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PHOTOGRAPHIC BINDER OF VINYL POLYMER OF ANTHRANILATE UNITS

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16 Claims

ABSTRACT OF THE DISCLOSURE

Light-sensitive palladium compounds when carried in a polymeric binder having recurring vinyl anthranilate units exhibit improved photographic properties.

This invention relates to novel photographic elements and processes. In a particular aspect it relates to photographic elements containing photosensitive palladium compounds and to processes for physically developing these elements.

Physical development comprises the intensification or development of a latent image by treating the latent image with a developer solution which contains a reducible metal compound and a reducing agent. In physical development, virtually all the metal in the resultant visible 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 the 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 silver physical developer solutions are extremely unstable. Thus, shortly after a physical developer solution is prepared by mixing silver salts and reducing agent, reduced silver begins to deposit rapidly, so that in a few hours the developer solution 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 copending Yudelson et al. application Ser. No. 653,025, filed July 13, 1967, there is described a photographic element and process which can be employed with physical developer solutions which are extremely stable under conditions of storage. This system is based on photosensitive palladium compounds which upon exposure to actinic radiation form catalytic centers or sites for the deposition of metal from these stable physical developer solutions. Unlike silver, the palladium sites formed on exposure catalyze the reduction of metal compounds which have good autocatalytic properties. Therefore, physical developer solutions which are extremely stable under storage conditions can be formulated with such metal compounds and employed in the above-mentioned process, thus avoiding the disadvantages associated with silver physical development.

It is an object of this invention to provide novel photographic elements and processes.

It is a further object of this invention to provide novel

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photographic elements which can be developed with stable physical developers.

It is another object of this invention to provide novel physically developable photographic elements which exhibit improved photographic speed.

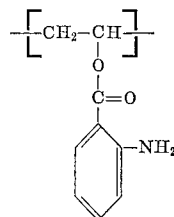
It is yet another object of this invention to provide novel physically developable photographic elements which can be stored without significant decay of the latent image formed on photoexposure.

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

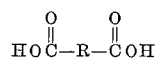
In accordance with this invention, I have found that my incorporating photosensitive palladium compounds in a polymeric binder having recurring vinyl anthranilate units, the photographic speed of the palladium compound is increased, the peak sensitivity of the palladium compound is shifted towards or into the visible region of the spectrum, and decay of the palladium latent image formed on photoexposure is minimized. Thus, the novel photographic elements of this invention comprise a layer of a polymer having recurring vinyl anthranilate units which contains a photosensitive palladium compound and the novel processes of this invention comprise photographically exposing such elements and then physically developing the palladium latent image thus formed with a stable physical developer.

The reason why improved and unexpected results are obtained when a vinyl anthranilate polymer is employed as a binder is not fully understood. While not wishing to be bound to any particular theory, it is possible that the palladium nuclei which are formed on photoexposure are protected by the anthranilate groups present in the binder and prevented from reforming as the palladium compound. In any event, and regardless of the reason therefor, photosensitive palladium elements employing a binder having recurring vinyl anthranilate units exhibit improved and unobvious properties over palladium photosensitive elements employing other binders.

The polymeric binders which exhibit the advantageous effects of the present invention are polymers comprising recurring units having the formula:



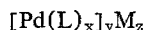
These polymers can be obtained by esterification of a hydroxyl-containing polymer, such as polyvinyl alcohol, with isatoic anhydride. Polymers containing from about 1 mole percent to about 30 mole percent of the vinyl anthranilate units are most useful, and polymers containing from about 5 to 15 mole percent of vinyl anthranilate units are preferred. In some instances it is desirable to improve the handling and coating properties of these polymers by incorporating therein additional groups. For example, groups derived from dicarboxylic acids having the formula



where R is an alkylene group of 1 to 6 carbon atoms (e.g., malonic acid, succinic acid, glutaric acid, etc.) can be attached to the polymer backbone to improve adhesion of the polymer to a support. Such polymers can be prepared by reacting the hydroxyl-containing polymer with a dicarboxylic acid or a dicarboxylic acid anhydride

prior to esterification with isoatoic anhydride. The polymers can contain up to 15 mole percent of such additional groups. A polymer which is particularly useful as a binder in the present invention is poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate). Reference is made to Smith and Copenhagen U.S. patent application entitled "Photographic Elements Containing Synthetic Polymeric Vehicles," Ser. No. 723,279, filed Apr. 22, 1968, for a further description of these polymers and the manner in which they are prepared.

The photosensitive palladium compounds which are useful in the practice of the present invention include salts and complexes of palladium which have the general formula:



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, ethylenediaminetetraacetic acid, etc., a nitrile such as nitrilotriethanol, benzonitrile, etc., an imine such as iminodiethanol, an oxime such as salicylaldehyde or hydrazide such as benzhydrazide, a phosphorus ligand such as triarylphosphine, trialkylphosphine, etc., an arsenic ligand such as triarylar sine, 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., an 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 $[\text{Pd}(\text{L})_x]$ 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.

Photosensitive elements useful in the practice of the present invention can be prepared by dispersing the palladium compound in the polymeric binder containing vinyl anthranilate units and then coating this photosensitive dispersion on a suitable support material. Alternatively, the polymeric binder can be coated on a support and then a solution of the photosensitive palladium compound can be imbibed into the binder.

Suitable support materials include paper, polyethylene-coated paper, porcelain, glass, polymeric films such as polystyrene film, cellulose nitrate film, cellulose acetate butyrate film, cellulose acetate propionate film, poly(ethylene terephthalate) film, poly(ethylene sebacate) film, poly(ethylene adipate) film, etc. and the like. These support materials can be coated or subbed with materials which aid adhesion of the binder to the support such as gelatin, polymers such as a terpolymer of methacrylic acid, itaconic acid, and vinylidene chloride, and the like.

The binder, or the palladium compound-binder dispersion, can be coated on the support by any well-known coating process such as hopper coating, doctor-blade coating, dip coating, swirl coating, spray coating, etc. Coating thicknesses will vary widely depending upon the particular application intended for the element. Normally, a coating thickness in the range of about 0.001 inch to about 0.01 inch is useful in the practice of the invention.

The amount of palladium compound present in the element can vary widely depending upon the particular application contemplated for the element. Amounts of palladium compound, calculated on the basis of palladium metal, as low as 2 mg. of palladium per square foot are adequate to provide useful images when using the development conditions described herein. The preferred coverage of palladium is in the range of 10 to 25 mg. of palladium per square foot. When the palladium compound is imbibed into the binder, the amount absorbed will depend upon such factors as the nature of the imbibing solution and its pH.

When using an imbibition technique, an aqueous solution of the palladium compound is prepared and then the binder-coated support is immersed into the solution in order for it to absorb palladium compound. It has been found that if the imbibing solution is acidic, the palladium compound is more easily imbibed into the binder and, once in the binder, the palladium compound exhibits greater photosensitivity. Extremely useful results have been observed when the pH of the imbibing solution is between about 2.5 and about 3.0. The acid used to adjust the pH of the imbibing solution should not react with the palladium compound nor displace ligands associated with the palladium compound. Such organic acids as p-toluenesulfonic acid are extremely useful for adjusting the pH of the imbibing solution. If the palladium compound contains a carboxylic acid ligand, the corresponding carboxylic acid can be employed to adjust the pH of the imbibing solution. Thus, if the palladium compound contains an oxalate ligand, oxalic acid could be used in adjusting the pH, if the palladium compound contains a malonate ligand, malonic acid could be used, etc.

Elements prepared according to the present invention can be exposed by techniques well known to those skilled in the art of photography. Since the compounds of this invention exhibit their greatest sensitivity in the blue and near ultraviolet regions of spectrum, light sources rich in such radiation are preferably employed. However, since the use of the polymeric binder containing recurring vinyl anthranilate units shifts the peak sensitivity of the palladium towards or into the visible region of the spectrum and increases the sensitivity of the compound in the visible region of the spectrum, white light sources can be used with practicable exposure times.

Exposure of the photosensitive palladium compound reduces the compound to nuclei of elemental palladium which act as catalytic centers or sites for the deposition of metal from a physical developer. Depending upon the light source and the particular palladium compounds, exposure times of from several seconds to several minutes give satisfactory latent images.

Development of the latent image in the exposed element can be effected by contacting the element with a physical developer, for example, by immersing the element in an aqueous solution of the physical developer. Suitable physical developers comprise a reducible heavy metal salt (e.g., a reducible salt of such metals as nickel, cobalt, iron, chromium or copper), a reducing agent for the heavy metal salt (e.g., formaldehyde, sodium hypophosphite, sodium hydrosulfite or potassium borohydride), and a complexing agent for heavy metal ions derived from the reducible heavy metal salt (e.g., a carboxylic acid such as malic acid, lactic acid, citric acid, aspartic acid or glycolic acid). Such physical developers are extremely stable under storage conditions, but in the presence of palladium

catalytic centers are reduced and deposit heavy metal on the palladium sites. The formulation of suitable physical developers and physical developer solutions is described in Yudelson et al. application Ser. No. 653,025 filed July 13, 1967. A particularly preferred class of physical developers are those described in copending Yudelson et al. application entitled "Photographic Physical Developers," Ser. No. 723,269 filed Apr. 22, 1968 in which the developer additionally comprises a complexing agent for palladium ions selected from the group consisting of gluconic acid, saccharic acid, and quinic acid. These physical developers are preferred because they are extremely stable even when contaminated with palladium ions.

The photosensitive compositions and elements of this invention find use in a wide variety of applications. Elements containing the photosensitive palladium compounds can be exposed to actinic radiation through a subject to be copied, such as a transparency, and then can be developed with an appropriate physical developer bath. In this manner the processes and elements of this invention can be used to produce positive and negative copies from originals and continuous tone and line negatives for a variety of uses for which systems based on silver are employed. Additionally, by appropriate selection of the reducible heavy metal incorporated in the physical developer bath, heavy metal images can be prepared which have properties which render them suitable for specialized applications such as the production of lithographic printing masters, electrically conducting images or patterns, and magnetic images or patterns.

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

EXAMPLE 1

A strip of gelatin subbed poly(ethylene terephthalate) film support is coated at a dry coverage of 200 mg./ft.² with poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate), in which the anthranilate and succinate groups are each present to the extent of 10 mole percent (prepared by the procedure described in Example 2 of Smith and Copenhagen patent application entitled "Photographic Elements Containing Synthetic Polymeric Vehicles," Ser. No. 723,279, filed Apr. 22, 1968). This coating is then imbibed for 10 minutes with a 0.5 percent solution of potassium dioxalato palladate (II) the pH of which has been lowered to 2.8 with oxalic acid. After drying, the film contains 53 mg./ft.² of potassium dioxalato palladate (II). The film is then exposed through a line copy negative for 15 seconds to an exposure unit drawing 1,000 watts distributed among a small fan and 28 tungsten bulbs. The bulbs are 2½ inches from the negative during exposure. The film is then developed by immersion for 3 minutes in a physical developer solution having the following composition:

	Mol/l.
Nickel chloride	0.1
Malic acid	0.4
Sodium hypophosphite	0.2
Gluconic acid	0.25
Ammonium hydroxide	0.75
Water to make 1 liter.	

A good quality positive print is obtained.

EXAMPLE 2

A sheet of gelatin subbed poly(ethylene terephthalate) film support is coated at a coverage of 350 mg./ft.² with poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate) as described in Example 1. A similar coating of gelatin on poly(ethylene terephthalate) film support is prepared. Both coatings are hardened by addition of 0.5 weight percent (based on the weight of the binder) of oxy-guar. The sheets are imbibed with a 0.5 percent solution of potassium dioxalato palladate (II) whose pH has been adjusted to 2.8 with p-toluenesulfonic acid. After dry-

ing, each coating contains approximately 50 mg./ft.² of potassium dioxalato palladate (II). Strips of these coatings are then exposed through a line copy negative for different lengths of time to the following light sources:

(A) Eight 8-watt black-light fluorescent tubes (General Electric F8T5-BL) spaced one inch from the negative and separated therefrom by a ⅛ inch clear Plexiglas plate, and

(B) Twenty-eight tungsten incandescent lamps (peak 450 millimicrons) arranged in four rows of seven bulbs per row. The exposure unit draws one thousand watts distributed among the 28 tungsten bulbs and a small fan. Exposure is through frosted glass at a distance of one inch from the tops of the bulbs. After exposure, the strips are developed by immersion for 3 minutes in a physical developer solution having the following composition:

	Mol/l.
Nickel chloride	0.1
Malic acid	0.4
Sodium hypophosphite	0.3
Gluconic acid	0.25
Ammonium chloride	0.4
Water to make 1 liter.	

The developer solution is adjusted to pH 9.0 with sodium hydroxide. Table I lists the exposures necessary to produce a dense black image (*D*=1.2) under these development conditions.

TABLE I

Binder	Exposure unit	
	A	B
Bone gelatin	15 sec.	5 min.
Poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate).	2 to 3 sec.	15 sec.

EXAMPLE 3

Coatings of gelatin and poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate) on poly(ethylene terephthalate) support are prepared as described in Example 2 and imbibed with a 0.5 percent solution of potassium dimesoxalato palladate (II). Both coatings contain approximately 65 mg./ft.² of this palladium complex. They are exposed for 1 minute through a 0.15 density wedge strip to an exposure unit composed of eight 8-watt black-light fluorescent tubes spaced 1 inch from the negative and separated from the negative by a ⅛ inch clear Plexiglas plate. The exposed coatings are then developed by immersion for 3 minutes in the physical developer solution described in Example 2. The coating employing the poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate) developed six steps whereas the coating employing the gelatin binder developed only 2 steps, thus indicating that the former is four times faster than the latter.

EXAMPLE 4

A 3 percent aqueous solution of poly(vinyl alcohol) (DuPont 71-30) is coated on a gelatin subbed poly(ethylene terephthalate) support to give a dry coverage of 300 to 350 mg./ft.². The coating is then hardened by exposure to a formaldehyde atmosphere. A 0.5 percent solution of potassium dioxalato palladate (II) whose pH has been adjusted to 2.8 with oxalic acid is imbibed into the poly(vinyl alcohol) coating and dried. The dried coating contains approximately 12 mg./ft.² of the palladium complex. A strip of this coating is exposed for 10 minutes through a line negative to the black-light exposure unit described in Example 3. It is then immersed in the physical developer solution described in Example 2 for 10 minutes. There is no sign of a visible image being developed on the coating. A second strip of this coating is exposed to a 350-watt Gates mercury arc through a line copy negative for 5 minutes. After exposure, the coating is immersed in the physical developer solution of Example 2 for 3 minutes. A good quality image appears on the coating.

7 EXAMPLE 5

This example illustrates the increase in spectral absorption and speed observed when a photosensitive palladium compound is coated in a poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate) binder. Coatings of potassium dioxalato palladate (II) are made in gelatin and in poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate) by the procedure described in Example 2 to give a palladium coverage of 20 mg./ft.² in each of the coatings. Spectral absorption of the coatings is then measured with a Beckman spectrophotometer. Table II, below, gives optical density, a measure of spectral absorption, of these coatings at various wavelengths after the spectral absorption characteristic of the binder has been subtracted.

TABLE II

Wavelength (mμ)	Gelatin binder	Optical density ¹
310.....	0.44	0.53
320.....	0.062	0.10
330.....	0.060	0
340.....	0.070	0
350.....	0.078	0
360.....	0.083	0.018
367.....	² 0.090	0.075
380.....	0.080	0.170
393.....	0.072	² 0.225
400.....	0.068	0.185
410.....	0.063	0.130
420.....	0.050	0.100
430.....	0.040	0.075
440.....	0.033	0.060
450.....	0.030	0.040
460.....	0.028	0.030

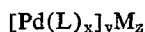
¹ Poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate) binder.
² Peak.

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

What is claimed is:

1. A photographic element comprising a support on which is coated a layer of a polymer having recurring vinyl alcohol and vinyl anthranilate units, said polymer layer containing a photosensitive palladium compound which upon exposure to actinic radiation forms catalytic centers for the deposition of metal from a physical developer solution.

2. A photographic element as defined in claim 1 wherein the photosensitive palladium compound has the formula:



where

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, metal ions and onium ions, and

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

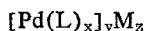
x is an integer from 0 through 4,

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.

3. A photographic element as defined in claim 1 wherein the photosensitive palladium compound has the formula:



where

L is a carboxylic acid ligand,

M is a cation,

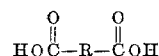
x is 2 or 4,

y is 1,

and z is 1 or 2.

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4. A photographic element as defined in claim 3 wherein the polymer includes units derived from a dicarboxylic acid having the formula



where R is an alkylene group of 1 to 6 carbon atoms.

5. A photographic element as defined in claim 3 wherein the polymer is poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate).

6. A photographic element as defined in claim 4 wherein the photosensitive palladium compound is selected from the group consisting of potassium dioxalato palladate (II), potassium dimalonato palladate (II), potassium dimesoxalato palladate (II) and potassium tetraoxamato palladate (II).

7. A photographic element comprising a support on which is coated a layer of poly(vinyl alcohol-co-vinyl anthranilate) in which the vinyl anthranilate units are present in amount of from about 1 mole percent to about 30 mole percent, said layer containing potassium dioxalato palladate (II).

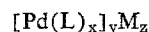
8. A photographic element comprising a support on which is coated a layer of poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate) in which the vinyl anthranilate and vinyl succinate units are present in amount of from about 5 mole percent to about 15 mole percent, said layer containing potassium dioxalato palladate (II).

9. A method of producing photographic images which comprises the steps of:

(a) exposing to actinic radiation a photosensitive element comprising a support on which is coated a layer of a polymer having recurring vinyl alcohol and vinyl anthranilate units, said polymer layer containing a photosensitive palladium compound which upon exposure to said actinic radiation forms catalytic centers for the deposition of metal from a physical developer solution, and

(b) developing the latent image thus formed with a physical developer comprising a reducible heavy metal salt, a complexing agent for heavy metal ions derived from said salt and a reducing agent for heavy metal ions derived from said salt.

10. A method as defined in claim 9 wherein the photosensitive palladium compound has the formula:



where

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,
metal ions and
onium ions, and

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

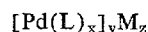
x is an integer from 0 through 4,

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.

11. A method as defined in claim 9 wherein the photosensitive palladium compound has the formula:



where

L is a carboxylic acid ligand,

M is a cation,

x is 2 or 4,

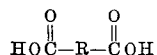
y is 1,

and z is 1 or 2.

12. A method as defined in claim 11 wherein the reducible heavy metal salt is selected from the group consisting of nickel salts, cobalt salts, iron salts, chromium salts, copper salts and mixtures thereof.

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13. A method as defined in claim 11 wherein the polymer includes units derived from a dicarboxylic acid having the formula



wherein R is an alkylene group of 1 to 6 carbon atoms.

14. A method as defined in claim 13 wherein the photosensitive palladium compound is selected from the group consisting of potassium dioxalato palladate (II), potassium dimalonato palladate (II), potassium dimesoxalato palladate (II) and potassium tetraoxamato palladate (II).

15. A method for producing photographic images which comprises the steps of

(a) exposing to actinic radiation a photosensitive element comprising a support on which is coated a layer of poly(vinyl alcohol-co-vinyl anthranilate), in which the vinyl anthranilate units are present in amount of from about 1 mole percent to about 30 mole percent, said layer containing potassium dioxalato palladate (II), and

(b) developing the latent image thus formed with a physical developer solution comprising an aqueous solution of a reducible salt of a heavy metal selected from the group consisting of nickel, cobalt, iron, chromium, copper and mixtures thereof, a reducing agent for heavy metal ions derived from said salt, and a complexing agent for heavy metal ions derived from said salt.

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16. A method for producing photographic images which comprises the steps of

(a) exposing to actinic radiation a photosensitive element comprising a support on which is coated a layer of poly(vinyl alcohol-co-vinyl anthranilate-co-vinyl succinate), in which the vinyl anthranilate and vinyl succinate units are present in amount of from about 5 mole percent to about 15 mole percent, said layer containing potassium dioxalato palladate (II), and

(b) developing the latent image thus formed by immersing the element in an aqueous solution of a physical developer comprising a reducible nickel salt, a reducing agent for nickel ions and a complexing agent for nickel ions.

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