has been dispersed, e.g., a metavanadate of one of the above-cited amines. This layer is exposed to ultraviolet light, the wavelength of which can be between 160 and 390 nm., and there is obtained directly a brown, visible image in exposed areas.

Any of the film-forming substances that are commonly used for preparing photographic layers can be utilized as the binder, e.g., ethyl cellulose, polystyrene, polyvinyl alcohol and other vinyl polymers, etc. The photosensitivity of amine metavanadates remains unchanged, regardless of whether the substance is simply in a solid state or dispersed in a binder; nor does the nature of the binder modify the photosensitivity.

According to the present invention there are several procedures for intensifying the image obtained by exposure of the element to ultraviolet light.

According to one procedure for intensifying the image, the image is heated, e.g., by exposing it to a source of infrared radiation. A change of color is observed, and the image becomes black. This is most likely due to the brown image areas, which contain the products of the photoreduction of the amine metavanadate, selectively absorbing the infrared radiation; this absorption causing local elevations in temperature and an intensification of the brown tints. Thus, very contrasty images are obtained, which display a good maximum density.

It is obvious that if the heat source that is used does not produce a selective intensification of the image areas, the image and the background will be blackened indifferently. Moreover, as their analysis by thermogravimetry shows, amine metavanadates are sensitive to heat and begin to decompose at temperatures between about 100° C. and 150° C.

After such a thermal intensification treatment the image can be stabilized by a simple washing in water, which removes the unexposed compound.

A second procedure for intensifying these images utilizes the reducing properties that the compounds which result from the photoreduction of the exposed metavanadate display with respect to certain metal ions. For example, when the exposed element is immersed in an aqueous ammoniacal solution of a silver salt, such as silver nitrate, there is formed in the exposed areas of the element a black, silver image. This intensification treatment simultaneously stabilizes the image, since the unexposed amine metavanadate is dissolved in the aqueous ammoniacal medium in the form of a soluble silver salt.

A variation of this second procedure comprises placing the exposed element of the invention in contact with a receiving sheet containing an easily reducible organic salt of silver, such as silver behenate. The two sheets are heated while they are kept in contact with each other, a silver image is formed on the receiving sheet in areas in contact with exposed areas of the element. Thus, in this case, a process of chemical intensification by heat transfer is utilized.

According to the process of this invention for obtaining a positive relief image, a layer of a hydrophilic colloid, such as gelatin containing a heterocyclic amine metavanadate is coated on a subbed support. After exposure, as described above, to ultraviolet radiation, the element is washed in water. The colloid in exposed areas disaggregates and separates from the support. Inasmuch as the washing in water leaves only the unexposed areas, a relief image is obtained which is a positive copy of the original, and this clearly distinguishes the process of the invention from processes in which insolubilization is effected in exposed areas, as with, for example, bichromated gelatin. Only metavanadates of amines, the basic nitrogen atom of which is a heterocyclic nitrogen atom, are suitable for carrying out this process of the invention.

The relief image that is obtained can be made visible by dyeing before or after removal of the colloid from exposed areas.

The following examples further illustrate the invention.

EXAMPLE 1

2 gm. of piperidine metavanadate are dispersed in 20 cc. of a 2.5 percent alcoholic solution of ethylcellulose. This dispersion is coated onto a paper support (80 gm./m². bond paper) at 0.05 mm. thickness. The photosensitive layer is kept in darkness, and then is exposed through a continuous-tone negative original to ultraviolet light with a 125 W Mazda MAF lamp at a distance of 25 cm. A positive, brown image is obtained after 30 seconds. The density of the image can be increased by increasing the exposure time.

EXAMPLE 2

The procedure of Example 1 is repeated, replacing the piperidine metavanadate with morpholine metavanadate. Under the same conditions, a similar image is obtained.

EXAMPLE 3

The procedure of Example 1 is repeated, except that the piperidine metavanadate is replaced with pyrrolidine metavanadate and the photosensitive element is exposed for 8 minutes through a line-negative original under the same conditions as those indicated in Example 1. A brown, positive image is obtained which is then exposed to a source of infrared radiation by placing it for 15 seconds in a "Thermofax Assistant Model 380" thermographic machine (manufactured by Minnesota Mining Manufacturing Company). This treatment produces a very contrasty black image of good density. The image is stabilized by washing in water which dissolves the unexposed pyrrolidine metavanadate.

EXAMPLE 4

Under the same conditions as those described in Example 3, a photosensitive element is prepared and exposed, this time

utilizing cyclohexylammonium metavanadate as the photosensitive component. A brown image is obtained which is intensified, by heat treatment in the manner of Example 3, to a black image with good density.

EXAMPLE 5

Under the same conditions as those described in Example 1, a photosensitive element is prepared containing a layer of piperidine metavanadate. After exposure, the photosensitive element, containing a visible brown image, is treated in a 15 percent silver nitrate ammoniacal aqueous solution. In a few seconds, the brown image turns into a silver image. This treatment at the same time stabilizes the image, since the unexposed piperidine metavanadate dissolves in the ammoniacal medium.

EXAMPLE 6

Under the same conditions as those described in Example 3, a photosensitive element is prepared and exposed, and is then placed in contact with a receiving sheet containing a layer of silver behenate. The two sheets are then heated at 130° C. by passing them, for 20 seconds, through a "107 Office Model" photocopier (manufactured by Minnesota Mining Manufacturing Company). In this way a black silver image is obtained on the receiving sheet.

EXAMPLE 7

2 gm. of piperidine metavanadate are dissolved in 20 ml. of a 5 percent aqueous solution of gelatin. The above solution is coated at 0.05 mm. thickness, on a cellulose triacetate support subbed with gelatin. The element is exposed for 10 minutes, in contact with and through a screened-positive original, to the source of ultraviolet radiation described in Example 1. By exposing the element through the support, the time of exposure is reduced to 2 minutes. The exposure through the support makes possible a preferential absorption by the portion of the photosensitive layer that is in contact with the support. The exposed layer is then placed in an aqueous solution of a Pure Blue Diazol 6B dye (C.I. 24410). It is then washed with water at a temperature below 32° C. The exposed areas are removed leaving the unexposed areas in the form of a dyed relief.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A process for the preparation of photographic images which comprises imagewise exposing to ultraviolet radiation a support bearing a layer of a hydrophilic film-forming binder containing an organic amine metavanadate of an amine having a pKa of at least 8, to obtain an image in exposed areas of the layer, and intensifying and fixing the image thus obtained.

2. A process as defined in claim 1 wherein the image is intensified by heating it.

3. A process as defined in claim 2, wherein heating is effected by exposing the layer to infrared radiation.

4. A process as defined in claim 3 wherein fixing of the image is effected by washing the layer with water.

5. A process as defined in claim 1 wherein the image is intensified by immersing the layer in a solution of a reducible silver salt to form a silver image in exposed areas of the layer.

6. A process as defined in claim 5 wherein the solution is an ammoniacal solution of silver nitrate.

7. A process as defined in claim 1 wherein the image is intensified by contacting the layer with a receiving sheet containing a reducible organic silver salt and heating the layer and receiving sheet to form a silver image on the receiving sheet.

8. A process as defined in claim 7 wherein the reducible organic silver salt is silver behenate.

9. A process for the preparation of a positive relief image which comprises the steps of imagewise exposing to ultraviolet radiation an element which comprises a support bearing a

layer of a hydrophilic colloid containing a heterocyclic amine metavanadate of an amine having a pKa of at least 8, to degrade the colloid in exposed areas, and washing the element with water to remove the colloid from exposed areas of the element.

10. A process as defined in claim 9 wherein the hydrophilic

colloid is gelatin.

11. A process as defined in claim 10 wherein the support is translucent and exposure is through the support.

12. A process as defined in claim 10 wherein the heterocyclic amine metavanadate is piperidine metavanadate.

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