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3,687,668

**PALLADIUM IMAGES BY HYDROGEN
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No Drawing. Filed Oct. 7, 1970, Ser. No. 78,946

Int. Cl. G03c 5/24

U.S. Cl. 96-48

9 Claims

ABSTRACT OF THE DISCLOSURE

Visible palladium images may be formed by treating imagewise exposed photosensitive elements with palladium (II) ion, and subsequently forming palladium metal on such imagewise formed palladium nuclei by reduction with hydrogen. Further, a heavy metal may be imagewise deposited on these palladium images by the use of stable heavy metal physical developers such as nickel, cobalt, iron, palladium, platinum, chromium, copper, etc. Suitable photosensitive elements comprise titanium dioxide, zinc oxide, lead chromate, lead oxide, lead molybdate, or copper oxide. Titanium dioxide is preferred.

BACKGROUND OF THE INVENTION

This invention relates to a process for the physical development of photographic images on a radiation-sensitive element, comprising a radiation-sensitive, non-silver, metal salt or oxide, and in one aspect, to a method for the deposition of palladium metal on a titanium dioxide photosensitive element. This invention further relates to a method for the deposition of stable nickel images on a titanium dioxide photosensitive element which has been treated to produce an initial visible image of palladium metal.

The phenomenon of physical development, i.e., the deposition of metals from an external source of metal ions, has long been of interest to the photographic industry. A great deal of effort has been centered about the formulation of stable physical developers for the deposition of silver. Until recently, this research has been largely unsuccessful, with the lifetime of such developers being measured in hours. Relatively stable silver physical developers have recently been devised, such as those disclosed in Cole, U.S. Pat. 3,390,998, issued July 2, 1968, which employs a combination of ionic surfactants and organic antifogants.

Stable metal-hypophosphite physical developers are well established and have found particular utility in photographic systems wherein palladium nuclei are photolytically generated. However, attempts to catalytically decompose such developers with photolytically or otherwise produced silver nuclei have thus far been unsuccessful. At present, the primary obstacle appears to be the relative ineffectiveness of silver as a catalyst for decomposition of such stable metal-hypophosphite physical developers.

Methods are known for recording an image pattern wherein the image-producing agent forms the image solely on contact with activated portions of a copy medium. Typically, a titanium dioxide layer is employed which may be exposed and treated with silver nitrate to form a visible image.

The present invention relates to a means for producing a visible palladium image upon a photosensitive element, in such a manner as to avoid non-selective metal deposition, and affording the stability and cost advantages of non-silver physical developers.

It is an object of this invention to produce visible palladium images using an imagewise exposed radiation-

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sensitive, non-silver, metal salt or oxide. It is a further object of this invention to deposit metal from stable physical developer solutions in an imagewise distribution.

Still a further object of this invention is to form palladium photographic images on a titanium dioxide light-sensitive element, and to form these images in such a way as to render them catalytically active, at room temperature, with respect to stable physical developer baths containing hypophosphite as the reducing agent.

The photosensitive non-silver metal salts and oxides employed in this invention include such materials as titanium dioxide, zinc oxide, lead chromate, lead molybdate, lead oxide, copper oxide, and mixtures thereof. The preferred materials are titanium dioxide and zinc oxide. Suitable photosensitive elements may comprise a dispersion of photosensitive material such as titanium dioxide, in a hydrophilic binder such as gelatin, or a hydrophobic binder such as polyvinylacetate.

Alternatively photosensitive elements may be employed which have been prepared by the vacuum deposition of the appropriate photosensitive material, or, by the oxidation of metal containing surfaces such as of titanium metal or of organic titanium compounds.

One class of photosensitive elements of this invention comprise a support having coated thereupon a binder-free light-sensitive layer comprising titanium dioxide. The light-sensitive titanium dioxide layers which are employed in the practice of the invention described herein may be thin, abrasion resistant layers of titanium dioxide, deposited, without a binder, upon a support material by vacuum deposition techniques.

The coating operation may be accomplished by well-known vacuum deposition techniques, such as those described for vacuum depositing silver halide as in U.S. Pat. 1,970,496. Typically the support material is placed within a sealable enclosure along with titanium dioxide. Alternatively, metallic titanium can be used as a source of titanium dioxide by introducing oxygen into the vacuum system. The enclosure is sealed, the pressure reduced, and the temperature elevated, which combination of conditions produces the sublimation of titanium dioxide micro-crystals upon such support material.

An alternative process for the preparation of titanium dioxide photosensitive materials comprises depositing upon a suitable support, by vacuum deposition, a titanium metal film. To form radiation sensitive titanium dioxide, the titanium bearing film is heated to a temperature of from about 400° C. to about 900° C. for a suitable period of time; generally between one half hour and ten hours.

Materials containing chemically bound titanium which are suitable for forming radiation-sensitive titanium dioxide coatings include organic titanates such as hydrolyzable aliphatic esters of titanate acid, and the polymers formed by hydrolysis thereof. These materials include water-sensitive tetra-alkyl esters such as the tetraisopropyl-, tetra-butyl-, tetra-stearyl-, and tetrakis-(2-ethylhexyl)-titanates. These esters when applied to a moist substrate or when present on a substrate in the presence of atmospheric moisture, are readily hydrolyzed to form polymers on the substrates.

Still other titanate materials which can be used for the formation of radiation-sensitive titanium dioxide films include certain chelated titanate structures such as the ammonium salt of titanium lactate or titanium acetylacetonate. These chelated materials are more resistant to hydrolysis than are the tetra-alkyl esters, but can also be used for the formation of titanium dioxide films.

The organic titanium compounds mentioned are conveniently applied to a substrate in the form of thin films, if liquid or a solution, suitably by dipping, spraying, painting, or the like. The compounds are soluble in organic

solvents including alcohols such as isopropanol, hydrocarbons such as hexane, heptane and benzene, and halogenated solvents such as trichloroethylene or carbon tetrachloride. Upon heating, thin transparent films of titanium dioxide are produced.

Still another alternative method for the preparation of titanium dioxide, zinc oxide, copper oxide, lead oxide, lead chromate or lead molybdate light-sensitive elements, is to disperse the photosensitive material in a suitable binder, and apply it to a substrate by typical solvent evaporation techniques. Various colloids may be employed, either alone or in combination, as vehicles and binding agents. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like. Suitable hydrophobic binders include polyvinylacetate, polyvinylbutyral, and the like.

If desired, the titanium dioxide coatings may be protected with a thin transparent film to prevent damage to the titanium dioxide. Conventional plastic materials, such as polyacrylates, can be used to provide such a coating, but should remain permeable to the solutions which are used for physical development of the image in the underlying titanium dioxide film. Gelatin is particularly suited for such a purpose. However, no protective film would be required for a titanium dioxide photosensitive layer prepared by the method disclosed in copending application Ser. No. 636,016 of Kennard et al., filed May 4, 1967, now Pat. No. 3,547,635. The coating method taught therein, and briefly described above, produces extremely thin adherent and abrasion resistant layers of vacuum deposited titanium dioxide.

The described photographic layers and other layers of a photographic element employed in the practice of this invention can also contain, alone or in combination with hydrophilic water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds, such as latex form, and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described for example in Nottorf U.S. Pat. 3,142,568, issued July 28, 1964; White U.S. Pat. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. 3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. 3,220,844, issued Nov. 30, 1965; Ream et al. U.S. Pat. 3,287,289, issued Nov. 22, 1966; and Dykstra U.S. Pat. 3,411,911, issued Nov. 19, 1968; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates; those which have cross-linking sites which facilitate hardening or curing; and those having recurring sulfobetaine units as described in Dykstra Canadian Pat. 774,054.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetate) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal, and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

Any of the above methods may be employed in preparing the radiation-sensitive element which is to be treated according to the method of this invention. Typically, in the past, such elements have been exposed and treated with silver nitrate to form a visible image. In the present invention, the means for making an initial visible image

avoids the expense and various disadvantages of a silver nitrate system.

In the present invention, visible palladium images are formed by treating an imagewise exposed element with palladium ions, thereby forming an imagewise distribution of palladium nuclei, and subsequently forming palladium metal on such imagewise formed palladium nuclei by reduction with hydrogen. Palladium ions can be provided by contacting the imagewise exposed elements with a solution, e.g. an aqueous solution, of a palladium halide or other salt such as, for example, palladium chloride or potassium tetrachloropalladate. In addition to the thus formed visible palladium image, additional metal may be further deposited on these images by the use of stable physical developers. Significantly, it has been found that if hydrogen is not provided by some means, no formation of visible palladium images is observed, and an imagewise distribution of metal is not obtained when the element is contacted with a stable physical developer.

Visible palladium metal is selectively formed only in exposed areas upon treatment of the nucleated sample with hydrogen. In areas of exposure, a low density image of palladium metal is obtained very rapidly when hydrogen is brought into contact with the palladium nuclei. This low density image may then be intensified to the desired level by physical development in a conventional nickel physical developer. Other conventional plating baths may also be employed, such as electroless palladium copper, or cobalt. It is noted, however, that no imagewise physical development of the nickel, etc., is observed on a palladium nucleated sample without visible palladium image formation caused by hydrogen reduction. Hydrogen may be provided, for example, by contacting the imagewise exposed element with a stream of hydrogen gas. Alternatively, the exposed element may be placed in a closed chamber in a hydrogen rich atmosphere, at a temperature between about 0° C. and about 25° C., at a pressure of from about one half to about two atmospheres. The time necessary for the formation of palladium metal may vary from a few seconds to several minutes, depending upon such factors as pressure, temperature, and image density.

The physical developer which is used in the practice of this invention may comprise an aqueous bath in which is dissolved a salt of a heavy metal, a complexing agent for the metal ions in said bath, and a reducing agent. The physical developer bath is catalyzed by palladium metal sites. The heavy metal deposited from the bath must itself be autocatalytic; that is, it must act as a catalyst for further deposition of metal from the developer. This is necessary in order that deposition and development will continue after the palladium metal sites are enveloped with heavy metal. With respect to the Periodic Table, suitable heavy metals can be selected from Group VII metals such as nickel, cobalt, iron, palladium and platinum, Group VI-B metals such as chromium and Group I-B metals such as copper, silver and gold. Almost any heavy metal salt which is a source of the desired heavy metal ions can be employed. Suitable heavy metal salts useful in the invention include heavy metal halides such as cobaltous bromide, cobaltous chloride, cobaltous iodide, ferrous bromide, ferrous chloride, chromium bromide, chromium chloride, chromium iodide, copper chloride, nickel chloride, nickel bromide, nickel iodide, gold chloride, palladium chloride and platinum chloride, heavy metal sulfates such as nickel sulfate, ferrous sulfate, cobaltous sulfate, chromium sulfate, copper sulfate, palladium sulfate and platinum sulfate, heavy metal nitrates such as nickel nitrate, ferrous nitrate, cobaltous nitrate, chromium nitrate and copper nitrate, and heavy metal salts of organic acids such as ferrous acetate, cobaltous acetate, chromium acetate and copper formate. Baths can be formulated based on a single heavy metal or based on mixtures of heavy metals. When more than one heavy metal is employed in the bath, the image which is de-

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posited will generally be an alloy of the two metals. Physical developers based on noble metals such as silver, gold, and platinum are relatively unstable and cannot be stored for long periods of time. However, such physical developers are operative in the processes of this invention and can be employed if the developer bath is prepared shortly before use.

The complexing agent employed in the physical developer bath should tie up the metal ions so that they show a lessened tendency to be reduced spontaneously. However, the complexing agent should not bind the metal ions so tightly that they will be unable to be reduced and deposited on the image sites in the presence of the catalyst. Suitable complexing agents include ammonium salts such as ammonium chloride, organic acids such as aspartic acid, malic acid, citric acid, glycolic acid, salts of organic acids such as sodium citrate, potassium citrate, sodium glycolate, potassium glycolate, sodium succinate, potassium succinate, potassium sodium tartrate, etc. A single complexing agent can be used or a combination of more than one complexing agent can be incorporated in the physical developer bath.

The reducing agent can be any compound which provides a ready source of electrons for the reduction of the metal ions and which does not otherwise interfere with development. Suitable reducing agents include hypophosphites such as sodium hypophosphite, manganous hypophosphite, potassium hypophosphite, etc., hydrosulfites such as sodium hydrosulfite, potassium hydrosulfite, calcium hydrosulfite, etc., and the like.

There can be added to the physical developer bath a variety of other materials such as buffering agents, acid or base to adjust the pH, preservatives, etc., in accordance with usual practices.

The proportions in which the various components of the physical developer are present in the bath can vary over a wide range. Suitable concentrations of metal salt in the developer bath are in the range of from about 0.01 to about 0.5 mole of metal salt per liter of bath. The upper limit of concentration is controlled by the solubility of the particular metal salt employed. Preferably, the bath is between about 0.05 molar and 0.25 molar with respect to metal salt. The relative proportions of metal salt and complexing agent are dependent upon the particular metal salt or salts and the particular complexing agent or agents which are employed. As a general rule sufficient complexing agent should be incorporated to bind the metal ions and lessen the tendency of the metal ions to be reduced prior to use of the developer. Depending upon the particular metal salt and complexing agent employed, the amount of complexing agent present can vary from about 4 moles to about 10 moles of complexing agent per mole of metal salt present. The reducing agent can be present in amounts of from about 0.1 mole to about 5 moles of reducing agent per mole of metal salt present.

The following examples illustrate the formation of visible palladium images and further development upon these images of a metal from a stable physical developer. These examples are intended to be illustrative only, and are not intended to limit this invention in any way.

EXAMPLE 1

Unsensitized titanium dioxide is coated upon a poly(ethylene terephthalate) film support employing polyvinyl acetate as a binder. The thus prepared element is exposed for 5 seconds at 400 footcandles illumination through a line copy negative using a 500 watt projection lamp. The exposed sample is immersed for nucleation, in a 0.1–0.2 percent aqueous solution of K_2PdCl_4 for 30 seconds, and squeegeed dry. The nucleated sample (containing no visible image) is then placed in a stream of hydrogen gas until the palladium image fully develops, a matter of a few seconds. The desired degree of nickel development is obtained by immersion for an appro-

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priate length of time in a nickel physical developer of the following composition:

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$NiCl_2 \cdot 6H_2O$ -----	23.8
Malic acid -----	53.6
Gluconic acid -----	50.0
$NaH_2PO_2 \cdot H_2O$ -----	21.2
NaOH to pH=5.0.	
NH_4OH (con.) to pH=10.0.	
Water to 1000 ml.	

High quality nickel images are obtained in this fashion, having D_{max} equal to 2.88, after 120 seconds of development time. Shorter development times produce lower densities. The visible palladium images formed upon hydrogen reduction of the palladium nucleated sample have D_{max} equal to 0.27–0.44. Similar results are obtained using photosensitive elements of zinc oxide, lead oxide, or copper oxide.

In contrast, a sample of the nucleated exposed titanium dioxide, as prepared above, is subjected to physical development in the above nickel physical developing solution, without hydrogen reduction of the palladium nuclei. In this case, no nickel deposition upon the element is observed.

EXAMPLE 2

Samples of titanium dioxide, as prepared above, are imbibed with a saturated, filtered aqueous solution of $PdCl_2$, and allowed to dry. Exposure and treatment with hydrogen gas as in Example 1 results in visible palladium images. These images are also subsequently enhanced by nickel physical development as in the preceding example. However, no visible palladium or nickel images form when a similar sample is treated with hydrogen prior to exposure or when the hydrogen reduction is omitted.

EXAMPLE 3

A sample of titanium dioxide is prepared, exposed, and nucleated as in Example 1 above, and immersed in the nickel physical developer of Example 1 which has been previously saturated by hydrogen gas. A visible image forms rapidly and is of comparable quality to those obtained in the previous examples. The developer is rendered inactive by degassing with nitrogen. Activity may be regenerated by again saturating the nickel developer bath with hydrogen. No images are obtained if hydrogen gas is not passed through the developer solution, or otherwise brought in contact with the nucleated element, again illustrating the criticality of hydrogen reduction.

EXAMPLE 4

The titanium dioxide elements as prepared and exposed as in Example 1 above are nucleated with palladium (II), platinum (II), silver (I), and gold (III). These samples are immersed in a physical developer bath having the following composition:

	Molar
Nickel chloride -----	0.1
Dimethylamineboran -----	0.1
Malic acid -----	0.4
pH adjusted to with NaOH 7.0.	

These titanium dioxide samples are all completely fogged in this developer. Introduction of a similarly prepared and exposed element bearing a palladium image, formed by hydrogen reduction of a palladium nucleated titanium dioxide sample, into this developer results in formation of a direct positive image. The palladium metal sites exhibit a long induction period (90–120 seconds) with regard to the deposition of nickel from this plating bath. However, the non-image areas containing palladium (II) are immediately reduced to palladium metal in this bath and these sites act as effective catalysts for decomposition of the developer, resulting in rapid metal deposition. By removal of the element from the bath prior to the

commencement of deposition upon the palladium image, a direct positive image may be obtained.

EXAMPLE 5

Visible palladium images formed by hydrogen reduction as in Example 1 are heated at 100° C. over phosphorous pentoxide under vacuum for 2 hours in order to remove chemisorbed or adsorbed hydrogen. The palladium images are themselves visually unaffected by this treatment. The results of subsequent development in the nickel developer employed in Example 1 are as follows:

Treatment	D _{max.} (before development)	Development time, seconds	D _{max.} (after development)
H ₂ O removed	0.44	60	0.44
Control	0.44	60	1.82

The above data reveal that removal of hydrogen from the palladium image inhibits nickel deposition, thus indicating that hydrogen absorbed by the palladium serves to initiate decomposition of the nickel bath. Significantly, treatment of a sample as described to remove hydrogen, followed by regasing with hydrogen gas, does not regenerate the catalytic effect present before the removal of hydrogen.

EXAMPLE 6

Incubation studies at 100° F., 94% relative humidity, for 48 hours indicate that the stability of nickel images, as prepared in Example 1, increases with increasing development time. The percentage of density loss decreases with increasing thickness of the developed nickel layer, as would be expected. Although palladium images appear to be essentially stable under these conditions, fog occurs in unexposed areas such that image discrimination is poor. These results are summarized as follows:

Incubation of Palladium and Nickel Images

Development time (sec.)	D _{max.} (before incubation)	D _{max.} (After incubation)	Percentage decrease
30	0.27	* 0.30	(^b)
45	0.32	0.28	38
60	0.52	0.32	38
90	0.84	0.56	32
120	2.26	1.76	22
120	2.88	2.50	13

* Fog. ^b Pd image only.

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

There is claimed:

1. A method for the deposition of visible palladium images which comprises imagewise exposing a radiation-sensitive element comprising a metal salt or oxide selected from the group consisting of titanium dioxide, zinc oxide, copper oxide, lead oxide, lead chromate, and lead molybdate, to a source of activating radiation, treating said imagewise exposed radiation-sensitive element with palladium ions to imagewise deposit palladium nuclei, and treating said element with hydrogen to form a visible imagewise distribution of palladium metal.
2. A method as set forth in claim 1 wherein said radiation-sensitive element comprises titanium dioxide.
3. A method as set forth in claim 1 wherein said radiation-sensitive element comprises zinc oxide.
4. A method as set forth in claim 1 wherein said palladium ions are provided by a solution comprising palladium chloride.
5. A method as set forth in claim 1 wherein said palladium ions are provided by a solution comprising potassium tetrachloropalladate.
6. A method as set forth in claim 2 wherein said palladium ions are provided by a solution comprising palladium chloride.
7. A method as set forth in claim 2 wherein said palladium ions are provided by a solution comprising potassium tetrachloropalladate.
8. A method as set forth in claim 1 wherein said palladium metal is formed in the presence of hydrogen gas at a pressure between about one half and about two atmospheres and a temperature between about 0° C. and about 25° C.
9. A method for the deposition of visible palladium images which comprises imbibing a photosensitive titanium dioxide element with a solution of palladium chloride, drying, imagewise exposing said element to activating radiation, and contacting said imagewise exposed element with hydrogen.

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