United States Patent

Yudelson et al.

[15] **3,650,748**

[45] **Mar. 21, 1972**

[54] **PHOTOGRAPHIC REPRODUCTION USING NOVEL PHYSICAL DEVELOPERS**

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[22] Filed: **Nov. 22, 1968**

[21] Appl. No.: **778,323**

[52] **U.S. Cl.** .....**96/48 PD,** 96/63, 96/66, 96/92, 96/93

[51] **Int. Cl.** **G03c 5/24,** G03c 1/64

[58] **Field of Search** .....96/48 PD, 63, 66, 92, 93

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[57] **ABSTRACT**

Processes for producing images by photoexposure, and stable physical developers employing borane reducing agents for use in such processes are described.

30 Claims, No Drawings

PHOTOGRAPHIC REPRODUCTION USING NOVEL PHYSICAL DEVELOPERS

This invention relates to photographic reproduction. In a particular aspect it relates to processes for reproducing images by physical development and to stable physical developers for use in such processes.

Physical development comprises the intensification or development of catalytic nuclei by treating the nuclei with a developer solution which contains a reducible metal compound and a reducing agent. In physical development, virtually all the metal in the resultant visual image is formed by the selective reduction of metal ions supplied by the reducible metal compound in the developer solution. It is desirable that the physical developer solution be so formulated that it is stable under conditions of storage, but that in the presence of a catalyst, such as a heavy metal latent image, it decomposes and deposits reduced metal on the catalytic sites. Once a catalytic site is enveloped with metal deposited from the developer solution, it is essential that the reduced metal be autocatalytic, that is, it too must catalyze the decomposition of the physical developer solution.

Physical development involving silver compounds is well known. However, such processes have not had any substantial commercial application, except in very specialized applications, due to the fact that known silver physical developer solutions are extremely unstable. Thus, shortly after a physical developer solution is prepared by mixing silver salts and reducing agents, reduced silver begins to deposit rapidly, so that in a few hours the bath is completely decomposed and is of no practical utility. This type of instability is inherent in silver physical developer solutions since the poor autocatalytic properties of silver metal require that silver physical developer solutions be formulated so as to be capable of depositing silver very rapidly, if inordinately long development times are to be avoided.

In Yudelson et al. copending application Ser. No. 653,025, filed July 13, 1967, there are described photographic systems which employ extremely stable physical developer solutions. Since the catalyst which initiates reduction and deposition of heavy metal salt from these stable Yudelson et al. physical developer solutions is palladium, the photographic systems described in that application employ as the light-sensitive latent image-forming component a light-sensitive palladium compound. While these systems are useful for a variety of image-forming processes, the necessity of using light-sensitive palladium compounds to produce the latent image prevents these systems from enjoying the advantages associated with other light-sensitive systems based on light-sensitive components other than palladium compounds.

Therefore, it is an object of this invention to provide novel processes for physical development of latent images.

It is a further object of this invention to provide processes for the production of photographic images from a variety of light-sensitive systems employing stable physical developers.

It is another object of this invention to provide novel physical developers which can be employed in developing latent images derived from many different light-sensitive components.

The above and other objects of this invention will be apparent to those skilled in the art from the further description of this invention which follows.

In accordance with the present invention, we have found that nuclei of such metals as palladium, silver, iron, copper, and the like, which are derived from photosensitive compositions, will catalyze the reduction and deposition of heavy metal salts from stable physical developer baths which employ borane reducing agents. Thus, in one embodiment of this invention, a process for photographic reproduction of images is provided in which catalytic metal nuclei are formed by a process which includes the step of photographic exposure, and in which the heavy metal nuclei are developed by contacting them with a physical developer bath comprising a reducible heavy metal salt, a complexing agent for heavy metal ions derived from the heavy metal salt, and a borane reducing agent. In another embodiment of this invention a stable physical developer bath is provided which comprises a reducible heavy metal salt, a complexing agent for heavy metal ions derived from the reducible heavy metal salt which complex these ions and prevent their spontaneous reduction in the absence of catalytic nuclei, and a borane reducing agent.

The borane reducing agents useful in the physical developer baths of this invention include amine boranes, phosphine boranes, arsine boranes, stibine boranes, etc., and can be represented by the formula:

$$ZBH_3$$

wherein Z represents an amine, such as an alkylamine, containing alkyl groups of one to 12 carbon atoms, for example, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, ethanolamine, diethanolamine, propylamine, dipropylamine, tripropylamine, 3-hydroxypropylamine, butylamine, amylamine, etc., a polyamine, for example, ethylenediamine-2-aminoethylamine, etc., a hydrazine, an aromatic amine, for example, aniline, etc., a cyclic amine, for example, pyridine, 2,6-lutidine, 3,4-lutidine, 2,4-lutidine, 2-ethylpyridine, 2,4-diethylpyridine, 2,6-diethylpyridine, 3,4-diethylpyridine, 2-propylpyridine, 4-propylpyridine, 3-propylpyridine, etc., a phosphine, such an an alkylphosphine containing alkyl groups of one to 12 carbon atoms, for example, methylphosphine, dimethylphosphine, trimethylphosphine, ethylphosphine, diethylphosphine, triethylphosphine, propylphosphine, dipropylphosphine, tripropylphosphine, butylphosphine, etc., an aryl phosphine, for example, phenylphosphine, etc., an arsine such as an alkylarsine containing alkyl groups of one to 12 carbon atoms, for example, methylarsine, dimethylarsine, trimethylarsine, propylarsine, butylarsine, amylarsine, etc., an arylarsine, for example, phenylarsine, etc., a stibine, such as an alkylstibine containing alkyl groups of one to 12 carbon atoms, for example, methylstibine, dimethylstibine, trimethylstibine, ethylstibine, diethylstibine, triethylstibine, propylstibine, butylstibine, etc., an arylstibine, for example, phenylstibine, etc.

Typical borane reducing agents which are useful in the practice of the present invention include dimethylamine borane, trimethylamine borane, diethylamine borane, triethylamine borane, t-butylamine borane, pyridine borane, 2,6-lutidine borane, ethylenediamine diborane, hydrazine diborane, dimethylphosphine borane, phenylphosphine borane, dimethylarsine borane, triethylarsine borane, phenylarsine borane, dimethylstibine borane, diethylstibine borane and phenylstibine borane.

The reducible heavy metal salt provides a source of metal which amplifies the catalytic nuclei formed on photoexposure. The heavy metal image formed must itself be autocatalytic, that is it must catalyze the further reduction and deposition of heavy metal ions from the physical developer solution. Heavy metals which have this property include those selected from Periodic Table Group VIII metals such as, nickel, cobalt, and iron, Group VI*b* metals such as chromium and Group I*b* metals such as copper. The reducible heavy metal ions are introduced into the physical developer as a water-soluble salt. Suitable water-soluble reducible heavy metal salts include heavy metal halides such as cobaltous chloride, cobaltous iodide, ferrous bromide, ferrous chloride, chromic bromide, chromic chloride, chromic iodide, cupric chloride, etc.; heavy metal sulfates such as nickel sulfate, ferrous sulfate, cobaltous sulfate, chromic sulfate, cupric sulfate, etc.; heavy metal nitrates such as nickel nitrate, ferrous nitrate, cobaltous nitrate, chromic nitrate, cupric nitrate, etc.; heavy metal salts of organic acids such as ferrous acetate, cobaltous acetate, chromic acetate, cupric formate, etc.; and the like. The physical developers can be based upon a single one of these reducible heavy metal ions, or upon a mixture of more than one of these reducible heavy metal ions.

The complexing agent for the reducible heavy metal ions in the physical developer should "tie up" the metal ions to such a degree that the ions are not reduced spontaneously in the presence of the reducing agent. However, the complexing

agent should not bind the metal ions so tightly that they will be unable to be reduced by the reducing agent in the presence of catalytic sites. Any complexing agent which satisfies these criteria is useful in the practice of the present invention. A preferred group of complexing agents are organic carboxylic acids such as monocarboxylic acids, dicarboxylic acid, hydroxycarboxylic acid, etc., for example, malic acid, lactic acid, succinic acid, citric acid, aspartic acid, glycolic acid, tartaric acid, ethylenediaminetetraacetic acid, gluconic acid, saccharic acid, quinic acid, and the like. More than one of these complexing agents can be employed in the physical developer solution, and when a light-sensitive system based on light-sensitive palladium compounds is employed, it is preferred that at least one of the complexing agents be gluconic acid, saccharic acid or quinic acid, since as indicated in Yudelson et al. U.S. Ser. No. 723,269, filed Apr. 22, 1968, the presence of such a complexing agent increases the useful life of the physical developer solution and reduces background fog in palladium light-sensitive elements.

The physical developer solutions can include, in accordance with the usual practices, a variety of other materials to facilitate maintenance and operation of the developer and to improve the quality of the developed image, such as acids and bases to adjust pH, buffers, preservatives, thickening agents, brightening agents, and the like. The rate of development can be increased, and hence the time of development decreased, by adding to the developer solution a surfactant such as an alkyl metal salt of a sulfated fatty acid, e.g., dodecyl sodium sulfate.

The proportions in which the various components of the physical developer are present in the developer solution can vary over a wide range. Suitable concentrations of reducible heavy metal salt can range from about 0.01 mole to about 1.0 mole of metal salt per liter of solution. The upper limit of concentration is controlled by the solubility of the particular metal salt employed. Preferably, the solution is about 0.1 molar to about 0.3 molar with respect to the heavy metal salt. The relative proportions of metal salt and complexing agent are dependent upon the particular heavy 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 "tie up" the reducible heavy metal ions which are in solution and to lessen the tendency of these metal ions to be reduced prior to use of the developer solution. Depending upon the particular heavy metal salt and the particular complexing agent which is employed, the amount of complexing agent present typically can vary from about 0.2 mole to about 10 moles of complexing agent per mole of metal salt present. Typically, the reducing agent can be present in amounts from about 0.01 mole to about 5 moles of reducing agent per mole of metal salt present in the solution. In order to permit the developer solution to be utilized for its maximum life, at least one equivalent of reducing agent should be present in the solution for each equivalent of reducible heavy metal salt.

The physical developers are operative over a wide range of pH. However, since the borane reducing agents undergo an acid catalyzed hydrolytic reaction which reduces their stability during storage, it is preferred that the physical developers be maintained at a moderately alkaline pH of about 8 to 11, and preferably of about 8.5 to 9.5. Nevertheless, the physical developers can be used under acidic conditions, as low as pH 3, if such conditions are advantageous for the particular photographic process in which they are used. The physical developer solution can be brought to the desired pH by addition of an appropriate amount of a suitable base; for example, ammonium hydroxide or sodium hydroxide, and can be maintained at the desired pH by addition of a suitable buffering system, for example, sodium carbonate and sodium bicarbonate. Other materials which can be used to adjust the pH to the desired range and buffers which will maintain the pH in that range can be readily determined by those skilled in the art.

As indicated above, a wide variety of photosensitive systems are useful in the processes of this invention. The essential requirement which they must satisfy to be useful in this invention is that they are capable of ultimately producing nuclei which are catalytic for the reduction and deposition of metal from the physical developer solution. Metals such as palladium, silver, copper, iron, nickel, cobalt, chromium, platinum, tin, zinc, and the like are catalytic, and photosensitive systems which are capable of producing nuclei of such metals can be employed in this invention. The majority of photosensitive systems useful in the processes of this invention can be divided into three types. The first type would include those systems in which catalytic nuclei are produced directly on photoexposure. Typical of such systems are those based on such radiation-sensitive metal compounds as radiation-sensitive palladium compounds and radiation-sensitive copper compounds in which photoexposure reduces the metal compound to nuclei of elemental metal. The second type would include those systems in which photoexposure yields a product which when reacted with a second compound produces catalytic nuclei which are derived either from the product of photoexposure, from the second compound, or from a combination of the two. An example of this type of system would be one in which photoexposed silver halide must be chemically developed and then activated to give a catalytic image. The third type would include those systems in which photoexposure yields a product which is noncatalytic or can be made noncatalytic, while the unexposed material is catalytic or can be made catalytic by chemical reaction. An example of such a system is one in which photoexposed silver halide is chemically developed to noncatalytic silver and the unexposed silver halide is reduced in the physical developer solution catalytic silver nuclei.

A more detailed description of representative photosensitive systems and the manner in which they are used in this invention follows.

One type of photosensitive element which can be used in this invention is one based on light-sensitive palladium compounds such as is described in copending Yudelson et al. Ser. No. 653,025, filed July 13, 1967. These elements employ as the light-sensitive component a light-sensitive palladium compound such as a salt or complex of palladium which has the general formula:

$$[Pd(L)_x bh]_y M_z$$

where L is a ligand such as a halogen ligand such as bromine, chlorine, or iodine, a carboxylic acid ligand such as a malonate group, an oxalate group, a mesoxalate group, an oxamate group, a mandelate group, etc., an aromatic ligand such as phenol, styrene, naphthol, etc., a nitrogen ligand such as ammonia, an amine such as methylamine, ethylamine, benzylamine, propanediamine, tetraethylenepentamine, aminoethanol, methylaminoethanol, aminonaphthol, bipyridine, phenanthroline, ethylenediamine-tetraacetic acid, etc., a nitrile such as nitrilotriethanol, benzonitrile, etc., an imine such as iminodiethanol, an oxime such as salicylaldoxime or a hydrazide such as benzhydrazide, a phosphorous ligand such as triarylphosphine, trialkylphosphine, etc., an arsenic ligand such as triarylarsine, trialkylarsine, etc., an antimony ligand such as triarylantimony, trialkylantimony, etc., and the like; M is an ion such as a hydrogen ion, an inorganic acid ion such as a chloride ion, a bromide ion, an iodide ion, a sulfate ion, a nitrate ion, a phosphate ion, etc., an organic acid ion such as an acetate ion, an acrylate ion, an oxalate ion, a malonate ion, etc., a metal ion such as a sodium ion, a potassium ion, a calcium ion, a strontium ion, an aluminum ion, etc., a onium ion such as those containing nitrogen, phosphorus or sulfur like a quaternary ammonium ion, a quaternary phosphonium ion, a tertiary sulfonium ion, etc., and the like, or M can be a $[Pd(L)_x]$ group; x is an integer from 0 through 4; y is an integer from 1 through 4; z is an integer from 0 through 2, and x and z are not 0 at the same time.

A particularly preferred group of photosensitive palladium compounds are those palladium complexes having the above

general formula, wherein L is carboxylic acid ligand, M is a cation, and x is 2 or 4, y is 1 and z is 1 or 2. Representative of such preferred palladium complexes are potassium dioxalato palladate (II), potassium dimalonato palladate (II), potassium dimesoxalato palladate (II), potassium tetraoxamato palladate (II) and potassium dimandelato palladate (II); alternatively named as potassium palladium oxalate, potassium palladium malonate, potassium palladium mesoxalate, potassium palladium oxamate and potassium palladium mandelate, respectively.

Suitable elements employing light-sensitive palladium compounds are described in the above-mentioned Yudelson et al. copending application Ser. No. 653,025, filed July 13, 1967, and in Yudelson copending application Ser. No. 723,278, filed Apr. 22, 1968. These elements contain the light-sensitive palladium compound imbibed in a porous support such as paper, coated paper, ceramic, gelatin, olefinic polymers such as polyvinyl alcohols, polyvinyl phthalates, polyvinyl anthranilates, carboxyl-containing polymers such as carboxymethyl cellulose, cellulose ether phthalates, cellulose ester succinates, cellulose ether malonates, copolymers of alkyl acrylates with acrylic acid, etc., and the like.

These elements are exposed by standard photographic techniques to yield nuclei of palladium in exposed areas, and are then developed by immersion in the physical developer bath. The paladium nuclei act as catalytic centers for the reduction and deposition of heavy metal from the bath and in exposed areas a heavy metal image is formed.

The above process employing light-sensitive palladium compounds is negative working, that is, a heavy metal image is formed in the exposed areas of the element while in the unexposed areas, corresponding to the original image, there is no deposition of metal from the physical developer bath. The light-sensitive palladium compounds can, however, be employed in a positive-working process in which a heavy metal image is formed in the unexposed areas of the element. In such a process the photosensitive element is exposed in the usual manner and is then contacted with a receiving sheet into which has been imbibed the physical developer. While the element and the receiving sheet are in contact, heat is applied so as to promote diffusion of unexposed palladium compound from the element to the receiving sheet. Contact temperatures of from 45° to 100° C. are suitable. In the unexposed areas of the element the palladium compound migrates from the element to the receiving sheet where it is reduced and catalyzes reduction of heavy metal salt from the developer in the receiving sheet. In the exposed areas of the element, because of the formation of palladium nuclei, there is a lower concentration of palladium compound, and hence there is smaller differential in concentration of palladium compound between the exposed areas of the element and the receiving sheet. This permits transfer of sufficient palladium compound to the receiving sheet from unexposed areas of the element before a significant amount of palladium compound has been transferred from exposed areas. The image formed on the receiving sheet can be used as such or it can be intensified by immersing the receiving sheet in a physical developer bath.

The physical developer solutions which are imbibed in receiving sheets for use in this positive-working embodiment normally differ somewhat from the physical developers described above. These physical developers contain a greater proportion of heavy metal salt and reducing agent and a lesser proportion of complexing agent. It is preferred that the raio of complexing agent to heavy metal salt be from about 0.5 mole to about 2.0 moles of complexing agent per mole of heavy metal salt, and that the raio of reducing agent to heavy metal salt be from about 1 to about 5 moles of reducing agent per mole of heavy metal salt. As discussed above, the ratios employed will vary somewhat depending upon the particular metal salt and particular complexing agent employed.

Another type of light-sensitive element which can be employed in the present invention is one which utilizes silver halide as the light-sensitive component. The silver halide can be employed as an emulsion in gelatin, in a polymeric binder, or in a mixture of gelatin and polymeric material. Since the silver produced by photographic exposure and conventional silver halide chemical development is not normally a catalyst for reduction and deposition of heavy metal salt from the physical developer solution, it is necessary that further processing be performed in order to form catalytic silver nuclei. Since silver does not form the final image, the silver halide elements employed in this embodiment need not have a large concentration of silver halide. Elements having a coverage of as little as 1 mg. of silver per square foot, or less, and preferably from about 2.5 to 15 mg. of silver per square foot can be satisfactorily employed. A low coverage of silver is in fact preferred since this eliminates the necessity of removing silver halide from nonimage areas. However, silver halide elements having a silver halide concentration in amounts typical for photographic elements can be employed in this invention if desired.

In one embodiment of this invention a negative image is produced by exposing an element comprising a support on which is coated silver halide in a suitable binder; developing the exposed areas of the element with an ordinary silver halide developer, such as one based on polyhydroxybenzene developers, aminophenol developers, ascorbic acid developers, pyrazolidone developers, and the like; removing the unexposed silver halide from the element; activating the developed silver with a suitable activator, such as a mineral acid (e.g., nitric acid, hydrochloric acid, sulfuric acid, sulfurous acid) a strong oxidizing agent (e.g., potassium ferricyanide, hydrogen peroxide), or a strong reducing agent (e.g., sodium borohydride); and then developing a heavy metal image by contacting the exposed silver halide element with a physical developer bath.

In another embodiment of this invention instead of activating the exposed, developed silver, the unexposed, undeveloped silver halide is removed from the element with a fixing bath and the exposed, developed silver is reconverted to silver halide in a silver rehalogenation bath containing an oxidizing agent and a source of halide ions, after which the element is contacted with a physical developer bath. The physical developer bath reduces the silver halide to provide catalytic silver nuclei, and heavy metal is deposited on these catalytic nuclei.

In yet another embodiment of this invention in which a silver halide element is employed, the exposed, developed silver is removed from the element with a bleach bath and an image is developed, utilizing the unexposed, undeveloped silver halide remaining in unexposed areas, by contacting the element with a physical developer bath. As in the preceding embodiment, the silver halide remaining in the element is reduced to form catalytic silver nuclei on which heavy metal is deposited. In this embodiment a positive image is obtained.

In yet another embodiment of this invention the ability of ferric ions to be reduced to ferrous ions on exposure to light is employed to provide catalytic nuclei useful in the invention. The ferrous ions formed on exposure act as a reducing agent for a suitable metal salt which yield catalytic nuclei. The strong reducing activity of photoreduced ferrous ions is known and has been employed in "brownprint" and related processes. The ferric salts useful in this invention include those employed in the "brownprint" processes and include inorganic ferric salts such as ferric chloride, and salts of organic acids such as ferric ammonium oxalate, ferric ammonium citrate, and the like. Suitable salts which can be reduced by the ferrous ions formed on photoexposure and which yield catalytic nuclei include silver salts such as silver nitrate, copper salts such as cupric chloride, gold salts such as sodium chloroaurate, platinum salts such as potassium chloroplatinite, palladium salts such as sodium chloropalladite, and the like. These salts can be admixed with the ferric salt; for example, a mixture of ferric chloride and cupric chloride yields a suitable light-sensitive composition which gives copper nuclei on photoexposure. Alternatively, the photosensitive element can contain the ferric salt and then after photoexposure the ele-

ment can be washed with a solution of the reducible metal salt; for example, exposing an element containing ferric ammonium oxalate, and then contacting this element with a silver nitrate solution yields catalytic silver nuclei in exposed areas of the element.

The processes of this invention can be employed to form images which are useful for many different purposes. Such uses include document copy and related uses, preparation of electrically conducting images which can be employed as printed circuits and the like, preparation of ink-receptive or ink-repellent images which can be employed in printing operations, preparation of images opaque to radiation in and near the infrared region of the spectrum which can be employed as the soundtrack on motion picture film, and many other uses which will be apparent to those skilled in the art.

The following examples are included for a further understanding of this invention.

EXAMPLE 1

Nuclei of copper, silver and palladium are prepared in paper supports by imbibing the paper with 1 percent solutions of cupric chloride, silver nitrate and palladous chloride, reducing the metal ions by immersion of the paper supports into a 1 percent sodium borohydride ($NaBH_4$) solution, and washing the nucleated supports in distilled water for 5 minutes. Strips of these nucleated supports are immersed in a physical developer bath having the following composition:

Nickel chloride	0.1 molar
Dimethylamine borane	0.1 molar
Malic acid	0.4 molar
pH adjusted to 7.0 with NaOH	

In this and succeeding example the borane reducing agent is added to the physical developer bath after adjustment of pH. All three of the nucleated strips cause the bath to deposit nickel on the paper surface after 5–10 minutes immersion at room temperature. The nucleated strips are also immersed in a physical developer bath which employs sodium hypophosphite as the reducing agent, having the following composition:

Nickel chloride	0.1 molar
Sodium hypophosphite	0.1 molar
Malic acid	0.4 molar
pH adjusted to 9.0 with NaOH	

No nickel deposition occurs on the silver or copper nucleated strips even after immersion in the bath for 18 hours. A nickel deposit forms on the palladium nucleated strip after 5 minutes immersion in the bath.

EXAMPLE 2

A strip of gelatin-coated poly(ethylene terephthalate) support (350mg. of gelatin/ft.^{2}) containing approximately 15 mg./ft.^{2} of potassium dioxalato palladate (II) is exposed through a line copy negative to an ultraviolet light source (eight 8-watt BL tubes, 2½inches from the print) for 60 seconds. It is then immersed in a physical developer bath which contains the following:

Nickel chloride	0.1 molar
Gluconic acid	0.65 molar
Ammonium chloride	1.0 molar
Dimethylamine borane	0.5 g./liter
pH adjusted to 10 with concentrated ammonium hydroxide	

The exposed element is immersed in the developer for 15 minutes to yield a high quality black image in the exposed areas of the film while the unexposed areas remain clear. When the dimethylamine borane is substituted with triethylamine borane, pyridine borane, dimethylphosphine borane, dimethylarsine borane or dimethylstibine borane, similar results are obtained.

EXAMPLE 3

A poly(ethylene terephthalate) film support coated with a gelatino-silver bromide layer (Ag = 8–10 mg./ft.^{2} and gelatin = 75–100 mg./ft.^{2}) is imagewise exposed and then developed for 30 seconds in a chemical developer (diluted 1: 2 with water) having the following composition:

Monomethyl-p-aminophenol sulfate	3.0 g.
Sodium sulfite (desiccated)	45.0 g.
Hydroquinone	12.0 g.
Sodium carbonate $\cdot H_2O$	80.0 g.
Potassium bromide	2.0 g.
Water to make	1 liter

Unexposed, undeveloped silver halide is then removed from the element by fixing for 5 minutes in a bath having the following composition:

Sodium thiosulfate	240.0 g.
Sodium sulfite (desiccated)	15.0 g.
28% Acetic acid	48.0 g.
Boric acid (crystalline)	37.5 g.
Potassium alum	75.0 g.
Water to make	1 liter

The element is then washed in tap water for 10 minutes, and dried. At this point, the silver image is not catalytic toward the physical developer described in Example 2. The sample is then immersed for 2 minutes in a rehalogenation bath consisting of:

Potassium ferricyanide	10.0 g.
Potassium bromide	10.0 g.
Water	80 ml.

After this rehalogenation treatment, the element is then immersed in the physical developer of Example 2. after ten minutes, a heavy nickel deposit covers the silver image.

EXAMPLE 4

A photographic paper coated with a gelatino-silver chloride emulsion and a photographic paper coated with silver chloride in a polyvinyl alcohol binder are exposed through a line copy negative on a printing box, and developed in the chemical developer of Example 3 (diluted 1: 2 with water) for 30 seconds, after which they are washed in running tap water for 10 minutes and dried. They are then immersed for 10 minutes in a physical developer bath having the following composition:

Nickel chloride	0.1 molar
Gluconic acid	0.6 molar
Dimethylamine borane	0.2 molar
pH adjusted to 9.0 with concentrated ammonium hydroxide	

The physical developer bath causes the silver halide in the nonexposed areas to be reduced to silver, after which nickel plates on this chemically reduced silver. Nickel does not plate on the silver that has been developed in the exposed areas. Such silver is not a catalyst for the reduction of the physical developer. Additional sheets of these photographic papers are exposed, developed as described above and they are then treated for 10 minutes in the following activating solutions after which they are placed into the above physical developer bath for 10 minutes.

A. 10 Percent Nitric acid
B. 10 Percent Hydrochloric acid
C. 10 Percent Sulfuric acid
D. 10 Percent Sulfurous acid
E. 10 Percent Potassium ferricyanide
F. 1 Percent Hydrogen peroxide
G. 1 Percent Sodium borohydride

In no case does the photographically produced silver in the paper having the polyvinyl alcohol binder become catalytic for the reduction by the physical developer. However, the activating baths cause the photographically produced silver in

the gelatino-silver halide paper to become catalytic for the reduction and deposition of nickel salts from the physical developer bath on the silver surface.

EXAMPLE 5

A gelatino-silver chloride paper is exposed through a line copy transparency and is then developed in the chemical developer of Example 3 (diluted 1: 2 with water) for 5 minutes followed by a brief rinse in tap water. The developed silver is then removed by immersing the element in the following bleach bath for 1 minute:

Potassium dichromate	80 g.
Sulfuric acid (concentrated)	22 ml.
Water to make	1 liter

The element is rinsed, and then put into the physical developer bath of Example 4 for 5 minutes. This causes the unexposed areas, which contain unexposed silver halide, to turn black and nickel plates out on these areas.

EXAMPLE 6

Example 5 is repeated using the following physical developer baths:

Nickel chloride	0.1 molar
Gluconic acid	0.6 molar
Butylamine borane	10 g./liter
pH adjusted to 9.0 with approximately 50 ml. of ammonium hydroxide (concentrated).	

An excellent copy of the original image, metallic in appearance, is produced with this development.

EXAMPLE 7

Example 5 is repeated using the following physical developer bath:

Cobaltous chloride	0.1 molar
Gluconic acid	0.6 molar
Dimethylamine borane	10 g./liter
pH adjusted to 9.0 with ammonium hydroxide (concentrated)	

After 5 minutes' development at room temperature, a heavy cobalt deposit covers the unexposed areas which contain unexposed silver halide.

EXAMPLE 8

A poly(ethylene terephthalate) film which has been coated with a gelatino-silver bromide layer (Ag = 55 mg./ft.^{2} and gelatin = 110 mg./ft.^{2}) is exposed through a line copy negative and developed in the chemical developer of Example 3 for 1 minute. It is then rinsed briefly in water and placed into the nickel physical developer of Example 4 for 10 minutes. This development causes the silver bromide which had not been developed (nonimage areas) to be reduced to silver which is a catalyst for the reduction of the nickel physical developer. The silver which had been chemically developed is inert toward the physical developer solution. The film, which now consists of gray-black silver in the exposed areas, and a heavy nickel layer in the unexposed background areas, is placed in the following bleach solution for 1 minute:

Potassium dichromate	20 g.
Sulfuric acid	10 ml.
Water to make	1 liter

This treatment removes the silver image, and at the same time barely affects the nickel layer.

EXAMPLE 9

A polyethylene-coated paper support which has been coated with a gelatino-silver chloride layer (Ag = 20 mg./ft.^{2}, gelatin = 20 mg./ft.^{2}) is exposed through a line copy negative developed in the chemical developer of Example 3 (diluted 1: 1 with water) for 1 minute, washed, and placed in the bleach solution of Example 8 for 1 minute. This treatment removes the silver image, and leaves the silver chloride intact to the nonimage areas. The sample is then placed in a copper physical developer bath having the following composition:

Cupric nitrate	0.03 molar
Gluconic acid	0.25 molar
Dimethylamine borane	10 g./liter
pH adjusted to 9.0 with ammonium hydroxide (concentrated)	

After 10 minutes' immersion in this bath at 50° C., a heavy copper deposit has formed in the areas which contained silver chloride producing an excellent reversal image. The copper layer has a resistance that is less than 0.1 ohm/square.

EXAMPLE 10

A cubic-grained silver bromoiodide gelatin emulsion containing 2.5 mole percent iodide is coated at coverages of 2.5, 5.0 and 10.0 mg. Ag/ft.^{2} on an imbibition transfer blank. The blank is a poly(ethylene terephthalate) film support on which is coated a layer of gelatin overcoated with a layer of a mixture of gelatin and copoly(styrene-methyl vinyl ketone-aminoguanidine) described in Minsk U.S. Pat. No. 2,882,156. This element is then exposed for 5 seconds to a 60-watt bulb at a distance of approximately one foot and developed in a chemical developer bath having the following composition:

Monomethyl-p-aminophenol sulfate	2.5 g.
Sodium sulfite (desiccated)	30.0 g.
Hydroquinone	2.5 g.
Sodium metaborate $\cdot 4H_2O$	10.0 g.
Potassium bromide	0.5 g.
Water to make	1 liter

The element is then washed and immersed for 10 minutes in a nickel physical developer bath of Example 4. A nickel image is formed in the unexposed areas.

EXAMPLE 11

A paper strip is imbibed with the following solution:

Ferric chloride	10.0 g.
Cupric chloride	5.0 g.
Water	85 ml.

After drying the element is exposed through a line copy negative to the light source described in Example 2 for 15 minutes. It is then immersed for 10 minutes in the physical developer bath of Example 4, after which a black nickel image is present in the exposed areas. The nonexposed areas are pale yellow.

EXAMPLE 12

A paper strip is imbibed with the ferric chloride-cupric chloride solution described in Example 11, dried, and exposed through a line copy negative to the light source used in Example 2 for 10 minutes. Another strip is sensitized and exposed in the same manner, but is also heated after exposure for 15 seconds at 130° C. Both samples are then developed in the physical developer bath described in Example 4 for 10 minutes at room temperature. After development, the sample which has been heated, contains a high quality black image in the exposed areas whereas the sample which had not been heated showed only a very faint image in the exposed areas.

EXAMPLE 13

The following solution is imbibed into a paper strip:

Ferric chloride	1.6 g.
Cupric chloride	0.4 g.
Mandelic acid	4.0 g.
Water	95.0 ml.

The strip is then dried, and exposed through a line copy negative for 1 minute to the light source described in Example 2. It is then developed for 10 minutes in the physical developer bath described in Example 4. An excellent black image on a white background is obtained in exposed areas.

EXAMPLE 14

An imbibition transfer blank of the type described in Example 10 is imbibed with the following solution:

Ferric ammonium oxalate	70 g.
Ferric ammonium citrate	170 g.
Diazopon AN (polyoxyethylated fatty alcohol manufactured by GAF Corp.)	5 ml.
Sulfamic acid	50 g.
Water	600 ml.
Natrosol (Hydroxy ethyl cellulose manufactured by Hercules Powder Co.)	5 g.
Acetone	10 ml.

The blank is then dried, exposed for 30 seconds to a 60-watt bulb at a distance of approximately one foot and bathed in a 0.1 molar silver nitrate solution. The element is developed for 5 minutes in the nickel physical developer bath of Example 4. A negative nickel image is obtained in the exposed areas of the element.

EXAMPLE 15

An imbibition transfer blank of the type described in Example 10 is imbibed in an aqueous acidic solution of potassium dioxalato palladate (II), dried, exposed for 5 seconds to a 60-watt bulb at a distance of approximately 1 foot, and developed for 15 minutes in the nickel physical developer bath of Example 4. A good quality negative image is obtained.

EXAMPLE 16

A paper strip is imbibed with a 5 percent cupric sulfate solution, dried and then exposed to a 400-watt Gates lamp (high-pressure mercury arc) for 45 minutes. It is then immersed in a physical developer bath having the following composition:

Nickel chloride	0.1 molar
Gluconic acid	0.4 molar
Dimethylamine borane	5.0 g./liter
pH adjusted to 11 with ammonium hydroxide.	

After immersion in this developer bath for 60 minutes, a nickel image appears in the exposed areas. Nickel did not deposit in unexposed areas.

EXAMPLE 17

A paper strip is imbibed with the following solution:

Cupric chloride	10 g.
2,7-Anthraquinonedisulfonic acid, disodium salt	3 g.
Water	87 ml.

After drying, the paper is exposed through a line copy negative to the light source described in Example 2 for 10 minutes. It is then heated at 130° C. for 15 seconds and is then immersed in the following physical developer bath for 10 minutes at room temperature:

Nickel chloride	0.1 molar
Gluconic acid	0.6 molar
Dimethylamine borane	0.17 molar
pH adjusted to 9.0 with concentrated ammonium hydroxide	

After immersion in this developer for 10 minutes, a black nickel image appears in the exposed areas. If the element is not heated after exposure, no image is observed after 10 minutes' immersion.

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 reproduction of images which comprises the steps of

a. forming on a photographic element by a progress which includes the step of exposure to actinic radiation, heavy metal nuclei which are catalytic for reduction and deposition of heavy metal from a borane physical developer, and

b. developing a heavy metal image by contacting the exposed element with a physical developer solution comprising:

1. a. a reducible heavy metal salt,

2. a carboxylic acid complexing agent for heavy metal ions derived from the heavy metal salt, and

3. a borane reducing agent.

2. A process as defined in claim **1** wherein :

the reducible heavy metal salt is of a metal selected from the group consisting of nickel, cobalt, copper, chromium, and iron,

and the borane reducing agent is selected from the group consisting of amine boranes, phosphine boranes, arsine boranes, and stibine boranes.

3. A process as defined in claim **1** wherein the catalytic heavy metal nuclei are formed by exposing an element containing a radiation-sensitive heavy metal salt to actinic radiation to form a latent image of catalytic heavy metal nuclei in exposed areas.

4. A process as defined in claim **2** wherein the catalytic heavy metal nuclei are formed by exposing to actinic radiation an element containing a radiation-sensitive heavy metal compound selected from the group consisting of radiation-sensitive copper compounds and radiation-sensitive palladium compounds to form a latent image of catalytic heavy metal nuclei in exposed areas of the element.

5. A process as defined in claim **4** wherein the radiation-sensitive palladium compound has the formula:

$[Pd(L)_x\mathbf{bh}]_yM_z$, wherein

L is a ligand,

M is selected from the group consisting of ions selected from the group consisting of

hydrogen ions,

inorganic acid ions,

organic acid ions,

metals ions, and

onium ions, and

$[Pd(L)_x\mathbf{bh}]$ groups,

x is an integer from 0 through 4,

y is an integer from 1 through 4,

z is an integer from 0 through 2, and

x and z are not 0 at the same time.

6. A process as defined in claim **4** wherein the radiation-sensitive palladium compound has the formula:

$[Pd(L)_x\mathbf{bh}]_yM_z$, wherein

L is a carboxylic acid ligand,

M is a cation,

x is 2 or 4,

y is 1, and

z is 1 or 2.

7. A process as defined in claim **6** wherein

the reducible heavy metal salt is of a metal selected from the group consisting of nickel, cobalt, and copper,

and the borane reducing agent is an amine borane reducing agent.

8. A process as defined in claim **6** wherein the radiation-sensitive palladium compound is selected from the group consist-

ing of potassium dioxalato palladate (II), potassium dimalonato palladate (II), potassium dimesoxalato palladate (II) and potassium tetraoxamato palladate (II).

9. A process as defined in claim 8 wherein

the reducible heavy metal salt is of a metal selected from the group consisting of nickel and cobalt,

and the borane reducing agent is an alkylamine borane.

10. A process as defined in claim 2 wherein the catalytic heavy metal nuclei are formed by

1. exposing to actinic radiation an element containing silver halide,
2. converting the exposed silver halide to elemental silver with a chemical developer,
3. removing unexposed silver halide from the element, and
4. converting the developed elemental silver to catalytic centers for physical development.

11. A process as defined in claim 10 wherein the photosensitive element comprises a support on which is coated a gelatino-silver halide emulsion.

12. A process as defined in claim 11 wherein the silver halide coverage is between about 2.5 and 15 mg. of silver per square foot.

13. A process as defined in claim 11 wherein developed elemental silver is converted to catalytic centers for physical development by contacting the element with a solution of an activating agent selected from the group consisting of mineral acids, strong oxidizing agents, and strong reducing agents.

14. A process as defined in claim 13 wherein the activating agent is selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, sulfurous acid, potassium ferricyanide, hydrogen peroxide and sodium borohydride.

15. A process as defined in claim 10 wherein the developed elemental silver is converted to catalytic centers for physical development by contacting the element with a rehalogenation bath to convert the elemental silver to silver halide and reducing the silver halide thus formed to catalytic silver nuclei by contacting the element with the physical developer solution.

16. A process as defined in claim 15 wherein the rehalogenation bath comprises a solution of potassium ferricyanide and potassium bromide.

17. A process for reproduction of images which comprises the steps of

a. forming on a photographic element heavy metal nuclei which are catalytic for the reduction and deposition of heavy metal from a borane physical developer by 1. 1. exposing to actinic radiation an element which comprises a support on which is coated a gelatino-silver halide emulsion,
   2. converting the exposed silver halide to elemental silver with a chemical developer,
   3. removing unexposed silver halide from the element and
   4. converting the developed elemental silver to catalytic centers for physical development by contacting the element with a solution of an activating agent selected from the group consisting of mineral acids, strong oxidizing agents and strong reducing agents, and

b. developing a heavy metal image by contacting the element with a physical developer solution comprising
   1. a reducible heavy metal salt of a metal selected from the group consisting of nickel, cobalt, and copper,
   2. a carboxylic acid complexing agent for heavy metal ions derived from the heavy metal salt, and
   3. an amine borane reducing agent.

18. A process for reproduction of images which comprises the steps of

a. forming on a photographic element heavy metal nuclei which are catalytic for the reduction and deposition of heavy metal from a borane physical developer by
   1. exposing to actinic radiation an element which comprises a support on which is coated a gelatino-silver halide emulsion,
   2. converting the exposed silver halide to elemental silver with a chemical developer,
   3. removing unexposed silver halide from the element and
   4. converting the developed elemental silver to catalytic centers for physical development by contacting the element with a rehalogenation bath to convert the elemental silver to silver halide which is reducible to catalytic silver nuclei when contacted with the borane physical developer, and

b. developing a heavy metal image by contacting the element with a physical developer solution comprising
   1. a reducible heavy metal salt of a metal selected from the group consisting of nickel and cobalt,
   2. at least one carboxylic acid complexing agent for heavy metal ions derived from the heavy metal salt, and
   3. an alkylamine borane.

19. A process as defined in claim 2 wherein catalytic heavy metal nuclei are formed by

1. exposing to actinic radiation an element containing silver halide,
2. converting the exposed silver halide to elemental silver with a chemical developer, and
3. reducing the silver halide in unexposed areas of the element to catalytic silver nuclei by contacting the element with the physical developer solution.

20. A process as defined in claim 19 which includes the step of removing the developed elemental silver from the element after chemical development.

21. A process as defined in claim 19 wherein the element comprises a support on which is coated a gelatino-silver halide emulsion.

22. A process as defined in claim 19 wherein the element comprises a support on which is coated silver halide carried in a binder comprising a mixture of gelatin and copoly-(styrene-methyl vinyl ketone-aminoguanidine).

23. A process as defined in claim 22 wherein the silver halide coverage is between about 2.5 and 15 mg. of silver per square foot.

24. A process as defined in claim 2 wherein catalytic heavy metal nuclei are formed by

1. exposing to actinic radiation an element containing a photoreducible ferric salt to reduce ferric ions in exposed areas of the element to ferrous ions, and
2. contacting the element with a heavy metal salt which is reducible by ferrous ions to catalytic heavy metal nuclei.

25. A process as defined in claim 24 wherein the heavy metal salt reducible by ferrous ions is a salt of a metal selected from the group consisting of silver, copper, gold, platinum, and palladium.

26. A process as defined in claim 25 wherein the photoreducible ferric salt is a mixture of ferric ammonium oxalate and ferric ammonium citrate.

27. A process for reproduction of images which comprises the steps of

a. forming on a photographic element heavy metal nuclei which are catalytic for the reduction and deposition of heavy metal from a borane physical developer by
   1. exposing to actinic radiation an element containing a mixture of ferric ammonium oxalate and ferric ammonium citrate to reduce ferric ions in exposed areas of the element to ferrous ions, and
   2. contacting the element with a solution of silver nitrate to form catalytic silver nuclei in exposed areas of the element and

b. developing a heavy metal image by contacting the element with a physical developer solution comprising
   1. a reducible heavy metal salt of a metal selected from the group consisting of nickel, cobalt and copper,
   2. a carboxylic acid complexing agent, and
   3. an amine borane reducing agent.

28. A physical developer for developing a heavy metal image on a photographic element containing catalytic heavy metal nuclei which comprises

1. a reducible heavy metal salt of a metal selected from the group consisting of nickel, cobalt, copper, chromium and iron.
2. a carboxylic acid complexing agent for heavy metal ions derived from the heavy metal salt, and

3. a borane reducing agent selected from the group consisting of phosphine boranes, arsine boranes and stibine boranes.

29. A physical developer for developing a heavy metal image on a photographic element containing catalytic heavy nuclei which comprises

1. a reducible heavy metal salt of a metal selected from the group consisting of copper, chromium and iron,
2. a carboxylic acid complexing agent for heavy metal ions derived from the heavy metal salt, and
3. a borane reducing agent selected from the group consisting of amine boranes, phosphine boranes, arsine boranes and stibine boranes.

30. A process for reproduction of images which comprises the steps of

a. forming on a photographic element heavy metal nuclei which are catalytic for the reduction and deposition of heavy metal from a borane physical developer by

1. exposing to actinic radiation an element comprising a support on which is coated a gelatino-silver halide emulsion,
2. converting the exposed silver halide to elemental silver with a chemical developer and
3. reducing the silver halide in unexposed areas of the element to catalytic silver nuclei, by contacting the element with a physical developer solution comprising a reducible heavy metal salt of a metal selected from the group consisting of nickel, cobalt and copper, a carboxylic acid complexing agent, and an amine borane reducing agent, and

b. developing a heavy metal image on said catalytic silver nuclei by deposition from said physical developer.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,650,748 Dated March 21, 1972

Inventor(s) Joseph S. Yudelson and Barbara F. Dernbach

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 45, "$\angle$ Pd(L)$_x$bh$\angle_y$M$_z$" should read ---$\angle$ Pd(L)$_x\angle_y$M$_z$---. Column 10, line 9, "to" should read ---in---. Column 12, Claim 5, line 46, "$\angle$ Pd(L)$_x$bh$\angle_y$M$_z$" should read ---$\angle$ Pd(L)$_x\angle_y$M$_z$---; Claim 5, line 55, "$\angle$ Pd(L)$_x$bh$\angle_y$M$_z$" should read ---$\angle$ Pd(L)$_x\angle_y$M$_z$---; Claim 6, line 63, "$\angle$ Pd(L)$_x$bh$\angle_y$M$_z$" should read ---$\angle$ Pd(L)$_x\angle_y$M$_z$---.

Column 14, line 67, Claim 27, after "agent" insert ---for heavy metal ions derived from the heavy metal salt, and---.

Signed and sealed this 11th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents