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PHOTOGRAPHER HARDENER-DEVELOPER COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Compositions comprising a chelate compound inorganic developing agent for silver halide and an organic aldehyde hardening agent for photographic hydrophilic colloid layers are used to advantage to combine in a single process step the hardening and developing steps in color processes.

This invention is related to photography, including developer compositions for use in rapid processing of color photographic materials and rapid processes for color photographic materials.

Multilayer, multicolor photographic materials are well known in the art. Some of these materials contain incorporated color-forming couplers in the appropriately sensitized silver halide emulsion layers. Usually a cyan-forming (e.g., phenolic or naphtholic) coupler is incorporated in the red-sensitized silver halide emulsion layer, a magenta-forming (e.g., 5-pyrazolone coupler is incorporated in the green-sensitized silver halide emulsion layer and a yellow-forming open chain (e.g., acylacetanilide, an acylacetamide, a pivalylacetanilide, a pivalylacetamide, etc.) coupler is incorporated in the blue-sensitive silver halide emulsion layer. Usually these layers are coated on a support in the same order mentioned, however, they are sometimes coated on the support in other orders. The other color materials do not contain incorporated couplers, so the appropriate coupler is usually incorporated in separate color developer solutions used to color develop the differently sensitized silver halide emulsion layers. Usually a cyan-forming coupler is incorporated in the developer used to form a cyan dye image in the red-sensitized layer, a magenta-forming coupler is used in the developer solution that forms the magenta image in the green-sensitive layer and a yellow-forming coupler is used in the developer solution that forms the yellow image in the blue-sensitive layer.

The processing of these color photographic materials requires a large number of photographic processing solutions that make it necessary to use rather large and expensive processing machines. Conventional color processes for color photographic materials that incorporate couplers require 15 different processing steps including solutions, washes and drying. Although the usual temperature for processing color photographic materials is about 75 to 80° F., processes are available for operation at about 100° F. The large number of steps required by these processes form the principal impediment for the practical design of mobile equipment for operating the process and is an impediment in existing equipment to change to a new process particularly higher temperature processes for more rapid processing.

Because of the prolonged period of time that the photographic material is held in contact with very high pH solutions it is necessary to treat the film being processed with a prehardener solution as the first step in order to prevent the photographic emulsions from reticulating or even separating from the support upon which they are coated, during the processing operation. Attempts to shorten processing times and reduce the number of steps by combining the prehardening function with the first developing function have not been possible. This has been especially true in the processing of color photographic materials which contain incorporated couplers because aldehydes used in the prehardening solutions as the active hardening agent reacted with the color-forming couplers at the pH's required for developer solutions. The reaction of aldehyde with coupler produces very undesirable stains and, of course, uses up the coupler so that it is not available for image formation where it is needed.

Photographic developer compositions are desired which make it possible to combine the prehardening and development functions in a single step so that the number of steps required in the processing of color material can be reduced.

Rapid color development processes are desired which require fewer process steps and shorter processing times than prior art processes.

It is therefore an object of my invention to provide a novel rapid color process and novel photographic developer compositions that make my rapid color process possible.

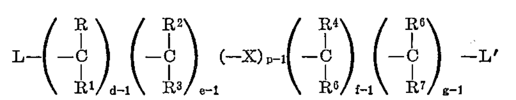
Another object is to provide a novel hardener-developer composition which is used to advantage in rapid color processing using fewer process steps.

Still other objects will become apparent from the following specification and claims.

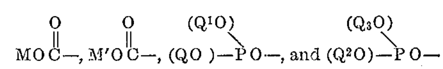
These and still other objects are accomplished according to my invention by making my hardener-developer compositions and using them in my rapid color process which has from two to five fewer process steps than conventional prior art processes. In the simplest form, my hardener-developer composition comprises a chelate compound inorganic developing agent for silver halide and a hardening agent for photographic hydrophilic colloid layers. My rapid process is made possible by a substitution of inorganic developers for the conventional organic developers which makes it possible to develop rapidly at low pH's and in the presence of hardening agents. In this way, the prehardening and development are accomplished in a single step which is not possible in conventional color processes because of the reaction of aldehyde hardeners with emulsion incorporated color-forming couplers at the high pH's required by organic developing agents.

The chelate compound, inorganic developing agents for silver halide used according to my invention include chelate compounds of a metal ion, such as, Ti^{+++}, V^{+++}, Fe^{++}, chelated by a polybasic compound having one of the formulas:

(I)



wherein L and L′ each represent radicals, such as



M and M′ each represent the same or different members, such as, hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., and an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc.; Q, Q^1, Q^2, and Q^3 each represent the same or different member, such as, hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., an ammonium group, e.g., dium, potassium, lithium, etc., an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc., an alkyl group, e.g., methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, etc., including an aralkyl group, e.g., benzyl, β-phenethyl, o-acetamidobenzyl, etc., and including a heterocyclylalkyl group, e.g. pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, etc., an aryl group, e.g., a naphthyl group, e.g., α-naphthyl, β-naphthyl, etc., a phenyl group, e.g., phenyl, o-, m-, p-tolyl, o-, p-carboxyphenyl, and water-soluble salts thereof, such as, sodium, potassium, etc., and a heterocyclic group, e.g., pyridinium, pyrrolyl, thiazolyl, oxazolyl, etc.; R, R^1, R^2, R^3, R^4, R^5, R^6 and R^7 each represent the same or different members, such as, hydrogen, hydroxpl, nitro, and an amino group, e.g., amino, N-methylamino, N-butylamino, N,N-diethylamino, anilino, etc., a halogen atom (e.g., chlorine, bromine, iodine, fluorine), a lower alkyl group, e.g., methyl, ethyl, propyl, butyl, etc., a lower alkoxy group, e.g., methoxy, ethoxy, propoxy, butoxy, etc., such that no single carbon atom in the chain contains more than one hydroxyl group, more than one amino group and more than one nitro group; *d, e, f,* and *g* each represent integers of from 1 to 4; *p* represents an integer of from 1 to 2; X represents a member, such as, oxygen, sulfur, a

$$-\overset{R^8}{\underset{R^9}{\overset{|}{\underset{|}{C}}}}-$$

radical, a $=NR^8$ radical, etc.; R^8 and R^9 each represent the same or different members, such as, hydrogen, a lower alkyl group, e.g., methyl, chloromethyl, hydroxyethyl, ethoxyethyl, bromoethyl, propyl, butyl, cyclopentyl, cyclohexyl, etc., including an aralkyl group, e.g., benzyl, β-phenethyl, o-acetamidobenzyl, etc., and including a heterocyclylalkyl group, e.g., pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, etc., an alkoxy group, e.g., methoxy, ethoxy, butoxy, etc., a phenyl group, e.g., phenyl, carboxyphenyl, tolyl, etc., a

$$-(CH_2)_{h-1}-L^2$$

group, etc.; *h* represents an integer of from 1 to 4; L^2 represents a group having the formula:

$$M_3O\overset{O}{\overset{\|}{C}}- \text{ or } (Q^4O)-\overset{(Q^5O)}{P}O-$$

M^2 represents a member selected from the class consisting of hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., and an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc.; Q^4 and Q^5 each represent the same or different member, such as, hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc., an alkyl group, e.g., methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, etc., including an aralkyl group, e.g., benzyl, β-phenethyl, o-acetamidobenzyl, etc., and including a heterocyclylalkyl group, e.g., pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, etc., an aryl group, e.g., a naphthyl group, e.g., α-naphthyl, β-naphthyl, etc., a phenyl group, e.g., phenyl, o-, m-, p-tolyl, o-, p-carboxyphenyl, and water-soluble salts thereof, such as, sodium, potassium, etc., and a heterocyclic group, e.g., pyridinium, pyrrolyl, thiazolyl, oxazolyl, etc.; and

(II)
$$\begin{array}{c} L(-CH_2)_{i-1}-N-(CH_2-)_{j-1}L^1 \\ | \\ Z \\ | \\ L^3(-CH_2)_{m-1}-N-(CH_2-)_{n-1}L^2 \end{array}$$

wherein L, L^1 and L^2 are as defined previously; L^3 represents a radical having the formula

$$M^3O\overset{O}{\overset{\|}{C}}- \text{ or } (Q^7O)-\overset{(Q^6O)}{P}O-$$

M^3 represents a member, such as, hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., and an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc.; Q^6 and Q^7 each represent the same or different member, such as, hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc., an alkyl group, e.g., methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, etc., including an aralkyl group, e.g., benzyl, β-phenethyl, o-acetamidobenzyl, etc., and including a heterocyclylalkyl group, e.g., pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, etc., an aryl group, e.g., a naphthyl group, e.g., α-naphthyl, β-naphthyl, etc., a phenyl group, e.g., phenyl, o-, m-, p-tolyl, o-, p-carboxyphenyl, and water-soluble salts thereof, such as, sodium, potassium, etc., and a heterocyclic group, e.g., pyridinium, pyrrolyl, thiazolyl, oxazolyl, etc.; *i, j, m* and *n* each represent integers of from 2 to 4; Z represents a member, such as,

$$-\left(\overset{R}{\underset{R^1}{\overset{|}{\underset{|}{C}}}}\right)_k-$$

group, a

$$\begin{array}{c} R \quad R^2 \qquad R^4 \quad R^6 \\ -C-C-N-C-C- \\ R^1 \quad R^3 \;|\; R^5 \quad R^7 \\ (CH_2)_h-L^4 \end{array}$$

group, a phenylene group, e.g., o-phenylene, p-phenylene, etc., and a cyclohexylene group; R, R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are as described previously; *h* is as described previously; *k* represents an integer of from 2 to 4; L^4 represents a radical, such as those of the formulas

$$M^4O\overset{O}{\overset{\|}{C}}- \text{ and } (Q^8)O-\overset{(Q^9O)}{\overset{|}{P}}O-$$

M^4 represents a member, such as, hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., and an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc.; Q^8 and Q^9 each represent a member, such as, hydrogen, an alkali metal, e.g., sodium, potassium, lithium, etc., an ammonium group, e.g., ammonium, triethanol ammonium, triethyl ammonium, etc., an alkyl group, e.g., methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, etc., including an aralkyl group, e.g., benzyl, β-phenethyl, o-acetamidobenzyl, etc., and including a heterocyclylalkyl group, e.g., pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, etc., an aryl group, e.g., a naphthyl group, e.g., α-naphthyl, β-naphthyl, etc., a phenyl group, e.g., phenyl, o-, m-, p-tolyl, o-, p-carboxyphenyl, and water-soluble salts thereof, such as, sodium, potassium, etc., and a heterocyclic group, e.g., pyridinium, pyrrolyl, thiazolyl, oxazolyl, etc.

Included among illustrative chelating agents used to advantage according to my invention are the following which illustrate polycarboxylic acids and polyphosphonic acids (and their salts) of Formula I:

(1) Nitrilotriacetic acid
(2) Nitrilotriacetic acid, trisodium salt
(3) Nitrilotriacetic acid, triammonium salt
(4) Oxalic acid
(5) Ammonium oxalate
(6) Malonic acid
(7) Chloromalonic acid
(8) Ethylmalonic acid
(9) Aminomalonic acid
(10) Bromomalonic acid
(11) Succinic acid
(12) Glutamic acid
(13) Glutamic acid, dipotassium salt
(14) Adipic acid
(15) Adipic acid, sodium salt
(16) Diglycolic acid
(17) Diglycolic acid, disodium salt
(18) Ethyliminodipropionic acid
(19) Ethyliminodipropionic acid, dipotassium salt
(20) Ethylene di(thioglycolic) acid
(21) Thiodiglycolic acid
(22) Malic acid
(23) Tartaric acid
(24) Citric acid

(25) Nitrilo-N,N,N-trimethylenephosphonic acid
(26) o-Carboxyanilino-N,N-dimethylenephosphonic acid
(27) Propylamino-N,N-dimethylenephosphonic acid
(28) 4-(N-pyrrolidino)butylamine-N,N-bis(methylenephosphonic acid)
(29) o-Acetamidobenzylamino-N,N-dimethylenephosphonic acid
(30) o-Toluidine-N,N-dimethylenephosphonic acid
(31) 2-pyridylamino-N′,N′-dimethylenephosphonic acid
(32) Tetraethyl methylenediphosphonate
(33) Tetraethyl octylidinediphosphonate
(34) Octylidinephosphonic acid
(35) Trisodium octylidine diphosphonate
(36) Triammonium tridecylidenediphosphonate
(37) Tetrabutyl-β,β-diethyl-β-methylethylidenediphosphonate
(38) Disodium cyclohexylmethylenediphosphonate
(39) Tetraethyl benzylidenediphosphonate
(40) Tetraphenyl o-phenylbenzylidenediphosphonate
(41) Dodecylbenzylidenediphosphonic acid
(42) Methylcarbonylbenzylidenediphosphonic acid
(43) Tetraethyl nonadecylidenediphosphonate
(44) Tetraethyl-1-pyrrolylidenediphosphonate
(45) Methylene diphosphonic acid, sodium salt

It is to be understood that any of the above acids can be in salt form, such as, sodium salt, potassium salt, ammonium salt, triethanol ammonium salt, triethyl ammonium salt, pyridinium salt, etc.

The following will illustrate typical examples of the polyamine polycarboxylic and polyamine polyphosphonic acid (and salt) chelating agents represented by Formula II:

(1) Ethylene diamine tetraacetic acid
(2) Ethylene diamine tetraacetic acid, tetrasodium salt
(3) Pentaacetic acid diethylene triamine
(4) Pentaacetic acid diethylene triamine, pentasodium salt
(5) Ethylene diamine-N,N,N′,N′-tetramethylenephosphonic acid
(6) 1,2-cyclohexanediamine-N,N,N′,N′-tetramethylenephosphonic acid
(7) 1,3-diaminopropanol-N,N,N′,N′-tetramethylenephosphonic acid
(8) 1,3-propanediamine-N,N,N′,N′-tetramethylenephosphonic acid
(9) 1,6-hexanediamine-N,N,N′,N′-tetramethylenephosphonic acid

It is to be understood that any of the above acids can be in salt form such as the sodium salt, potassium salt, ammonium salt, triethanol ammonium salt, triethyl ammonium salt, pyridinium salt, etc.

The chelating compound inorganic developing agents of my invention are advantageously prepared by contacting the metal ion, preferably Ti^{+++}, V^{+++} or Fe^{++}, with an aqueous solution of my chelating compounds including those of Formulas I and II. The metal ions are advantageously supplied by dissolving any suitable water-soluble salt of the metal desired including, for example, a halide, e.g., chloride, bromide, fluoride, iodide, a sulfate, etc. Illustrative examples of salts used to advantage include:

(1) Titanium trichloride,
(2) Titanium tribromide,
(3) Titanium triiodide,
(4) Titanous sulfate,
(5) Titanous oxalate,
(6) Vanadium trichloride,
(7) Vanadium tribromide,
(8) Vanadium triiodide,
(9) Vanadium trifluoride,
(10) Ferrous sulfate,
(11) Ferrous chloride,
(12) Ferrous bromide, etc.

These and other sources of my metal ions and my chelating agents have been described in the chemical literature and are well known.

My chelate compound inorganic developing agents are prepared and isolated in the dry form, such as, titanous oxalate, for example, and supplied as a single component to be added to the hardening agent or alternatively the appropriate chelating agent and an appropriate source of the desired metal ion are supplied as separate components that are added to the hardening agent to prepare my hardener developer compositions. My compositions are advantageously prepared and stored in the dry form for ease of storage and shipping or can be prepared directly from the raw materials in a concentrated solution form or as a working developer solution. My chelate compound inorganic developing agents or the components used to make them are readily water-soluble and my dry compositions are easily and quickly made up into the concentrated solution form for subsequent dilution for the working developer solution.

Any of the organic aldehyde hardening agents used in photographic processing to harden hydrophilic colloids, such as, gelatin and gelatin substitutes are used to advantage in my hardener developer compositions. Organic aldehyde hardening agents used to advantage include those represented by the formulas:

$$\mathrm{H\overset{O}{\overset{\|}{C}}{-}H},\ \text{a}\ \mathrm{H\overset{O}{\overset{\|}{C}}{-}R^{10}{-}\overset{O}{\overset{\|}{C}}H},\ \mathrm{H_3C\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3}\ \text{and}\ \mathrm{CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}H}$$

wherein R^{10} represents a divalent member, e.g., an alkylene group (e.g., ethylene, 1-methylethylene, 1-butylethylene, 1,1-dimethylethylene, 1,2-dimethylethylene, 1-methoxyethylene, 1-methyl-2-methoxyethylene, 1-butoxyethylene, propylene, 1-methylpropylene, 1-butylpropylene, 1-methyl-2-methylpropylene, 1-methyl-2-ethoxypropylene, 1-butoxypropylene, butylene, 1-methylbutylene, 1-methoxybutylene, 1-hydroxybutylene, 2-hydroxybutylene, 1-hydroxyethylene, 1-hydroxypropylene, 1,2-cyclopentylene, 1,3-cyclopentylene, 1,2-cyclobutylene, 1,3-cyclobutylene, etc.), a vinylene group (e.g., vinylene, 1-methylvinylene, 1-butylvinylene, 1,2-dimethylvinylene, 1-methoxyvinylene, etc.), a dimethylene ether residue, a dimethylenethioether residue, a dimethyleneselenaether residue, a dimethyleneamino residue, etc. Illustrative aldehyde hardening agents include the following:

(1) Formaldehyde,
(2) Glutaraldehyde,
(3) β-Methylglutaraldehyde,
(4) α-Methylglutaraldehyde,
(5) α-Butoxyglutaraldehyde,
(6) α-Methyl-β-ethoxyglutaraldehyde,
(7) α,α-Dimethylglutaraldehyde,
(8) α,β-Dimethylglutaraldehyde,
(9) Maleic dialdehyde,
(10) Butylmaleic dialdehyde,
(11) Succinaldehyde,
(12) Methylsuccinaldehyde,
(13) Methoxysuccinaldehyde,
(14) β-Isopropoxysuccinaldehyde,
(15) Cyclopentanedicarboxaldehyde,
(16) Thiobisacetaldehyde,
(17) Iminobisacetaldehyde,
(18) Oxybisacetaldehyde,
(19) Selenobisacetaldehyde,
(20) N-methylaminobisacetaldehyde-HCl, etc.

These aldedhydes are known in the chemical art. It is to be understood that the bisulfite addition complexes of the above and and other aldehydes are used advantageously as the hardening agent in my hardener-developing compositions. One aldehyde, a mixture of an aldehyde and its bisulfite addition complex, mixtures of two or more aldehydes or mixtures of aldehydes and bisulfite addition complexes of aldehydes are used to advantage as the hardening agent in my compositions. Aldehyde precursors which hydrolyze in acid solution to release an aldehyde are also used to advantage. For example, dimethoxytetrahydrofuran is used to advantage to form succinaldehyde in my compositions.

My developer compositions advantageously have pH's in the range from about 0.5 to about 6.9. The preferred range being from about 4 to about 5.5.

The concentration of the components of my hardener-developer composition are advantageously used over a wide range. The optimum concentration can be readily determined by methods well known in the art and need not be discussed further here. Usually sufficient chelating compound inorganic developing agent is included in my composition to produce a concentration in the range from about 1 to about 400 grams per liter when dissolved and sufficient aldehyde hardening agent(s) to produce a concentration in the range of from about 0.1 to about 60 grams per liter when dissolved in water. When the chelating agent and the water-soluble metal salt used to make my chelate compound inorganic developing agents are to be supplied as separate components in my compositions (rather than a single chelate compound inorganic developing agent) a sufficient amount of the chelating agent is provided to produce a concentration in the range of from about 0.1 to about 200 grams per liter and a sufficient amount of the water-soluble metal salt is provided to produce a concentration in the range of from about 1 to about 400 grams per liter when disolved in water.

The following examples will still further illustrate the hardener-developer compositions and the rapid color processes of my invention, however, it is to be understood that these examples are not to limit the scope of my invention.

EXAMPLE 1

Hardener-developer compositions are prepared containing mixtures of titanium trichloride, ethylenediaminetetraacetic acid, tetrasodium salt, and formaldehyde alone and in combination with succinaldehyde as indicated in Table I below.

TABLE I

Component:	Range of amounts of component in composition
Titanium trichloride ----------g--	1 through 400
Ethylenediaminetetraaectic acid, tetrasodium salt ----------g--	0.1 through 200
Formaldehyde (37%) ------ml--	1 through 150
Succinaldehyde ----------g--	0 through 34
pH of a water solution of this composition ----------	0.5 through 6.9

Multilayer color film containing incorporating cyan-forming coupler in the red-sensitive layer, magenta-forming coupler in the green-sensitive layer and a yellow-forming coupler in the blue-sensitive layer is exposed to a color image. One piece of the exposed color film is given the ECO-2 Process steps listed in Table II below. The processing solutions used are those described in the "Manual for Processing of Ektachrome Commercial Film (Process ECO-2)" published by and available from Motion Picture and Education Markets Division, Eastman Kodak Company, Rochester, N.Y. 14650. Ektachrome is a registered trademark of Eastman Kodak Company. Other pieces of the exposed color film are given my process steps listed in Table III below using one liter hardener-developer solutions prepared from compositions of Table I. The other solutions, e.g., neutralizer, reversal bath, color developer, acid stop, bleach, fix, and stabilizer are the same as used in the ECO-2 Process for the respective steps.

TABLE II

ECO-2 Process

Step:	Process time
(1) Prehardener ----------	2'35"
(2) Neutralizer ----------	31"
(3) First developer ----------	3'20"
(4) Acid stop ----------	'31"
(5) Wash ----------	31"
(6) Reversal bath ----------	31"
(7) Wash ----------	31"
(8) Color developer ----------	3'37"
(9) Acid stop ----------	31"
(10) Wash ----------	1'02"
(11) Bleach ----------	1'33"
(12) Fix ----------	1'33"
(13) Wash ----------	1'02"
(14) Stabilizer ----------	31"
(15) Dry	

TABLE III

Hardener-developer process of my invention

Step:	Process time
(1) Hardener-developer ----------	3'00"
(2) Neutralizer ----------	31"
(3) Wash ----------	31"
(4) Reversal bath ----------	31"
(5) Wash ----------	31"
(6) Color developer ----------	3'37"
(7) Acid stop ----------	31"
(8) Wash ----------	1'02"
(9) Bleach ----------	1'33"
(10) Fix ----------	1'33"
(11) Wash ----------	1'02"
(12) Stabilizer ----------	31"
(13) Dry.	

Good quality color pictures are obtained by using my hardener-developer solutions having the concentration ranges of the components given in Table I in place of the prehardner, first developer and acid stop bath used in ECO-2 Process. The preferred concentrations are:

Titanium trichloride—26 g./l.
Ethylenediaminetetraacetic acid, tetrasodium salt—88 g./l.
Formaldehyde (37%)—14 ml./l.
Succinaldehyde—5 g./l.
pH of 3.8—5 g./l.

This example is repeated using hardener-developer compositions of Table I in which dimethoxytetrahydrofuran in the range from 0 to 50 milliliters is substituted in place of succinaldehyde (0 to 34 grams). Comparable results are obtained using hardener-developer solution prepared from these compositions. The preferred concentration of dimethoxytetrahydrofuran is found to be 8 milliters per liter of solution. The processes used in this example are operated at about 100° F., however, my process can be operated in the temperature range of from about 65° F. to about 212° F. by making appropriate adjustment of the processing step times. The optimum time for each process step is determined by methods well known in the art.

EXAMPLE 2

Similar results are obtained when Example 1 is repeated using my hardener-developer composition in the 10-step process listed below in Table IV in place of the 13-step process listed in Table III of Example I.

TABLE IV

Process step:	Time
(1) Hardening developer	3'00"
(2) Neutralizer	31"
(3) Color developer containing t-butylamine borane for reversal	3'20"
(4) Acid stop	31"
(5) Wash	1'02"
(6) Bleach	1'33"
(7) Fix	1'33"
(8) Wash	1'02"
(9) Stabilizer	31"
(10) Dry.	

Similar results are also obtained by replacing steps 6 and 7 in Table IV with a single blix step. A blix for this is advantageously made by combining fix and bleach solutions immediately before application to the film. The color developer containing t-butylamine borane used in this process has the composition.

Benzyl alcohol—6.0 cc.
Sadium hexametaphosphate—2.0 g.
Sodium sulfite, anhydrous—5.0 g.
Trisodium phosphate—40.0 g.
Potassium bromide—0.25 g.
0.1% solution of potassium iodide—10.0 cc.
Sodium hydroxide—6.5 g.
Color developer [1]—11.33 g.
Ethylenediamine sulfate—7.8 g.
Citrazinic acid—1.5 g.
t-Butylamine borane—0.1 g.
Water to make—1.0 liter.

[1] 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.

EXAMPLE 3

Hardener-developer compositions are prepared containing mixtures of titanous oxalate and succinaldehyde indicated in Table V.

TABLE V

Component:	Range of amount from, g.
Titanous oxalate	1 to 200
Succinaldehyde	0.5 to 34
pH of aqueous solution	0.5 to 6.9

Example I is repeated using one liter solutions of the compositions of Table V in place of the compositions of Table I. The results obtained in this example are similar to those obtained in Example I.

EXAMPLE 4

Hardener-developers are prepared having the compositions indicated in Table VI.

TABLE VI

Component:		Range of amount from
Titanium trichloride	g.	1 to 400
Diethylenetriamine pentaacetic acid, pentasodium salt	g.	0.1 to 200
Formaldehyde (37%)	ml.	0.3 to 6
Succinaldehyde	g.	0 to 34
pH (of aqueous solution of above components)		0.5 to .69

Example 1 is repeated using one liter solutions of the compositions of Table VI in place of the compositions of Table I. The results obtained in this example are similar to those obtained in Example 1. The preferred composition of Example 4 is found to have sufficient titanium trichloride to produce a concentration of 26 grams per liter, sufficient diethylenetriamine pentaacetic acid, pentasodium salt to produce a concentration of 160 milliliters per liter, sufficient formaldehyde to produce a concentration of 5.2 grams per liter and sufficient succinaldehyde to produce a concentration of 8 grams per liter when dissolved in the solution.

EXAMPLE 5

Example 1 is repeated using a hardener-developer having the composition shown in Table VII in place of that shown in Table I.

TABLE VII

Component:		Amount
Titanium trichloride	g.	15
Ethylenediaminetetraacetic acid, tetrasodium salt	g.	90
Sodium sulfate	g.	100
Sodium bromide	g.	2
Formaldehyde (37%)	ml.	25
Succinaldehyde	g.	2.7
Sodium acetate	g.	20
pH		4.8

The results obtained in this example are similar to those obtained in Example 1. Temperatures of about 212° F. are preferred for purposes of rapid access to the processed film, however, temperatures down to 65° F. are advantageously used in conventional processing machines. At 212° F. it is possible to process Ektachrome film by using a hardener-developer solution of this example in the 8-step process described in Example 2 in a total time of less than two minutes in equipment of much greater simplicity of design than was previously possible because of the greatly reduced number of process steps.

EXAMPLE 6

Example 1 is repeated using a hardener-developer having the composition shown in Table VIII.

TABLE VIII

Component:	Range of amount of component from, g.
Ferrous sulfate	1 to 200
Diethylenetriamine pentaacetic acid, pentasodium salt	0.1 to 200
Succinaldehyde	0.3 to 34

Hardener-developer compositions prepared from mixtures shown in Table VIII give results comparable to those in Example 1.

Similarly, it can be shown that any of the other chelate compound inorganic developing agents for silver halide formed by chelating Ti^{+++}, V^{+++}, or Fe^{++} with any of the chelating agents of Formulas I and II are used with any of the hardening agents of my invention as the hardener-developer composition in my rapid color process. The following example will illustrate the use of my hardener-developer composition as a replacement for the prehardener, wash and first developer steps in a color process for a color film that does not contain incorporated color-forming couplers.

EXAMPLE 7

Exposed multilayer color film not containing color-forming couplers is advantageously processed in a K–12A process using my hardener-developer solutions, such as those described in Examples 1 through 6, in place of the K–12A process, prehardener, wash, and first developer solution.

As the hardener-developer solutions are used the Ti^{+++}, V^{+++}, or Fe^{++} ions in the chelate (developing agent) are oxidized to the Ti^{++++}, V^{++++}, or Fe^{+++} ions, respectively. The oxidized developing agents in my hardener-developer solutions are advantageously reduced (to the lower valence state) by electrolysis, using conventional equipment. Aldehyde hardening agent can be added to the electrolytically rejuvenated solution as is necessary and the hardener-developer solution reused to harden-develop additional photographic material. This is an important advantage provided by use of my hardener-developer compositions that is not provided by conventional developer solutions with organic developers used in prior art color processing.

My hardener-developer compositions are valuable for use in my rapid color processes. These hardener-developer compositions are characterized by having pH's in the range of from 0.5 to 6.9 which makes them particularly valuable for combining the hardening and development steps in a color process for processing color materials containing incorporated couplers because at their pH's the aldehyde hardening agents do not react with the color-forming coupler. This is a very valuable technical advance since prior art developer solutions used in color processing require higher pH's where any aldehyde present would react very detrimentally or disastrously with color-forming couplers present in the photographic element, thus making it impossible to combine the prehardening and developing functions in a single step.

The invention has been described in detail with particular 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 as defined in the appended claims.

I claim:

1. A hardener-developer composition comprising:

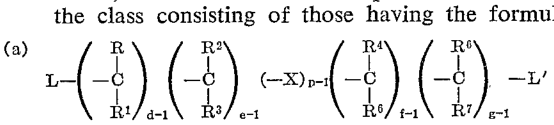
(1) a Ti^{+++}, V^{+++} or Fe^{++} chelate compound inorganic developing agent for silver halide and

(2) an organic aldehyde hardening agent for gelatin.

2. A hardener-developer composition comprising:

(1) a chelate compound product of reacting a salt of a metalion selected from the class consisting of Ti^{+++}, V^{+++}, and Fe^{++} with a compound selected from the class consisting of those having the formulas:

(a)



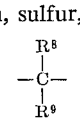
wherein L and L′ represent radicals selected from the class consisting of those having the formulas

$$MO\overset{O}{\overset{\|}{C}}—,\ M^1O\overset{O}{\overset{\|}{C}}—,\ (Q^1O)(QO)—PO—$$

and

$$(Q^3O)(Q^2O)—PO—$$

M and M^1 represent members selected from the class consisting of hydrogen, an alkali metal and an ammonium group; Q, Q^1, Q^2 and Q^3 repersent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; R, R^1, R^2, R^3, R^4, R^5, R^6 and R^7 each represent a member selected from the class consisting of hydrogen, hydroxyl, an amino group, nitro, halogen, a lower alkyl group, and a lower alkoxy group, such that no single carbon atom in the chain contains more than one hydoxyl group, more than one amino group and more than one nitro group; *d, e, f* and *g* represent intergers of from 1 to 4; *p* represents an interger of from 1 to 2; X represents a member selected from the class consiting of oxygen, sulfur, a



radical, and a $=NR^8$ radical; R^8 and R^9 each represent members selected from the class consisting of hydrogen, a lower alkyl group and a

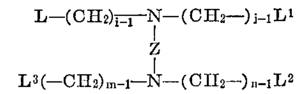
$$—(CH_2)_{\overline{h-1}}L^2$$

group; *h* represents an integer of from 1 to 4; and L^2 represents a radical selected from the class consisting of those having the formulas

$$M^2O\overset{O}{\overset{\|}{C}}— \text{ and } (Q^5O)(Q^4O)—PO—$$

M^2 represents a member selected from the class consisting of hydrogen, an alkali metal and an amonium group; Q^4 and Q^5 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group and a heterocyclic group; and

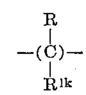
(b)



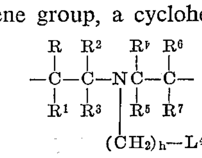
wherein L, L^1 and L^2 are as defined previously; L^3 represents a radical selected from the class consisting of those having the formulas

$$M^3O\overset{O}{\overset{\|}{C}}— \text{ and } (Q^6O)(Q^7O)—PO—$$

M^3 represnts a member selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group and a heterocyclic group; Q^6 and Q^7 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; *i, j, m* and *n* each represent intergers of from 2 to 4; Z represents a group selected from the class consisting of a



group, a phenylene group, a cyclohexylene group and a



group; R, R^1, R^2, R^3, R^4, R^5, R^6, and R^7 are as described previously; *h* is as described previously; *k* represents an interger of from 2 to 4; and L^4 represents a radical selected from the class consisting of those having the formulas

$$M^4O\overset{O}{\overset{\|}{C}}— \text{ and } (Q^9O)(Q^8O)—PO—$$

M^4 represents a member selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group and a heterocyclic group; Q^8 and Q^9 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; and

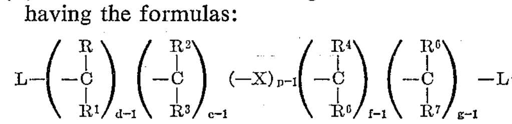
(2) at least one aldehyde hardening agent for gelatin.

3. A hardener-developer composition comprising:

(1) a water-soluble salt which upon solution in water forms ions selected from the class consisting of Ti^{+++}, V^{+++}, Fe^{++} and ions selected from the class consisting of chloride, bromide, iodide, fluoride, and sulfate;

(2) a water-soluble chelate agent selected from those having the formulas:

(a)



wherein L and L′ represent radicals selected from the class consisting of those having the formulas

$$MO\overset{O}{\overset{\|}{C}}—\ \ M^1O\overset{O}{\overset{\|}{C}}—(Q^1O)(QO)—PO—$$

and

$$(Q^3O)(Q_2O)—PO—$$

M and M^1 represents members selected from the class consisting of hydrogen, an alkali metal and an ammonium group; Q, Q^1, Q^2 and Q^3 represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an ary group, and a heterocyclic group; R, R^1, R^2, R^3, R^4, R^5, R^6 and R^7 each represent a member selected from the class consisting of hydrogen, hydroxyl, an amino group, nitro, halogen, a low alkyl group, and a lower alkoxy group, such that no single carbon atom in the chain contains more than one hydroxyl group, more than one amino group and more than one nitro group; *d, e, f* and *g* each represent integers of from 1 to 2; X represents a member selected from the class consisting of oxygen, sulfur, a

$$-\underset{R^9}{\overset{R^8}{\underset{|}{\overset{|}{C}}}}-$$

radical, and a $=NR^8$ radical; R^8 and R^9 each represent members selected from the class consisting of hydrogen, a lower alkyl group and a

$$-(CH_2)_{h-1}-L^2$$

group; *h* represents an integer of 1 to 4; and L^2 represents a radical selected from the class consisting of those having the formulas

$$M^2O\overset{\overset{O}{\|}}{C}- \text{ and } (Q^4O)-\overset{\overset{(Q^5O)}{|}}{P}O-$$

M^2 represents a member selected from the class consisting of hydrogen, an alkali metal and an ammonium group; Q^4 and Q^5 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; and

(b)
$$\begin{array}{c} L(-CH_2)_{i-1}-N-(CH_2-)_{j-1}L^1 \\ | \\ Z \\ | \\ L^3(-CH_2)_{m-1}-N-(CH_2-)_{n-1}L^2 \end{array}$$

wherein L, L^1 and L^2 are as defined previously; L^3 represents a radical selected from the class consisting of those having the formulas

$$M^3O\overset{\overset{O}{\|}}{C}- \text{ and } (Q^7O)-\overset{\overset{(Q^6O)}{|}}{P}O-$$

M^3 represents a member selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group and a heterocyclic group; Q^6 and Q^7 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; *i, j, m* and *n* each represent integers of from 2 to 4; Z represents a group selected from the class consisting of a

$$-(\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}})_k-$$

group, a phenylene group and a cyclohexylene group, and a

$$\begin{array}{c} R\ \ R^2\ \ \ \ R^4\ R^6 \\ -\underset{R^1}{C}-\underset{R^3}{C}-N\underset{R^5}{C}-\underset{R^7}{C}- \\ | \\ (CH_2)_h-L^4 \end{array}$$

group; R, R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are as described previously; *h* is as described previously; *k* represents an integer of from 2 to 4; and L^4 represents a radical selected from the class consisting of those having the formulas

$$M^4O\overset{\overset{O}{\|}}{C}- \text{ and } (Q^8O)-\overset{\overset{(Q^9O)}{\backslash}}{P}O-$$

M^4 represents a member selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group and a heterocyclic group; Q^8 and Q^9 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; and

(3) at least one aldehyde hardening agent.

4. A hardener-developer composition of claim **2** in which the chelate compound is titanous oxalate and the said hardening agent is succinaldehyde.

5. A hardener-developer composition of claim **3** in which the hardening agent contains an aldehyde selected from the class consisting of formaldehyde, a succinaldehyde, a glutaraldehyde, a maleic dialdehyde, a cyclopentane dicarboxaldehyde, and a bisulfite addition complex of said aldehydes.

6. A hardener-developer composition of claim **3** containing a sufficient amount of the said water-soluble salt to produce a concentration in the range of from about 1 to about 400 grams per liter, a sufficient amount of the said chelating agent to produce a concentration in the range of from about 0.1 to about 200 grams per liter, and a sufficient amount of the said aldehyde hardening agent to produce a concentration in the range from about 0.1 to about 60 grams per liter when dissolved in water.

7. A hardener-developer composition of claim **3** in which the said salt is titanium trichloride, the said chelating agent is ethylenediamine tetraacetic acid, tetrasodium salt.

8. A hardener-developer composition of claim **3** in which the said salt is titanous sulfate, the said chelating agent is nitrilotriacetic acid, trisodium salt, and the said hardening agent is succinaldehyde.

9. A hardener-developer composition of claim **3** in which the said salt is titanium trichloride, the said chelating agent is diethylene triamine pentaacetic acid, pentasodium salt and the said hardening agent is a mixture of formaldehyde and succinaldehyde.

10. A hardener-developer composition of claim **3** in which the said salt is ferrous sulfate, the said chelating agent is diethylene triamine pentaacetic acid, penasodium salt and the hardening agent is succinaldehyde.

11. An aqueous hardener-developer solution in accordance with claim **21** comprising titanium trichloride in the concentration range from about 1 to about 400 grams per liter, diethylene triamine pentaacetic acid, pentasodium salt in the concentration range of from about 0.1 to about 200 grams per liter, formaldehyde in the concentration range from about 0.3 to about 6 ml. per liter and succinaldehyde in the concentration range from 0 up to about 34 grams per liter.

12. An aqueous hardener-developer solution of claim **11** containing 26 grams per liter of titanium trichloride, 160 ml. per liter of diethylene triamine pentaacetic acid, pentasodium salt, 5.2 grams per liter of formaldehyde and 8 grams per liter of succinaldehyde.

13. An aqueous hardener-developer solution in accordance with claim **21** comprising:

15 g./l. of titanium trichloride,
90 g./l. of ethylenediamine tetraacetic acid, tetrasodium salt,
9 m./l. of formaldehyde,
2.7 g./l. of succinaldehyde,
100 g./l. of sodium sulfate,
20 g./l. of sodium acetate,
said solution having a pH of about 4.8

14. A rapid process for simultaneously hardening and developing a silver image in an exposed color photographic element, said process comprising contacting said element with an aqueous hardener-developer having a pH of about 4 to 6.9 and a temperature of 65 to 212° F. comprising:

(1) a Ti^{+++}, V^{+++} or Fe^{++} chelate compound inorganic developing agent for silver halide and

(2) an organic aldehyde hardening agent for gelatin.

15. A rapid process for simultaneously hardening and developing a silver image in an exposed color photographic element, said process comprising contacting the said element with an aqueous hardener-developer solution having a pH in the range of from about 4 to about 6.9 and temperature 65–212° F. and containing:

(1) a chelate compound product of reacting a salt of a metal ion selected from the class consisting of Ti^{+++}, V^{+++}, and F^{++} with a poly basic compound selected from the class consisting of those having the formulas:

(a) $$L-\left(\begin{array}{c}R\\ |\\ -C\\ |\\ R^1\end{array}\right)_{d-1}\left(\begin{array}{c}R^2\\ |\\ -C\\ |\\ R^3\end{array}\right)_{e-1}(-X)_{p-1}\left(\begin{array}{c}R^4\\ |\\ -C\\ |\\ R_9\end{array}\right)_{f-1}\left(\begin{array}{c}R^6\\ |\\ -C\\ |\\ R^7\end{array}\right)_{g-1}-L'$$

wherein L and L′ represent radicals selected from the class consisting of those having the formulas

$$MO\overset{O}{\overset{\|}{C}}-,\ M'O\overset{O}{\overset{\|}{C}}-,\ (QO)-\overset{(Q^1O)}{\overset{|}{P}}O-,\ \text{and}\ (Q^2O)-\overset{(Q^3O)}{\overset{|}{P}}O-$$

M and M′ represent members selected from the class consisting of hydrogen, an alkali metal and an ammonium group; Q, Q^1, Q^2 and Q^3 represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; R, R^1, R^2, R^3, R^4, R^5, R^6 and R^7 each represent a member selected from the class consisting of hydrogen, hydroxyl, an amino group, nitro, halogen, a lower alkyl group, and a lower alkoxy group, such that no single carbon atom in the chain contains more than one hydroxyl group, more than one amino group and more than one nitro group; *d*, *e*, *f* and *g* each represent integers of from 1 to 4; *p* represents an integer of from 1 to 2; X represents a member selected from the class consisting of oxygen, sulfur, a

$$\begin{array}{c}R^8\\ |\\ -C-\\ |\\ R^9\end{array}$$

radical, and a $=NH^8$ radical; R^8 and R^9 each represent members selected from the class consisting of hydrogen, a lower alkyl group and a

$$-(CH_2)_{h-1}-L^2$$

group; *h* represents an integer of from 1 to 4; and L^2 represents a radical selected from the class consisting of those having the formulas

$$M^2O\overset{O}{\overset{\|}{C}}-\ \text{and}\ (Q^4O)-\overset{(Q^5O)}{\overset{\diagdown}{P}}O-$$

M^2 represents a member selected from the class consisting of hydrogen, an alkali metal and an ammonium group; Q^4 and Q^5 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; and

(b) $$\begin{array}{c}L(-CH_2)_{i-1}-N-(CH_2)_{t-1}L^1\\ |\\ Z\\ |\\ L^3(-CH_2)_{m-1}-N-(CH_2-)_{n-1}L^2\end{array}$$

wherein L, L^1 and L^2 are as defined previously; L^3 represents a radical selected from the class consisting of those having the formulas

$$M^3O\overset{O}{\overset{\|}{C}}-\ \text{and}\ (Q^7O)-\overset{(Q^6O)}{\overset{\diagdown}{P}}O)$$

M^3 represents a member selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group and a heterocyclic group; Q^6 and Q^7 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; *i*, *j*, *m* and *n* each represent integers of from 2 to 4; Z represents a group selected from the class consisting of a

$$-\left(\begin{array}{c}R\\ |\\ C\\ |\\ R^1\end{array}\right)_k-$$

group, a phenylene group, a cyclohexylene group and a

$$\begin{array}{ccccccccc} & R & & R^2 & & & R^4 & & R^6\\ & | & & | & & & | & & |\\ - & C & - & C & - N - & & C & - & C\ -\\ & | & & | & | & & | & & |\\ & R^1 & & R^3 & | & & R^5 & & R^7\\ & & & & (CH_2)_h-L^4 & & & & \end{array}$$

group; R, R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are as described previously; *h* is as described previously; *k* represents an integer of from 2 to 4; and L^4 represents a radical selected from the class consisting of those having the formulas

$$M^4O\overset{O}{\overset{\|}{C}}-\ \text{and}\ (Q^8O)-\overset{(Q^9O)}{\overset{\diagdown}{P}}O-$$

M^4 represents a member selected from the class consisting of hydrogen, an alkali metal, an ammonium group; an alkyl group, an aryl group and a heterocyclic group; Q^8 and Q^9 each represent members selected from the class consisting of hydrogen, an alkali metal, an ammonium group, an alkyl group, an aryl group, and a heterocyclic group; and

(2) at least one aldehyde hardening agent for gelatin.

16. A rapid process of claim **15** in which the said poly basic compound is present in a concentration range of from about 0.1 to about 200 grams per liter and the said aldehyde hardening agent is present in a concentration range of from about 0.1 to about 60 grams per liter.

17. A rapid process for simultaneously hardening and developing a silver image in an exposed color photographic element, said process comprising contacting said element with an aqueous hardener-developer having temperature of 65–212° F. comprising:

15 g./l. of titanium trichloride,
90 g./l. of ethylenediamine tetraacetic acid, tetrasodium salt,
9 m./l. of formaldehyde,
2.7 g./l. of succinaldehyde,
100 g./l. of sodium sulfate,
20 g./l. of sodium acetate,

said solution having a pH of about 4.8

18. A rapid process for processing an exposed color photographic element, said process comprising the steps of contacting the said element with:

(1) an aqueous hardening developer having a pH of about 4 to 6.9 and a temperature of about 65 to 212° F. comprising:
  (a) a Ti^{+++}, V^{+++} or Fe^{++} chelate compound inorganic developing agent for silver halide and
  (b) a hardening agent,
(2) a neutralizer,
(3) a color developer containing t-butylamine borane,
(4) an acid stop,
(5) wash,
(6) a bleach,
(7) a fix,
(8) wash and
(9) a stabilizer.

19. A composition for hardening gelatin and developing exposed photographic silver halide comprising:

(1) a chelate compound of a metal ion selected from the group consisting of Ti^{+++} and Fe^{++} chelated by a water-soluble polycarboxylic acid selected from the group consisting of a polyamine polyacetic acid and oxalic acid; and
(2) an organic aldehyde having a formula selected from the group consisting of:

$$H\overset{O}{\overset{\|}{C}}H\ \text{and}\ H-\overset{O}{\overset{\|}{C}}-R^{10}-\overset{O}{\overset{\|}{C}}-H$$

wherein R^{10} is a lower alkylene radical.

20. A hardener-developer composition for hardening photographic hydrophilic colloid layers and developing exposed photographic silver halide comprising:

(1) a chelate compound of a metal ion selected from the group consisting of Ti^{+++}, V^{+++} and Fe^{++} chelated by a water-soluble polybasic acid selected from the class consisting of a polycarboxylic acid, a polyphosphonic acid and water-soluble salts of said polybasic acids; and

(2) at least one hardening agent for photographic hydrophilic colloid layers selected from the class consisting of formaldehyde, acrolein, dimethylglyoxyl, a succinaldehyde, a glutaraldehyde, a maleic dialdehyde, a cyclopentane dicarboxaldehyde, a cyclobutane dicarboxaldehyde, and a bisulfite addition complex of said aldehydes.

21. An aqueous hardener-developer solution comprising:

at least one aldehyde, and a chelate compound produced by reacting a water soluble polyaminopolyacetic acid or a water soluble salt thereof with titanium trichloride, said solution having a pH of about 4 to about 6.9.

22. An aqueous hardener-developer solution in accordance with claim **21** wherein said chelate compound is of ethylenediamine tetraacetic acid or of diethylene triamine pentaacetic acid, or sodium salts thereof.

23. A rapid process for simultaneously hardening and developing a silver image in an exposed color photographic element, said process comprising contacting such an element with the aqueous hardener-developer solution of claim **21** at a temperature of about 65 to 212° F.

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