Novel photographic elements and processes are described. Active sites for physical development are created by the action of a sensitizing compound on a reducible metal salt.

25 Claims, No Drawings
PHOTOGRAPHIC ELEMENTS AND PROCESSES

This invention relates to novel photographic elements, compositions and processes.

Physical development comprises the intensification or development of catalytic nuclei, e.g., by treating the nuclei with a developer solution which contains a reducible metal compound and a reducing agent. In physical development, virtually all of 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 storage conditions, but that in the presence of a catalyst such as a metallic latent image, it decomposes and deposits reduced metal on the catalytic sites. Once a catalytic site is enveloped with metal deposited from developer solution, it is essential that the reduced metal be auto-catalytic, that is it too must catalyze the decomposition of the physical developer solution.

The catalytic nuclei used in the formation of the latent image are generated by several techniques. One method involves the formation of active sites for subsequent physical development by using a light sensitive metal salt as the nucleating agent precursor. When subjected to actinic radiation, the metal in the salt is reduced to zero valency, thus forming the nuclei or active sites for further physical development. A disadvantage in the use of this technique is that very often, long exposure times are required. A second method involves the use of metal salts as nucleating agent precursors which are not necessarily light sensitive. A light sensitive sensitizer is used in conjunction with these compounds. When subjected to actinic radiation, the sensitizer reduces the metal in the salt to the elemental state thus providing active sites for subsequent physical development. Difficulty has been encountered in finding sensitizers which are stable upon storage. Photographic elements containing such sensitizers frequently have exhibited extremely poor keeping characteristics.

It is therefore an object of this invention to provide novel photographic elements which are developable with physical developers.

It is a further object of this invention to provide photographic processes utilizing the novel elements developed herein.

It is a further object of this invention to provide novel photographic compositions.

An additional object of the invention is to provide novel photographic elements having good keeping properties.

It is still another object of this invention to provide novel elements having good photographic speeds.

These and other objects are accomplished with photographic elements having a support which contains (a) a metallic salt nucleating agent precursor which is capable of forming active or catalytic sites for subsequent physical development and (b) a sensitizer which is a photosensitive compound containing a heterocyclic nitrogen atom which is substituted by either an alkyl or an acyl group. When such an element is exposed to actinic radiation, the sensitizer causes the metallic salt nucleating agent precursor to form catalytic sites for physical development. The action of the light-struck sensitizer on the metal salt comprising the nucleating agent precursor causes reduction of the metal in the salt. It is the metal in reduced form which provides the active or catalytic sites. This subsequent physical development may be accomplished for example with any of the conventional physical developers.

The use of the novel photographic elements of this invention provides reproductions having high resolution. Additionally, such elements are characterized by a high inherent photolytic speed which is directly attributable to the high speeds of the sensitizers employed. Another advantage residing in the use of the described elements is their broad spectral response. The various sensitizers which can be used in the elements have varying spectral responses, so such a particular sensitizer or combination of sensitizers can be used depending on the nature of the activating radiation. The sensitizers incorporated in the elements of the invention are relatively stable under ambient conditions and thus the novel elements have good “keeping” properties. An additional advantage is that the metallic salt nucleating agent need not be a light sensitive material. Thus, a host of inexpensive metal salts can be used as nucleating agents provided they are responsive to the sensitizers described herein.

Typical sensitizing compounds of this invention can have one of the general formulas:

wherein:

- $R_1$ can be any of the following:
  - a methine linkage terminated by a heterocyclic nucleus of the type contained in cyanine dyes, e.g., those set forth in Mees and James, “The Theory of the Photographic Process,” MacMillan, 3rd ed., pp. 198-232; the methine linkage can be substituted or unsubstituted, e.g., $-\text{CH} = \text{CH}(\text{C}_2\text{H}_4)$, $-\text{CH} = \text{CH} = \text{CH} = (-\text{CH} = \text{CH} = \text{CH} =)$, etc.;
  - an alkyl radical preferably containing one to eight carbon atoms including a substituted alkyl radical;
  - an aryl radical including a substituted aryl radical such as a phenyl radical, a naphthyl radical, a tolyl radical, etc.;
  - a hydrogen atom;
  - an acyl radical having the formula

wherein $R_4$ is hydrogen or an alkyl group preferably having one to eight carbon atoms;

- f. an aminovinyl radical such as a radical having the formula

wherein $R_5$ is hydrogen, acyl or alkyl, or

- g. a styrly radical including substituted styrly radicals, e.g.,

wherein $R_5$ is hydrogen, alkyl, aryl, amino including dialkylamino such as dimethylylamino;

$R_4$ can be either of the following:

- a. a methine linkage terminated by a heterocyclic nucleus of the type contained in merocyanine dyes, e.g., those set forth in Mees and James (cited above); the methine linkage can be substituted or unsubstituted;

- b. an allylidene radical including a substituted allylidene radical such as a cyanoallylidene radical, an alkylcarboxy-allylidene radical or an alkylsulfonfallylidene radical;

$R$ can be either:

- a. an alkyl radical preferably having one to eight carbon atoms such as methyl, propyl, ethyl, butyl, etc., including a substituted alkyl radical such as sulfoalkyl, e.g., $-(\text{CH}_3)_2\text{SO}_2-$, an aralkyl, e.g., benzyl or pyridinato-oxalylalkyl salt, e.g., $\text{CH}_3\text{H}_2\text{O}-\text{Y}$ wherein Y is substituted or unsubstituted pyridinium salt; or

- b. an acyl radical, e.g.

wherein $R_4$ is an alkyl radical preferably having one to eight carbon atoms or aryl radical, e.g., methyl, ethyl, propyl, butyl, phenyl, napththyl, etc.
The preferred sensitizing compounds of the invention have one of the following structures:

(A) \[
\begin{align*}
N(\text{CH-Ch})_n \rightarrow C \rightarrow \text{L-M}L \rightarrow C \rightarrow \text{N-R}_2
\end{align*}
\]

(B) \[
\begin{align*}
N(\text{CH-Ch})_n \rightarrow C \rightarrow \text{L-M}L \rightarrow C \rightarrow \text{N-R}_2
\end{align*}
\]

(C) \[
\begin{align*}
N(\text{CH-Ch})_n \rightarrow X \rightarrow \text{L-M}L \rightarrow X \rightarrow \text{N-R}_2
\end{align*}
\]

(D) \[
\begin{align*}
N(\text{CH-Ch})_n \rightarrow X \rightarrow \text{L-M}L \rightarrow X \rightarrow \text{N-R}_2
\end{align*}
\]

(E) \[
\begin{align*}
N(\text{CH-Ch})_n \rightarrow C \rightarrow \text{L-M}L \rightarrow C \rightarrow \text{N-R}_2
\end{align*}
\]

(F) \[
\begin{align*}
N(\text{CH-Ch})_n \rightarrow C \rightarrow \text{L-M}L \rightarrow C \rightarrow \text{N-R}_2
\end{align*}
\]

wherein Q_1, Q_2, and Q_3 each represent the nonmetallic atoms necessary to complete a sensitizing or desensitizing nucleus containing five or six atoms in the heterocyclic ring, which nucleus can contain at least one additional hetero atom such as oxygen, sulfur, selenium or nitrogen, i.e., a nucleus of the type used in the production of cyanine dyes, such as the following representative nuclei: a thiazole nucleus, e.g., thiazole, 4-methylthiazole, 3-ethylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 4- or 5-nitrobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 6-nitrobenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-chloro-6-nitrobenzothiazole, 4-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-methyl-5-ethoxybenzothiazole, 4-ethoxybenzothiazole, 4-ethylbenzothiazole, 5-phenoxazolone, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylenbenzoxazole, 5- or 6-nitrobenzoxazole, 5-chloro-6-nitrobenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 5,6-dimethoxybenzoxazole, 5-ethylbenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 5-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, \(\alpha\)-naphthoxazole, \(\beta\)-naphthoxazole, nitro group substituted naphthoxazoles, etc.; a selanole nucleus, e.g., 4-methylselanole, 4-nitroselanole, 4-phenylselanole, benzoeselanole, 5-chlorobenzoeselanole, 5-methoxybenzoeselanole, 5- or 6-nitrobenzoeselanole, 5-chloro-6-nitrobenzoeselanole, tetrahydrobenzoeselanole, \(\alpha\)-naphthoeselanole, \(\beta\)-naphthoeselanole, nitro group substituted naphthoeselanoles, etc.; a thiazole nucleus, e.g., thiadiazole, 4-methylthiazole, etc.; a pyridine nucleus, e.g., 2-pyridine, 3-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine, nitro group substituted pyridines, etc.; a quinoline nucleus, e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 6-nitro-2-quinoline, 8-chloro-2-quinoline, 8-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4,5-dimethoxyquinoline, 4-quinoline, 7-methyl-4-quinoline, 8-nitro-4-quinoline, 1-isoquinoline, 6-nitro-1-isoquinoline, 3,4-dihydro-1-isoquinoline, 3-isoquinoline, etc.; a 3,3-dialkylindolinediene nucleus, preferably having a nitro or cyano substituent, e.g., 3,3-dimethyl-5 or 6-nitroindolenine, 3,393 -dimethyl-5 or 6-cyano-indolene, etc.; and an imidazole nucleus, e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazol, benzimidazole, 1-alkylbenzimidazole, 1-alkyl-5-nitrobenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-alkyl-\(\alpha\)-naphthimidazole, 1-aryl-\(\beta\)-naphthimidazole, 1-alkyl-5-methoxy-\(\alpha\)-naphthimidazole, or, an imidazo[4,5-b]quinoline nucleus, e.g., 1-alkylimidazo[4,5-b]quinoline, 6-chloro-1-ethylimidazo[4,5-b]-quinoxaline, etc.; 1-alkenylimidazo[4,5-b]quinoxaline such as 1-alkylimidazo[4,5-b]quinoxaline, 6-chloro-1-ethylimidazo[4,5-b]quinoxaline, etc.; 1-arylquinoxaline, 1-alkenylimidazo[4,5-b]quinoxaline, such as phenylimidazo[4,5-b]quinoxaline, 6-chloro-1-phenylimidazo[4,5-b]quinoxaline, etc.; a 3,3-dialkyl-3H-pyrrolo-[2,3-b]pyrindine, 3,3-diethyl-3H-pyrrolo[2,3-b]pyridine, etc.; a thiazolo[4,5-b]quinoline nucleus, \(R_3\) represents an alkyl group, including substituted alkyl (preferably a lower alkyl containing from one to four carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., and substituted alkyl groups (preferably a lower alkyl containing from one to four carbon atoms), such as a hydroxalkyl group, e.g., \(\beta\)-hydroxyethyl, \(\omega\)-hydroxybutyl, etc., an alkoxalkyl group, e.g., \(\beta\)-methoxyethyl, \(\omega\)-butoxybutyl, etc., a carboxylalkyl group, e.g., \(\beta\)-carboxyethyl, \(\omega\)-carboxybutyl, etc., an alkoxyl group, e.g., methoxy, ethoxy, etc., a sulfalkyl group, e.g., \(\beta\)-sulfethyl, \(\omega\)-suflybutyl, etc., a sulfalkylalkyl group, e.g., \(\beta\)-sulfatoethyl, \(\omega\)-sulfatoxybutyl, etc., an acyloxyalkyl group, e.g., \(\beta\)-acetoxyethyl, \(\omega\)-acetoxypropyl, etc., an oxaloxybutyl, etc., an alkoxybenzene-alkyl group, e.g., \(\beta\)-methoxybenzethoxyethyl, \(\omega\)-ethoxybenzethoxybutyl, etc., an aralkyl group, e.g., benzyl, phenethyyl, etc., an alkyl group, e.g., allyl, 1-propenyl, 2-butyl, etc., a 5-alkyl group, e.g., phenyl, tolyl, naphthyl, methoxyphenyl, chlorophenyl, etc.; \(Q_3\) represents the nonmetallic atoms required to complete a 5 to 6 membered heterocyclic nucleus, typically containing a hetero atom selected from nitrogen, sulfur, selenium, and oxygen, such as a 2-pyrazolin-5-one nucleus (e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.; an oxazole nucleus (e.g., 3-phenyl-5(4H)-oxazolone, 3-methyl-5(4H)-oxazolone, 3-ethyl-5(4H)-oxazolone, etc.; an oxindole nucleus (e.g., 1-alkyl-2,3-dihydro-2-oxindoles, etc.), a 2,4,6-triketohexahydropyrimidine nucleus (e.g., barbituric acid or 5,6-thiobitaric acid as well as their 1-alkyl derivatives, e.g., 1-ethyl, 1-propyl, 1-heptyl, etc.) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-disopropyl, 1,3-dicyclohexyl, 1,3-di(\(\beta\)-methoxyethyl), etc.) or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxy-
R₈ is an alkyl isonitroxy radical having one to eight carbon atoms in the alkyene chain including an alkylidenooxy radical and an arylenebisoxy radical e.g., ethylisoxenoy, trimethylenoxenoy, tetramethylenoxenoy, propylenoxenoy, 5-ethylenidenoxy, phenylenebisethoxy, etc.

R represents either (1) an alkyl radical including a substituted allyl radical (having one to four carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, aralkyl such as benzylic, sulfoalkyl such as β-sulfoethyl, ω-sulfobutyl, ω-sulfoxypropyly; or (2) an acyl radical, e.g.,

\[ \text{wherein } R₈ \text{ is an alkyl including a substituted allyl or an aryl radical such as methyl, phenyl, naphthyl, propyl, benzylic, etc.} \]

Typical sensitizing compounds included in the scope of this invention are the following:

1. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid anhydride
2. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid tetrafluoroborate
3. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid idoxide
4. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid tetrafluoroborate
5. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid idoxide
6. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid perchlorate
7. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid tetrafluoroborate
8. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid hydroxide
9. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid perchlorate
10. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid tetrafluoroborate
11. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid perchlorate
12. 3-ethyl-1-methoxy-4',5'-benzo-2-pyridocarboxylic acid perchlorate
13. 3-ethyl-1-methoxy-4',5'-benzo-2-pyridocarboxylic acid tetrafluoroborate
14. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid tetrafluoroborate
15. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid hydroxide
16. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid tetrafluoroborate
17. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid tetrafluoroborate
18. 3-ethyl-1-methoxy-2'-pyridocarboxylic acid perchlorate
19. 3-ethyl-1-methoxy-4',5'-benzo-2-pyridocarboxylic acid perchlorate
20. 3-ethyl-1-methoxy-4',5'-benzo-2-pyridocarboxylic acid perchlorate
21. 3-ethyl-1-methoxy-4',5'-benzo-2-pyridocarboxylic acid hydroxide
22. 3-ethyl-1-methoxy-4',5'-benzo-2-pyridocarboxylic acid tetrafluoroborate
coated on a support using any of the known coating methods. Supporting materials can be any of the known materials for this purpose, such as film base (e.g., cellulose nitrate film, cellulose ester film, etc.), plastic supports (e.g., polyethylene, polyethylene terephthalate, etc.) paper including resin treated papers, metal, glass, and the like.

Suitable binders for incorporating the organic compounds include any of the water-permeable materials, such as gelatin or other hydrophilic materials, such as colloidion, albumin, cellulose derivatives, synthetic resins such as poly(vinyl alcohol) and the like.

In preparing the coating compositions described herein, the binder and sensitizer are dispersed in a suitable aqueous vehicle such as water. The amount of sensitizer employed ranges from about 0.1% to about 5.0% by weight based on the weight of the total coating composition. The amount of vehicle employed ranges from about 5.0% to about 60% by weight, based on the weight of the total coating composition.

Coating thicknesses of the composition on a support can vary widely. Normally, a wet coating thickness in the range of about 0.001 inch to about 0.01 inch is useful in the practice of this invention. A preferred range of coating thickness is from about 0.002 inch to about 0.006 inch before drying. Greater thicknesses can vary widely depending on the particular application desired for the photographic element. After the composition is coated, the elements are dried at slightly elevated temperatures for one hour or more.

The photographic elements prepared in the manner described above are then exposed in an imagewise manner to a pattern of actinic radiation. The radiation causes the sensitizer to become an active reducing agent in the areas which have been exposed. The exposure time varies depending on the nature of the light source and the sensitizer used. Generally, however, exposure times vary from about 0.1 to about 60 or more seconds. Upon completion of the exposure step, the element is contacted with a solution of one of the metallic salt nucleating agent precursors described above. The contacting can be accomplished by any of several known techniques such as swabbing the solution on the surface of the element or by immersing the element in the solution. The metal salt is reduced by the sensitizer in the exposed areas of the element thus creating active or catalytic sites for subsequent physical development.

In an alternate embodiment, the photographic element is prepared by coating a composition containing a binder, a sensitizer, a carrier and the metallic salt nucleating agent precursor. In situations of this type, the nucleating agent precursor is present in an amount ranging from about 0.1% to about 50% by weight of the total coating composition. Exposure of an element of this type causes activation of the sensitizer in the light struck regions and immediate successive reduction of the metal salt to form active nuclei. In this embodiment, a separate solution containing the nucleating agent precursor is not necessary.

The exposed element containing the active or catalytic sites is then developed by any of the known physical development processes. The particular process or physical developer employed is dependent on the nature of the active sites created, certain physical developers being more suitable for specific classes of reduced metallic salts than others. Typical physical developers are described in U.S. Pat. No. 3,404,980, British Pat. No. 1,143,021, U.S. Ser. No. 653,025 filed July 13, 1967 by Yudelson et al.; U.S. Ser. No. 723,278 filed Apr. 22, 1968 by Yudelson; U.S. Ser. No. 778,323 filed Nov. 22, 1968 by Yudelson et al., Photographic Science and Engineering, Volume 13, No. 1.

The mechanism or theory pertaining to the function of the sensitizer on the metal salt is not completely understood. However, it is believed that when the sensitizer is struck by actinic radiation, it is decomposed or fragmented to several different fractions. Some of these fractions are reducing agents for the metal salt. The particular route of the fragmentation reaction is believed to be somewhat dependent upon the structure of the original compound. However, based upon observations, it is believed that the route followed, when a sensitizer of this invention (such as the one given below) is exposed to actinic radiation, is the following:

\[
\text{I} + \text{CHO} \rightarrow \text{CH}_2\text{O} + \text{I}^- \\
\text{H}^+ + \text{CH}_2\text{O}
\]

In this instance the aldehyde fragment is believed to cause the reduction of the metal salt as to form active sites for physical development.

In preparing the photographic elements of this invention, a sensitizer is dispersed in a suitable binder and then the mixture
will continue after the active sites are enveloped with heavy metal. With respect to the Periodic Table, suitable heavy metals can be selected from Group VIII metals such as nickel, cobalt, iron, palladium and platinum, Group VI B metals such as chromium and Group IB 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, silver bromide, silver chloride, silver 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 deposited 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 latent image sites in the presence of the catalyst. Suitable complexing agents include ammonium compounds such as ammonium hydroxide or chloride, organic acids such as aspartic acid, malic acid, citric acid, glycine acid, salts of organic acids such as sodium citrate, potassium citrate, sodium glycinate, potassium glycinate, sodium succinate, potassium succinate, potassium tartarate, 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. A general criteria for a reducing agent useful in the physical developers of the present invention is that the potential of the chemical coupler of the reducing agent, written as follows:

Reducing agent $\rightarrow$ Products + electrons must be more positive than that for the metal or metals which are to be deposited from the bath. For example, the potential for the nickel coupler:

$$\text{Ni}^{2+} \rightarrow \text{Ni}^{2+} + 2 \text{ electrons}$$

is $+0.277$ volts for acidic solutions. It is necessary for the reducing agent to possess a potential that is greater, i.e., more positive, than $+0.277$ volts in order that it be capable of reducing nickel ions in the bath. Suitable reducing agents include formaldehyde, hypophosphites such as sodium hypophosphate, manganous hypophosphate, potassium hypophosphite, etc., hydrosulfites such as sodium hydrosulfite, potassium hydrosulfite, calcium hydrosulfite, etc., borohydrides such as sodium borohydride, potassium borohydride, etc., borane amines such as dimethylborane amine, etc., hydrazines, 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 1.0 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 0.2 mole 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 moles to about 5 moles of reducing agent per mole of metal salt present.

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

**EXAMPLE 1**

A solution containing 0.025 grams of 2-β-anilinovinyl-1-methoxyoxa-2-pyridocarbo cyanine perchlorate (Compound 26) and 5.0 grams of a 10 percent aqueous gelatin solution is coated on paper using a 3 mil coating knife. The element is dried and then exposed to a negative image transparency for about 10 seconds using a 400 watt mercury light source at a distance of 1.5 inch. The exposed element is then swabbed with an ammonical silver nitrate solution (prepared by adding 0.1N AgNO₃ solution to a 28% NH₄OH solution in an amount sufficient to cause the resultant cloudy mixture to become clear), washed with water and dried. The active sites thus created are next physically developed by immersing the element in a silver physical developer such as that described in U.S. Pat. No. 3,409,432 (Example 2). A dark brown image is obtained in those areas which had been initially exposed.

**EXAMPLE 2**

Example 1 is repeated except the active sites are formed by swabbing the surface of the exposed element with an acidic solution of palladium chloride (0.10 gm. PdCl₂, 4.0 ml. of 0.01 N HCl). After drying, the element is physically developed in the same manner as described in Example 1. A sharp, dark image is obtained in those areas which had been initially exposed.

**EXAMPLE 3**

Example 2 is repeated except that the active sites are physically developed using a nickel developer as described in Example 4 of U.S. Ser. No. 778,323 filed Nov. 22, 1968 by Yudelson et al. The reproduction once again has a sharp dark image.

**EXAMPLE 4**

Example 2 is repeated except the sensitizer employed is 3-ethyl-1'-methoxyoxa-2-pyridocarbo cyanine perchlorate (Compound 1). Again a reproduction is obtained having sharp, dark images.

**EXAMPLE 5**

Example 1 is repeated using 3'-ethyl-1-methoxy-2-pyridothiacyanine iodide (Compound 3) as the sensitizer. A very satisfactory reproduction is obtained.

**EXAMPLES 6-12**

Example 3 is repeated using various sensitizers. The sensitizers used and the quality of the reproduction are described in the following Table 1.

**TABLE 1**

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Quality of Reproduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>Sharp, dark images</td>
</tr>
<tr>
<td>Compound 2</td>
<td>Sharp, dark images</td>
</tr>
<tr>
<td>Compound 3</td>
<td>Sharp, dark images</td>
</tr>
</tbody>
</table>


### EXAMPLE 13

A solution containing 0.025 grams of 2-β-anilinovinyl-1-methoxypyridinium p-toluene sulfonate, 5.0 grams of a 10 percent aqueous gelatin solution and 0.10 grams of palladium chloride is coated on paper using a 3 mil coating knife. The element is dried and then exposed in a manner described in Example 1. The active sites created by the exposure are physically developed with the developer described in Example 6 of U.S. Pat. No. 3,404,980. A good dense image is obtained.

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.

We claim:

1. A photographic element comprising a support having thereon a metallic salt nucleating agent precursor capable of forming active sites for physical development and a photosensitive compound containing a heterocyclic nitrogen atom which is substituted by a member selected from the group consisting of an alkoxy group and an acyloxy group.

2. A photographic element comprising a support having thereon a metallic salt nucleating agent precursor capable of forming active sites for physical development and a photosensitive compound having a formula selected from the group consisting of:

3. The element as defined in claim 2 wherein Z represents the atoms necessary to complete a 5 to 6 membered heterocyclic nucleus.

4. The element as defined in claim 2 wherein Z represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus and a quinoline nucleus.

5. The element as defined in claim 2 wherein Z represents the atoms necessary to complete a 5 to 6 membered heterocyclic nucleus.

6. A photographic element comprising a support having thereon a metallic salt nucleating agent precursor capable of forming active sites for physical development and a photosensitive compound having a formula selected from the group consisting of:

7. The photographic element of claim 6 wherein said photosensitive compound has the formula:

8. The photographic element of claim 6 wherein said photosensitive compound has the formula:
3,649,275

13

wherein R, \( R_m \), Q2, L, G, X, m and n are defined in claim 6.
9. The photographic element of claim 6 wherein said photosensitive compound has the formula:

\[
\begin{array}{c}
\text{Q2} \\
\text{R} \quad \text{N}^- \\
\text{R}_m \\
\text{OR} \quad \text{X}^-
\end{array}
\]

wherein R, \( R_m \), Q2, X and \( R_m \) are defined in claim 6.

10. The photographic element of claim 6 wherein said photosensitive compound has the formula:

\[
\begin{array}{c}
\text{Q2} \\
\text{R} \quad \text{N}^- \\
\text{R}_m \\
\text{OR} \quad \text{X}^-
\end{array}
\]

wherein R, \( R_m \), Q2, X and \( R_m \) are defined in claim 6.

11. The photographic element of claim 6 wherein said metallic salt nucleating agent precursor is a salt of a metal selected from the group consisting of silver, gold, copper, platinum, palladium, iron, nickel, cobalt, chromium, mercury, lead, tin and zinc.

12. A photographic element comprising a support having thereon a metallic salt nucleating agent precursor capable of forming active sites for physical development and a photosensitive compound which is a 2-\( \beta \)-anilinovinyl-1-methoxypyrindium salt.

13. The element of claim 12 wherein said metallic salt nucleating agent precursor is a silver salt.

14. The element of claim 12 wherein said metallic salt nucleating agent precursor is a palladium salt.

15. A process for forming a physically developable latent image comprising (a) providing a photographic element comprising a support having thereon a metallic salt nucleating agent precursor capable of forming active sites for physical development and a photosensitive compound containing a heterocyclic nitrogen atom which is substituted by a member selected from the group consisting of an alkyl group, and an acyloxy group, and (b) exposing said element to a pattern of actinic radiation thus forming a physically developable latent image.

16. A process for forming a physically developable latent image comprising (a) providing a photographic element comprising a support having thereon a metallic salt nucleating agent precursor capable of forming active sites for physical development and a photosensitive compound having a formula selected from the group consisting of:

\[
\begin{array}{c}
\text{Z}^- \\
\text{R}_m \\
\text{OR} \quad \text{X}^-
\end{array}
\]

wherein:

\( R_m \) is selected from the group consisting of:

\[\begin{align*}
&\text{a. a methine linkage terminated by a heterocyclic nucleus} \\
&\text{of the type contained in cyanine dyes,} \\
&\text{b. an alkyl radical,} \\
&\text{c. an anilinovinyl radical,} \\
&\text{d. a hydrogen atom,} \\
&\text{e. an aryl radical,} \\
&\text{f. an aldehyde group,} \\
&\text{g. a styryl radical;}
\end{align*}\]

\( R_m \) is selected from the group consisting of:

\[\begin{align*}
&\text{a. a methine linkage terminated by a heterocyclic nucleus} \\
&\text{of the type contained in merocyanine dyes} \\
&\text{and an acyl radical;}
\end{align*}\]

\( X^- \) is an acid anion; and

\( Z \) represents the atoms necessary to complete a 5 to 6 membered heterocyclic nucleus, and (b) exposing said element to a pattern of actinic radiation thus forming a physically developable latent image.

\[\begin{align*}
&\text{17. The process of claim 16 wherein } Z \text{ represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus and a quinoline nucleus.} \\
&\text{18. The process as defined in claim 16 wherein } R_m \text{ is a methine linkage terminated by a 5 to 6 membered heterocyclic nucleus.} \\
&\text{19. The process as defined in claim 16 wherein said nucleating agent precursor is a salt of a metal selected from the group consisting of silver, gold, copper, platinum, palladium, iron, nickel, cobalt, chromium, mercury, lead, tin and zinc.} \\
&\text{20. A process for forming a physically developable latent image comprising (a) providing a photographic element comprising a support having thereon a photosensitive compound containing a heterocyclic nitrogen atom which is substituted by a member selected from the group consisting of an alkyl group, and an acyloxy group,} \\
&\text{b. exposing said element to a pattern of actinic radiation, and} \\
&\text{c. contacting the exposed element with a solution of a metallic salt nucleating agent precursor thus forming a physically developable latent image.} \\
&\text{21. A process for forming a physically developable latent image comprising (a) providing a photographic element comprising a support having thereon a photosensitive compound having a formula selected from the group consisting of:}
\end{align*}\]

\[
\begin{array}{c}
\text{Z}^- \\
\text{R}_m \\
\text{OR} \quad \text{X}^-
\end{array}
\]

wherein:

\( R_m \) is selected from the group consisting of:

\[\begin{align*}
&\text{a. a methine linkage terminated by a heterocyclic nucleus} \\
&\text{of the type contained in cyanine dyes,} \\
&\text{b. an alkyl radical,} \\
&\text{c. an anilinovinyl radical,} \\
&\text{d. a hydrogen atom,} \\
&\text{e. an aryl radical,} \\
&\text{f. an aldehyde group,} \\
&\text{g. a styryl radical;}
\end{align*}\]

\( R_m \) is selected from the group consisting of:

\[\begin{align*}
&\text{a. a methine linkage terminated by a heterocyclic nucleus} \\
&\text{of the type contained in merocyanine dyes and an acyl radical;} \\
&\text{b. an allylidene radical;}
\end{align*}\]

\( X^- \) is an acid anion; and

\( Z \) represents the atoms necessary to complete a 5 to 6 membered heterocyclic nucleus, (b) exposing said element to a pattern of actinic radiation and (c) contacting the exposed element with a solution of a metallic salt nucleating agent precursor thus forming a physically developable latent image.

\[\begin{align*}
&\text{22. The process of claim 21 wherein } Z \text{ represents the atoms necessary to complete a member selected from the group consisting of a pyridine nucleus and a quinoline nucleus.} \\
&\text{23. The process as defined in claim 21 wherein } R_m \text{ is a methine linkage terminated by a 5 to 6 membered heterocyclic nucleus.} \\
&\text{24. The process as defined in claim 21 wherein said nucleating agent precursor is a salt of a metal selected from the group consisting of silver, gold, copper, platinum, palladium, iron, nickel, cobalt, chromium, mercury, lead, tin and zinc.} \\
&\text{25. A photographic composition comprising a metallic salt nucleating agent precursor capable of forming active sites for physical development and a photosensitive compound containing a heterocyclic nitrogen atom which is substituted by a member selected from the group consisting of an alkyl group and an acyloxy group.}
\end{align*}\]