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PHOTOGRAPHIC ELEMENT-DEVELOPER SYSTEM

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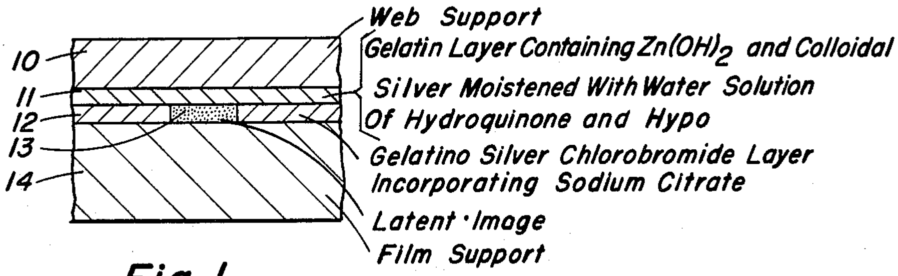

Fig. 1

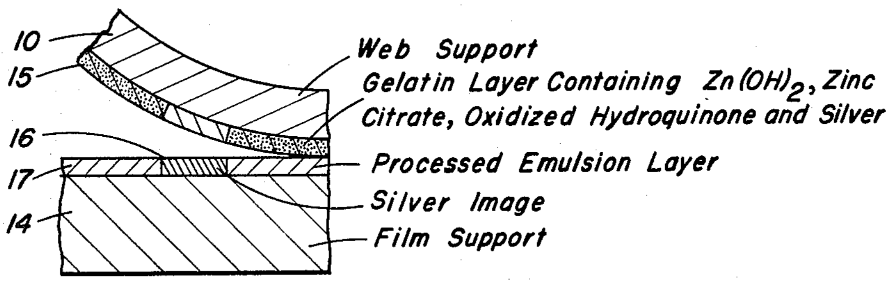

Fig. 2

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PHOTOGRAPHIC ELEMENT-DEVELOPER SYSTEM

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The present invention relates to photography and more specifically to a novel photographic element-developer combination.

In the conventional photographic system a light-sensitive photographic element containing a silver halide emulsion layer is exposed to an image, then the exposed silver halide is developed to a silver image by a highly alkaline aqueous developer solution. Such a developer contains a developing agent, a preservative, such as sodium sulfite, alkali to activate the developing agent and may contain other material such as sodium bromide, antifoggants, etc, to give the desired photographic development characteristics. The alkali is an essential part of the developer since a developer solution containing all the normal constituents but no alkali, produces very little if any silver image development in an exposed photographic element. Thus the developing agent or agents in a developer solution must be activated by incorporating an alkali in the solution. In general, the developer activity increases as the amount of alkali in the developer is increased, that is, as the pH of the solution is increased above 7.5.

In another development system the latent image bearing light-sensitive silver halide emulsion layer is developed by a web process in which a processing element incorporating an aqueous solution of a developing agent, alkali and a preservative such as sodium sulfite is squeeged onto the silver halide emulsion layer, then when the development is complete, the processing element is separated from the emulsion layer leaving a silver image. Tregillus et al. in U.S. Serial 835,473, filed August 24, 1959, describe a novel improved web process which combines the development and stabilization in one step by incorporating in the processing element a nucleating agent and a silver halide solvent along with the developing agent and alkali. In this process, the exposed silver halide is developed to a silver image in the emulsion layer while the unexposed silver halide is converted by the silver halide solvent from the processing element into a soluble complex which diffuses from the emulsion layer into the processing element where it is precipitated as silver by the nucleating agent. Thus when the processing element is stripped from the silver image bearing emulsion, it leaves the emulsion layer substantially free of silver halide.

Prior art processing elements used for web processing do not keep as long as desired after being soaked in the developer solutions used because their high pH causes the gelatin to hydrolyze.

The developing agents either in alkaline developer solutions or in processing elements which contain alkaline developer solutions are susceptible to aerial oxidation. In general, the stability of the developer solutions decreases markedly as their pH is increased.

It is therefore an object of this invention to provide a novel light-sensitive photographic element which is developable by developer solutions or by developer solution incorporating processing elements that do not contain alkali.

Another object is to provide a novel light-senstive photographic element which is developable in water or in an aqueous solution which does not contain alkali, and may or may not contain developing agents.

Another object is to provide a novel light-sensitive photographic element containing silver halide and a very slightly soluble metal hydroxide, such that the photographic element is developed by a low alkali inactive developer solution per se or by a processing element incorporating this solution, containing a developing agent and an alkali-releasing reagent consisting of a sodium or potassium salt which reacts with the metal hydroxide in the photographic element to produce a stable less dissociated compound than the metal hydroxide and release sufficient hydroxyl ions in the photographic element to activate the developing agent and cause vigorous development of the exposed silver halide.

Another object is to provide a novel light-sensitive photographic element containing silver halide and an alkali-releasing agent which is developed by a low alkali inactive developer solution per se or a processing element incorporating such a solution containing a developing agent and a very slightly soluble nonalkaline metal hydroxide to produce a stable less dissociated compound than the metal hydroxide and to release sufficient hydroxyl ions to activate the developing agent and cause vigorous development of the exposed silver halide.

Another object is to provide a web process utilizing processing elements having greatly improved keeping life compared to prior art processing elements.

Another object is to provide a novel light-sensitive photographic element and a processing element which, when brought in contact with each other in the presence of water or water containing a developing agent, will result in photographic development of the photographic elements.

Another object is to provide a process for developing the novel photographic element or our invention by using a low alkali inactive developer solution which contains a developing agent and sodium or potassium salt which reacts with the very slightly soluble metal hydroxide incorporated in the photographic element to produce a less dissociated compound than the metal hydroxide and release hydroxyl ions to activate the developing agents.

Still another object is to provide a novel photographic element that is developed by a low alkali inactive developer solution that is substantially more stable than the conventional developers.

Other objects will become apparent from the following specification and claims.

These and other objects are accomplished by using the photographic element-developer combination of our invention.

Our photographic element in its simplest form consists of a support coated with an organic hydrophilic layer containing light-sensitive silver halide and an alkali-releasing agent consisting of a very slightly water-soluble metal hydroxide having the formula:

I $$Z(OH)_n$$

or an alkali-releasing reagent having the formula:

II $$XY$$

such that (1) when the alkali-releasing agent $Z(OH)_n$ is incorporated in the photographic element, the alkali-releasing reagent XY is incorporated in the developer solution or in the processing element if a web process is used, and (2) when the alkali-releasing reagent XY is incorporated in the photographic element, the alkali-releasing agent $Z(OH)_n$ is incorporated in the processing element; in these formulae: Z represents a metal atom that forms a compound that is substantially less dissociated than $Z(OH)_n$ and releases hydroxyl ions from $Z(OH)_n$ by the reaction with the atom or group Y of the compound XY, X represents a sodium or potassium atom, Y represents a citrate radical, an oxalate radical, a fluorine atom, a ferricyanide radical, a tartrate radical, a sulfite radical, an ethylenedinitrilo tetraacetate radical, a 1:3-diamino-2-propanol tetraacetate radical, and other aliphatic nitrogenous poly-carboxylate radicals, such as a trimethylaminetricarboxylate radical, a di-ω,ω'-methylamino-diethylaminedicarboxylate radical, a di-ω,ω'-dimethylamino-diethylaminetetracarboxylate radical, and etc., and n is the integer 2, 3, or 4 which has the same numerical value as the valence of metal atom Z in the compound $Z(OH)_n$.

Alternatively, our photographic element may consist of a support coated on one side with a light-sensitive organic hydrophilic layer containing a silver halide and a second organic hydrophilic layer containing the compound $Z(OH)_n$ or the compound XY coated over the said sensitive layer, or the emulsion layer containing $Z(OH)_n$ or XY may be coated on the support with the light-sensitive layer coated over the $Z(OH)_n$ or XY containing layer.

The activator solution of the invention in its simplest form is composed of water or an aqueous solution which may or may not contain developing agents but which does not contain any alkali. The solution may contain the compound XY.

The low alkali processing element or processing web of our invention in its simplest form consists of a hydrophilic layer incorporating an alkali-releasing agent, $Z(OH)_n$ if the alkali-releasing reagent, XY, is incorporated in the photographic element or in the activator solution, or the processing element consists of a hydrophilic layer incorporating an alkali-releasing reagent XY if the alkali-releasing agent, $Z(OH)_n$, is incorporated in the photographic element.

In one embodiment of our process, a photographic element containing light-sensitive silver halide and a very slightly soluble metal hydroxide of Formula I is developed with a low alkali, inactive developer solution. The developing agent and compound XY of Formula II in the developer solution, diffuse into the emulsion layer of the photographic element. A reaction between compound XY and $Z(OH)_n$ results in the simultaneous formation of a compound that is less dissociated than the metal hydroxide which has the formula:

III ZY

and X^+ and OH^- in which X, Y, and Z are as previously defined. The hydroxyl ions produced in the emulsion layer activate the developing agent and the exposed silver halide in the emulsion layer is vigorously developed to form a silver image.

In another embodiment of our invention, the photographic element described above is developed by contacting it with a moist processing element consisting of a hydrophilic layer that has been soaked in a water solution of a developing agent and a compound XY. Developing agent and compound XY diffuse from the hydrophilic layer into the silver halide emulsion layer of the photographic element where $Z(OH)_n$ and XY react to produce a less dissociated compound than the metal hydroxide and release hydroxyl ions which activate the developing agent and cause vigorous development. After development, the processing element is separated from the developed photographic element.

In another embodiment of our invention, the alkali-releasing reagent XY is incorporated in the photographic element which is developed by contacting it with the moist hydrophilic layer of a processing web or element that incorporates an alkali-releasing agent $Z(OH)_n$ and which is soaked in a water solution of a developing agent just prior to use.

In this process the alkali-releasing reagent in the photographic element dissolves, diffuses to the hydrophilic layer where it reacts with the slightly soluble metal hydroxide thus releasing sufficient hydroxyl ions to activate the developing agent and cause silver image development. After development, the processing element is separated from the developed photographic element.

In another embodiment of our invention, all of the chemicals required for development are incorporated in dry form in the two elements, that is, in the photographic element and the web, so when they are brought together in the presence of a film of moisture that may be applied to either or both elements before they are contacted, development will occur. For example, the developing agent may be in either the photographic element or in the processing element, the compound XY may be in either element while the compound $Z(OH)_n$ is incorporated in the other element.

In still another embodiment of our invention, the processing element or web is designed to develop and also fix the developed photographic image. Such webs contain in addition to the chemicals already indicated, an incorporated silver nucleating or precipitating agent, and either contain a silver halide solvent or are soaked in a solution containing a silver halide solvent prior to use. As described previously, the photographic element and web may together contain all the chemicals needed for development and fixing so that after exposure to an image, the photographic element may be developed and fixed simply by contacting it with the web in the presence of a film of moisture. After processing, the two elements are stripped apart to expose the photographic image. Such a web may be designed solely for developing and fixing a negative silver image in the photographic element or it may be designed so that it will accomplish this in addition to producing a good usable positive silver image in the web.

The blocked alkali system of our invention may be utilized not only in silver image transfer processes, such as described above, but may also be utilized in color transfer processes as a source of alkali. For this purpose the XY compound may be in the photographic element and the $Z(OH)_n$ compound in the web or the XY compound may be in the web and $Z(OH)_n$ in the photographic element. Color transfer processes in which our blocked alkali system is valuable include those using non-diffusing couplers which form upon development a diffusible dye which diffuses to the web (which may contain a mordant), such as is described in Whitmore et al. in U.S. Serial 734,141, filed May 9, 1958, now abandoned, Whitmore et al., U.S. Serial 756,597, filed August 22, 1958, now abandoned, Williams et al., U.S. Serial 780,710, filed December 16, 1958, now abandoned, etc., and diffusing dye developer processes in which the diffusible dye developer is immobilized in regions of development while dye developer in regions of no development diffuses to the web to form the color image, such as is described in British Patent No. 804,971, published November 26, 1958.

Among the very slightly soluble metal hydroxides ($Z(OH)_n$) we have found valuable for incorporation in our photographic elements or in the processing elements to generate hydroxyl ions needed to activate the developing agent during development are the following:

Cadmium hydroxide
Aluminum hydroxide
Zinc hydroxide
Titanium hydroxide
Lead hydroxide

Typical examples of compounds having Formula II, valuable for use in our invention, are as follows:

Sodium citrate
Potassium citrate
Sodium oxalate
Potassium oxalate
Sodium fluoride
Potassium fluoride
Sodium ferrocyanide
Potassium ferrocyanide
Sodium tartrate
Potassium tartrate
Sodium sulfite
Potassium sulfite

Ethylenedinitrilo tetraacetic acid tetra sodium salt
Ethylenedinitrilo tetraacetic acid tetra potassium salt
Ethylenedinitrilo tetraacetic acid trisodium salt
Ethylenedinitrilo tetraacetic acid tripotassium salt
1:3-diamino-2-propanol tetraacetic acid tri sodium salt
1:3-diamino-2-propanol tetraacetic acid tri potassium salt
1:3-diamino-2-propanol tetraacetic acid tetra sodium salt
1:3-diamino-2-propanol tetraacetic acid tetra potassium salt

In addition to these, the alkail metal salts of other aliphatic nitrogenous poly-carboxylic acids, such as trimethylamine-tricarboxylic acid, and di-ω,ω'-methylamino-diethylamine-dicarboxylic acid, of U.S. Patent 2,168,181, di-ω,ω'- dimethylamino-diethylamine-tertacarboxylic acid, etc. are used to advantage.

The preparation of 1:3-diamino-2-propanol tetraacetic acid is described in Henn et al., U.S. Patent 2,656,273, issued October 20, 1953. Alkali metal salts of other aliphatic nitrogenous polycarboxylic acids useful in our invention may be found in the book "Organic Sequestering Agents" by S. Chaberek and A. E. Martell, published in 1959 by John A. Wiley & Sons in the United States (Library of Congress Catalogue Card Number 58–13455) and by Chapman & Hall in London.

The tetra sodium or potassium salt of ethylenedinitrilo tetraacetic acid dissociates in water solution to produce a pH which may be sufficient to bring about a certain amount of development even in the absence of the alkali-releasing agent $Z(OH)_n$. In such instances, it is the increase in the rate and extent of development produced by the release of hydroxyl ions resulting from the reaction of the tetra sodium or potassium salt of ethylenedinitrilo tetraacetic acid with the compound $Z(OH)_n$ that makes these salts valuable for use in our invention.

In some instances it may be advantageous to use combinations of the alkali-releasing reagent, XY, rather than a single compound.

The photographic emulsions used in practiceing our invention are of the developing-out type.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelation, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, Sheppard et al. U.S. Patent 1,623,499, issued April 5, 1927, and Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroptatinate, and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibtion, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951 and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, and Damschroder et al. U.S. Patent 2,642,361, issued June 16, 1953. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β-aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, isued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950 and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950 and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; VanLare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; or with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948 and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reyolds U.S. Patents 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2–28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or the polymethylene bis-benzothiazolium salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954; the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958; and the carboxymethylmercapto compounds of Murray, Reynolds and VanAllan U.S. Patent 2,819,965, issued January 14, 1958.

The emulsions may also contain speed increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; or the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955; or the quaternary ammonium salts and polyethylene glycols of Piper U.S. Patent 2,886,437, issued May 12, 1959; as well as the thiopolymers of Graham and Sagal U.S. application Serial No. 779,839, now U.S. Patent 3,046,129, filed December 12, 1958, and the Dann and Chechak U.S. application Serial No. 779,874, now U.S. Patent 3,046,134, filed December 12, 1958.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. Patent 2,960,404, issued November 15, 1960; an ester of any ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. Patent 2,904,434, issued September 15, 1959; bis-(ethoxy diethylene glycol succinate) as described in Gray U.S. Patent 2,940,854, issued June 14, 1960; or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsions may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo (2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride as described in Allen and Carroll U.S. Patents 2,725,294, and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonoxy)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness Canadian Patent 588,451, issued December 8, 1959; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. Patent 2,950,197, issued August 23, 1960; 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959; or bisisocyanate as described in Henn et al. U.S. patent application Serial No. 805,357, now U.S. Patent No. 3,103,437, filed April 10, 1959.

The emulsions may contain a coating aid such as saponin; a lauryl or oleyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert.octylphenoxypentaethoxy)-glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, now U.S. Patent 3,038,804, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate as described in Knox and Stenberg U.S. patent application Serial No. 691,125, now U.S. Patent 2,992,108, filed October 21, 1957, or a sodium salt of an alkylarylpolyether sulfonate of Baldsiefen U.S. Patent 2,600,831, issued June 17, 1952.

The addenda which we have described may be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions, they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U. S. Patent 2,698,794, issued January 4, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

These may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,698,236, issued December 28, 1954 and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. patent application Serial No. 586,705, now U.S. Pat. No. 3,020,155, filed May 23, 1956. They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951 and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 17, 1957 and 554,935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, granted July 24, 1956 and Whitmore and Mader U.S. patent application Serial No. 734,141, filed May 9, 1958. They may also be used in emulsions intended for use in a monobath process such as described in Haist et al. U.S. Patent 2,875,048, issued February 24, 1959, and in web-type processes, such as the one described in Tregillus et al. U.S. patent application Serial No. 835,473, now U.S. Patent 3,179,517, filed August 24, 1959.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide or an imidized polyacrylamide as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issed February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382, of Illingsworth, Dann and Gates, issued September 16, 1958.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation. Combinations of these antifoggants, sensitizers, hardeners, etc., may be used.

Any of the materials used for supports in conventional photographic elements containing light-sensitive silver halide emulsion layers may be used for supports in the photographic elements of our invention. For example, transparent supporting material such as glass, cellulose acetate, polyethylene terephthalate, polystyrene, the polycarbonates, etc., are used as supports for coating our photographic elements that are to be used for making transparencies. Opaque materials such as paper, baryta coated paper, polyethylene coated paper, or any of the transparent materials listed above which have been made opaque with an incorporated opaque pigment or which have been made opaque by means of a coating containing an opaque pigment may be used for coating the photographic elements for print purposes.

Our photographic element may be provided with a conventional antihalation layer which may be coated either under the emulsion layers already described or on the backside of the support. Also conventional light filtering layers may be used in making our photographic elements.

The following examples will illustrate typical photographic elements of our invention but are not to be considered as limiting the scope of the invention.

EXAMPLE 1

A cellulose acetate support was coated with an emulsion layer containing 200 mg. of $Zn(OH)_2$ per square foot and 750 mg. of gelatin per square foot of support. This coating was dried and then coated over with a high speed gelatin-bromoiodide emulsion prepared for coating by adding a solution of saponin. This emulsion was coated at 390 mg. of silver per square foot and 500 mg. of gelatin per square foot.

EXAMPLE 2

A high contrast gelatin-chlorobromide emulsion was prepared for coating by adding a solution of saponin. This material was coated at 250 mg. of silver per square foot and 500 mg. of gelatin per square foot over a gelatin layer containing 200 mg. of $Zn(OH)_2$ per square foot and 750 mg. of gelatin per square foot previously coated and dried on a cellulose acetate support.

We have found that the above compounds such as sodium citrate are used to advantage in our developer solutions in the concentration range of 12 g. per liter to 120 g. per liter. When used at concentrations below 12 g. per liter, nonuniform development has been noted which causes a mottled appearance in the developed image. The preferred range of concentrations for these compounds is from 40 to 50 g. per liter.

Any of the conventional developing agents or combinations of these developing agents may be used in our developer solutions. These include such developing agents as hydroquinone and substituted hydroquinones which are substituted on the 2,3,5- or 6- carbons or any combination of these with lower alkyl groups such as methyl, ethyl, propyl, butyl, etc., with lower alkoxy groups, halogen atoms such as chlorine, bromine, fluorine, and other groups commonly used as substituents; resorcinal; catechol; ascorbic acid; the aminophenols such as p-methylaminophenol sulfate; the 3-pyrazolidones such as are described in Haist et al., U.S. 2,875,048, issued February 24, 1959; the phenylenediamines; etc.

Other materials may be added to the developer solutions such as the sequestering agents of Henn U.S. 2,625,476, issued January 13, 1953, and Henn et al. U.S. 2,656,273, issued October 20, 1953, the stabilizers of Haist et al., U.S. 2,875,048, issued February 24, 1959, antifoggants commonly used such as benzotriazole, development restrainers such as alkali bromides, iodides, etc.

During the development reaction, the compound of Formula II in the developer diffuses into the emulsion layer of the photographic element and reacts with the very slightly soluble metal hydroxide incorporated there to produce a less dissociated compound than the metal hydroxide and release hydroxyl ions that activate the development reaction. The release of hydroxyl ions is illustrated by the following table which shows the increase in pH produced by the reaction of representative hydroxides and XY compounds of Formula II.

Table I

Metal hydroxide and its pH	Compound of Formula II and its pH	pH of Mixture	pH Change
Aluminum hydroxide-7	Sodium citrate-7.4	11.3	+3.9
Do	Potassium oxalate-7.5	10.0	+2.5
Do	Potassium fluoride-8.4	12.8	+4.4
Zinc hydroxide-7	Sodium citrate-7.4	11.4	+4.0
Do	Potassium oxalate-7.5	11.0	+3.5
Do	Potassium fluoride-8.4	11.1	+2.7
Do	Potassium ferrocyanide-9.5	11.9	+2.4
Do	Potassium tartrate-8.7	10.8	+2.1
Do	Ethylenedinitrilotetraacetic acid trisodium salt-8.2.	11.75	+3.5
Do	Ethylenedinitrilotetraacetic acid tetrasodium salt-10.5.	12.3	+1.8
Titanium hydroxide-7	Potassium oxalate-7.5	9.0	+1.5
Do	Potassium fluoride-8.4	9.9	+1.5
Lead hydroxide-7	Sodium citrate-7.4	8.9	+1.5
Do	Sodium sulfite-10.1	11.7	+1.6
Do	Potassium oxalate-7.5	10.4	+2.9
Lead hydroxide-9.9	Potassium fluoride-9.5	11.0	+1.1
Lead hydroxide-8.0	Ethylenedinitrilotetraacetic acid trisodium salt-8.2.	12.8	+4.6
Do	Ethylenedinitrilotetraacetic acid tetrasodium salt-10.5.	13.2	+2.7
Cadmium hydroxide-7	Ethylenedinitrilotetraacetic acid trisodium salt-8.2.	12.5	+4.3
Do	Ethylenedinitrilotetraacetic acid tetrasodium salt-10.5.	12.9	+2.4

The developer solution used for developing our photographic elements such as is illustrated by Examples 1 and 2, in general, have the formula of any of the conventional developer solutions used for silver halide development. However, in order to use the system according to our invention so that its full benefits may be derived, the developer formulae conventionally used are altered by eliminating the alkali normally present in the formula and by adding a compound having Formula II, XY. These developers are low alkali and inactive compared to usual photographic developers. Because of their low alkali content they are considerably more stable than normal developers.

Although all of these alkali releasing reagents are valuable, some of them are particularly noteworthy when their own pH is relatively low and yet they produce upon reaction with the slightly water-soluble metal hydroxide a relatively large increase in pH. Of particular interest is the trisodium salt of ethylenedinitrilotetraacetic acid, for example, which reacts with lead hydroxide to produce a pH increase of 4.6 units. The alkali metal salts, particularly the trialkali metal salts of ethylenedinitrilotetraacetic acid are preferred alkali releasing reagents for use in the processing web (receiving sheet) for developing photographic elements of our invention which contain a slightly water-soluble metal hydroxide in a process which requires only the addition of water to the photographic element before it is contacted with the dry processing web. Such a process is illustrated by Examples 23 and 24.

The following typical developer will illustrate developer solutions useful in our invention.

EXAMPLE 3

Constituent:		Amount
Water	ml	500
p-Methylaminophenol sulfate	g	2.5
Sodium sulfite (desiccated)	g	30.0
Hydroquinone	g	2.5
Potassium bromide	g	0.5
Sodium citrate	g	12.0
Water to 1.0 liter.		

The photographic element-developer combination of our invention is illustrated by the following examples.

EXAMPLE 4

The photographic element of Example 1 was exposed to light through a step wedge image and developed for 5 minutes in a developer similar to the developer of Example 3 but containing no sodium citrate, then fixed in a conventional sodium thiosulfate fixing bath, washed, and dried. This control element-developer combination gave a speed which was assigned a value of 100 and had a γ of 0.34, and a fog level of 0.04.

EXAMPLE 5

The photographic element of Example 1 was exposed to light through a step-wedge image and developed for 5 minutes in the developer of Example 3, fixed in a conventional sodium thiosulfate fixing bath, washed and dried. This element-developer combination produced a relative speed (i.e. a speed relative to the speed of 100 in Example 4) of 175, a γ of 0.34, and a fog level of 0.04.

EXAMPLE 6

Another sample of the photographic element of Example 1 was exposed and processed as in Example 4 but the ing that the developer contained 24 g. per liter of sodium citrate instead of 12 g. per liter to give an image with a relative speed (i.e. a speed relative to the speed of 100 in Example 4) of 187, a γ of 0.32 and a fog level of 0.04.

A sample of a photographic element like that of Example 1 but without the layer under the emulsion layer containing zinc hydroxide, was exposed and given the same process used above (in Example 6) to produce an image having a relative speed of only 91, a γ of 0.21 and a fog level of 0.04.

EXAMPLE 7

Another sample of the photographic element of Example 1 was exposed and procesed as in Example 4 but the developer used contained 36 g. per liter of sodium citrate instead of 12 g. per liter. The image had a relative speed of 190, a γ of 0.34 and a fog level of 0.04. The relative speed relates to 100 in Example 4.

EXAMPLE 8

The high contrast photographic element of Example 2 was exposed and processed by the method used in Example 4. This control element-developer combination produced an image with a speed which was assigned a value of 100, a γ of 1.66 and a fog level of 0.03.

EXAMPLE 9

Another sample of the photographic element of Example 2 was exposed and processed by the same method used in Example 5 to give a relative speed (i.e. a speed relative to the speed of 100 in Example 8) of 126, a γ of 3.50 and a fog level of 0.05.

EXAMPLE 10

Similarly, another sample of the photographic element of Example 2 was exposed and processed as in Example 6 to give a photographic result having a relative speed (i.e. a speed relative to the speed of 100 in Example 8) of 131, a γ of 2.95 and a fog level of 0.07.

EXAMPLE 10*a*

Another sample of the photographic element of Example 2 was exposed and processed as in Example 7 to give a photographic result having a relative speed (i.e. a speed relative to the speed of 100 in Example 8) of 133, a γ of 2.70, and a fog level of 0.06.

The novel photographic element-developer combination of our invention is particularly valuable for use in web processing systems. In such systems the low alkali developer compositions used are not only advantageous because of the improved developer stability but especially because of the prolonged keeping life of processing webs presoaked in this developer. The gelatin layer of prior art webs soaked in conventional developers of moderate pH hydrolyzes after short storage periods. Hydrolysis results in deterioration of the gelatin layer and in a loss of alkalinity which reduces the ability of the web to process photographic silver halide emulsion layers. Our webs have about twice the keeping life of prior art webs which are currently used with processing solutions having a pH of about 9.3 to 9.5, and our webs have about four times the keeping life of a prior art processing web using an alkaline processing solution with a pH of 10.5.

The processing elements or webs of the present invention comprises a hydrophilic organic colloid layer. The hydrophilic layers may be employed alone if they have sufficient strength to be self-supporting; or if desired, they may be coated on suitable film supports. The film supports and any subbing layers should preferably be inert to the chemicals in the processing solution and it is desirable in some cases that such supports be hydrophobic in nature as well. Suitable hydrophilic organic colloids include gelatin, cellophane, polyvinyl alcohol, hydrolyzed cellulose acetate, cellulose ether phthalate, carboxylated rubber, and similar materials. Particularly useful hydrophilic materials are gelatin and a copolymer made up of 80 percent acrylic acid and 20 percent ethyl acrylate. It is essential for best results in the operation of the web process that the hydrophilic layer be readily separable from the emulsion layer of the film to be processed.

It is important that the web be composed of a material which will swell and absorb aqueous solutions and that the extent of this absorption be sufficient to accommodate enough of each processing ingredient to obtain substantially complete development and fixation, or development alone if fixation or stabilization is to be accomplished by a separate step. In general, processing webs designed to develop and fix the photographic element must have the capacity to absorb at least 4.5 grams of a suitable processing solution per square foot of the web. Webs absorbing from about 5 to 10 grams of processing solution are usually satisfactory for processing slow or moderate speed chlorobromide emulsions while higher capacities may be required for silver bromoiodide emulsions or emulsions having large amounts of silver halide per unit area of emulsion. An upper practical limit of processing solution absorption would be about 25 grams per square foot.

It is important when it is desired to store webs containing processing solution that any tendency of the webs to exude liquid should be minimized. Exudation may appear as small droplets of liquid growing upon the surface of a soaked web after excess processing solution has been removed with a squeegee. These droplets may make it difficult to achieve intimate contact between the web and the silver halide emulsion layer. The otherwise preferred acrylic acid-ethyl acrylate webs have a greater tendency than gelatin to exude processing solution. It has been found that this tendency can be minimized by coating the copolymer on a suitable support at a coverage of about 2 grams per square foot and then hardening the copolymer to the point where it will absorb only the amount of solution needed without more than about 300 percent swelling of the copolymer layer. Webs which are required to absorb more than 6 or 7 grams of processing solution per square foot may need to have more than 2 grams of the copolymer per square foot of support. A suitable hardener is bis(2,3-epoxypropoxyethyl)ether used in amounts between 0.5 and 2.5 percent based on the weight of the copolymer.

Webs used to fix as well as develop the photographic element also contain incorporated silver precipitating agents in the hydrophilic layer. These may be physical development nuclei or chemical precipitants including (a) heavy metals, especially in colloidal form, and the salts of these metals, (b) salts, the anions of which form a silver salt less soluble than the silver halide of the photographic emulsion to be processed, or (c) nondiffusing polymeric materials with functional groups capable of combining with and insolubilizing silver ion. Suitable silver precipitating agents for use in the invention are disclosed in Rott U.S. Patent 2,352,014, Yutzy and Yackel U.S. Patent 2,740,717, and in Yackel et al. United States patent application Serial No. 586,705, filed May 23, 1956. More specifically, useful silver precipitating agents include sulfides, selenides, polysulfides, polyselenides, thiourea and its derivatives, mercaptans, stannous halides, silver, gold, platinum, palladium, and mercury, colloidal sulfur, aminoguanidine sulfate, aminoguanidine carbonate, arsenous oxide, sodium stannite, substituted hydrazines, xanthates, and the like. Polyvinyl mercapto-acetate is an example of a non-diffusing polymeric silver precipitant. Heavy metal sulfides such as lead, silver, zinc, nickel, antimony, cadmium, and bismuth sulfides are useful, particularly the sulfides of lead and zinc alone or in admixture, or complex salts of these with thioacetamide, dithiooxamide, or dithio-biuret. The heavy metals and the noble metals particularly in colloidal form are especially effective. Other silver precipitating agents will occur to those skilled in the art.

The particular means employed to precipitate silver in the hydrophilic layer will depend on the demands of simplicity, ease of fabrication, compatibility, and the effect on the photographic quality of the light-sensitive element to be processed. As indicated, silver precipitating agents may be materials that act as nuclei or will form nuclei which are sites for physical development upon which metallic silver from the soluble silver complexes may be deposited by the action of developing agents. Those silver precipitants that will form metallic silver directly or form insoluble silver salts may be incorporated in the hydrophilic layer in sufficient quantity to supply stoichiometric amounts for reduction or precipitation of silver ion, rather than in the considerably lower quantities used to promote physical development or catalytic decomposition.

The concentrations of silver precipitants in the hydrophilic layer of the web must at least be sufficient to insure positive and complete removal of undeveloped silver halide from the light-sensitive element to be processed. However, it has been found that a very considerable degree of control of the sensitometric properties of the image in web processed photographic material can be obtained through choice of the silver precipitant and by adjusting its concentration. For example, Carey-Lea silver nuclei incorporated in the hydrophilic layer of the web to give a coverage of 3 mg. of silver nuclei per square foot is sufficient to cause complete removal of substantially all undeveloped silver halide from a silver chlorobromide negative material processed by such a web. As this coverage is increased up to 120 mg. of silver nuclei per square foot, negative fog is lowered and the processing rate increases. Furthermore, the use of lead sulfide nuclei in a gelatin layer at a coverage of 8 mg. per square foot has been found to result in higher negative contrast when the same photographic material is processed. In turn, increasing the coverage of lead sulfide nuclei will increase the contrast but lower the speed of the processed negative image, while lowering maximum density.

Webs used for processing alkali-releasing reagent incorporating silver halide emulsion layers have alkali-releasing agent incorporated uniformly throughout the hydrophilic layer of the web or incorporated in a second hydrophilic layer coated over or under the main hydrophilic layer.

The web should incorporate at least enough alkali-releasing agent per unit area to release the hydroxyl ions required for processing a unit area of silver halide emulsion. Since hydroxyl ions are needed to raise the pH of the solution, in the hydrophilic layer of the web, and in the silver halide bearing hydrophilic layer of the photographic element to the pH required by the development reaction as well as for the reduction of exposed silver halide to silver, it is obvious that the hydroxyl ions needed may vary considerably depending on these factors for the particular web, photographic element, etc., to be used. In practice it has been found necessary to use more than the amount of alkali-releasing agent theoretically needed to supply these hydroxyl ions. Similarly, when the alkali-releasing agent is incorporated in the photographic element instead of the web, it is necessary to use an excess over the theoretical amount required. It appears that some of the alkali-releasing agents such as zinc hydroxide may become dehydrated during coating and drying of the hydrophilic layer so that it cannot quickly give up its hydroxyl ions.

If the web is to be used to process more than one batch of the photographic element, then enough alkali-releasing agent must be incorporated for the number of processes desired. The amount of hydroxyl ions released in the process is controlled by the amount of the alkali-releasing reagent that is incorporated in the photographic element. The preferred amount of alkali-releasing reagent incorporated in the photographic element will react with the alkali-releasing agent to produce enough hydroxyl ions to raise the pH of the system to the processing pH and neutralize the hydrogen ions generated by the silver reduction.

Webs used for processing alkali-releasing agent incorporating photographic elements may incorporate the alkali-releasing reagent, however, the reagent is usually contained in the processing solution that the web is soaked in prior to use.

The webs are soaked in an aqueous processing solution containing (1) a developing agent or combination of developing agents, (2) an alkali-releasing reagent when this is not already incorporated in the web and is to be supplied by the web, (3) a silver halide solvent when development and fixing are to be accomplished by a one step web process, and (4) other materials when needed such as potassium iodide, antifoggants, buffering agents, etc.

Among the developing agents useful are those described previously as used in our low alkali inactive developer solutions, sulfur dioxide clathrates of developing agents such as hydroquinone-sulfur dioxide clathrate, pyrogallal, gallic acid, the diamino phenols such as 2,4-diaminophenol, 3,4-diaminophenol hydrochloride, etc., the triaminophenols such as 2,4,6-triaminophenol, etc., glycine and glycine derivatives such as N-(p-hydroxyphenyl)-glycine, etc., the ene-diols such as ascorbic acid and especially the 1-phenyl-3-pyrazolidones. Especially useful combinations of developing agents include mixtures of monomethyl-p-aminophenol sulfate and hydroquinone; 1-phenyl-3-pyrazolidone and hydroquinone; and 4,4-dimethyl-1-phenyl-3-pyrazolidone and hydroquinone.

Silver halide solvents useful in the processing solution include the alkali metal thiosulfates such as sodium thiosulfate, potassium thiosulfate, etc., the alkali thiocyanates, alkali selenocyanates, thioglycerol, aminoethanethiols, p,p′-dithiasuberic acid, etc. Sodium thiosulfate pentahydrate is a preferred solvent. It may be used advantageously in the range of from 2 to 25 g. per l.

In another embodiment of our invention the negative and the web together contain all the processing chemicals requiring only water for activation. The web in this process serves as a receiving sheet upon which a positive image is formed after the negative image is formed in the negative.

The following examples will further illustrate how our invention is used in the development of photographic silver halide emulsion layers with a web processing system. Examples 12, 13, and 14 illustrate how to determine the proper amount of potassium fluoride to incorporate in our photographic emulsion layer.

EXAMPLE 11

A web material was prepared consisting of, on each square foot, 2 g. of gelatin, 10 mg. of Carey-Lea silver, and 0.124 g. aluminum hydroxide coated on a polyester support. A biostat and a coating aid were included in the coating solution.

The web material was soaked for 3 minutes at 70° F. in a developer solution comprised of:

	G.
Sodium sulfite	8.0
Hydroquinone	3.5
Sodium thiosulfate	1.6
4,4-dimethyl-1-phenyl-3-pyrazolidone	0.2

Water to 250.0 cc.

EXAMPLE 12

A negative was prepared consisting of, on each square foot, 0.5 g. gelatin, 0.15 g. silver as silver chlorobromide, and 0.160 g. potassium fluoride, coated on a cellulose acetate support. A hardener and coating aid were included in the coating solution.

The web of Example 11 was brought in contact with the negative material. After remaining in contact for 10 minutes the two sheets were stripped apart. The negative was completely developed and cleared.

EXAMPLE 13

A negative was prepared as in Example 12, except that it contained 0.080 g. potassium fluoride per square foot.

The web of Example 11 was brought in contact with this negative material. After remaining in contact for 10 minutes, the two sheets were stripped apart. The negative was partially developed and cleared.

EXAMPLE 14

A negative was prepared as in Example 12 except that the potassium fluoride was omitted.

The web of Example 11 was brought in contact with this negative material. After remaining in contact for 10 minutes, the sheets were stripped apart. Very little development occurred in this negative.

EXAMPLE 15

The following example will illustrate the reaction that took place in a web process system when the negative contained an alkali releasing agent. The components used in the following composition were equivalent to those contained in 33.3 square feet of web and negative coating.

Into 200 cc. of water 4.1 g. of aluminum chloride was dissolved. To the aluminum chloride solution 15.5 cc. of 4 N sodium hydroxide was added. The pH at this point was 7.0. The following developer components were added to the above aluminum hydroxide solution:

	G.
Sodium sulfite	8.0
Hydroquinone	3.5
Sodium thiosulfate	1.6
4,4-dimethyl-1-phenyl-3-pyrazolidone	0.2

The additions caused the pH to become 8.4. At thi point 19.5 cc. of 4 N potassium fluoride was added. Th pH increased to 10.25. The increase in pH from 8. before the addition of potassium fluoride to 10.25 afte the addition of potassium fluoride indicated that enoug hydroxyl ion was released to activate the developer.

EXAMPLE 16

A web material was prepared in which each squar foot consisted of 2 g. gelatin, 1.2 mg. lead sulfide nucle and 0.3 g. zinc hydroxide, coated on a cellulose acetat support. A biostat, a hardener, and a coating aid wer included in the coating solution.

The web material was soaked for 3 minutes at 70° F in a developer solution comprised of:

	G
Sodium sulfite	8.
Hydroquinone	3.
Sodium thiosulfate	3.
1-phenyl-4,4-dimethyl-3-pyrazolidone	0.

Water to 350.0 cc.

EXAMPLE 17

A set of negative emulsion coatings were made on a cellulose acetate support in which each square foot consisted of 0.5 g. gelatin and 0.15 g. silver as silver chlorobromide, together with a hardener and a coating aid. The negatives contained also sodium citrate, according to the following schedule.

Coating:	Sodium citrate, gram/foot^2
A	0
B	0.150
C	0.300
D	0.450

Samples of the negatives were exposed and then rolled in contact with strips of the wet web of Example 16. After a contact period of 10 minutes, the sandwiches were separated. Negative A showed very little development and no fixation, as would be expected in the absence of the hydroxide-releasing reagent. Negative B was partially developed and cleared, while Negative C was almost fully developed and cleared. Complete development and fixation were found in Negative D, indicating that sufficient hydroxide-releasing reagent was contained within the emulsion coating.

EXAMPLE 18

A web was prepared as in Example 16, except that it contained 0.6 g. zinc hydroxide/ft.^{2}.

The web material was soaked for 3 minutes at 85° F. in a developer solution comprised of:

	G.
Sodium sulfite	8.0
Hydroquinone	4.0
Sodium thiosulfate	8.0
1-phenyl-4,4-dimethyl-3-pyrazolidone	0.5

Wated to 250.0 cc.

EXAMPLE 19

A set of negative emulsion coatings were made as in Example 17, but the sodium citrate was replaced by (ethylenedinitrilo)tetraacetic acid tetrasodium salt which had been neutralized to a pH of 6.9 with sulfuric acid. The (ethylenedinitrilo)tetraacetic acid tetrasodium salt is available from Geigy Chemical Corporation under the trade name Sequestrene. The coatings were prepared according to the following schedule.

Coating:	Sequestrene, gram/foot^2
A	0
B	0.30
C	0.45

Samples of the negatives were exposed and then rolled in contact with strips of the wet web of Example 18. After a contact period of 10 minutes, the sandwiches were separated. Very little development and no fixing had occurred in Negative A. Negative B was almost completely developed and fixed, while Negative C showed complete development and fixation. It was evident that the Sequestrene formed a complex ion with the zinc, thereby releasing hydroxide ions which activated the development reactions.

The following two examples comprise a system in which barium carbonate represents the slightly water-soluble source of alkalinity and sodium sulfate the releasing reagent. By the formation of insoluble barium sulfate, carbonate ions are released which, by hydrolysis, provide hydroxide ions for the development reactions.

EXAMPLE 20

A web material was prepared in which each square foot consisted of 2 g. gelatin and 2.0 mg. lead sulfide nuclei coated on a polyethylene terephthalate support. A hardener and a coating aid were included in the coating.

The web material was soaked for 3 minutes at 68° F. in a processing solution comprised of:

	G.
Sodium sulfite	4.0
Hydroquinone	4.0
4,4-dimethyl-1-phenyl-3-pyrazolidone	0.25
Sodium thiosulfate	8.0
Sodium sulfate	20.0
Wated to 250.0 cc.	

EXAMPLE 21

On a cellulose acetate support was coated a gelatin silver chlorobromide emulsion in which each square foot consisted of 0.75 g. gelatin, 0.15 g. silver, and 0.40 g. barium carbonate. A hardener and a coating aid were included in the coating solution.

The negative material was exposed and then brought in contact with the wet web of Example 20, where it was allowed to remain for 10 minutes. On stripping the two sheets apart, appreciable development and fixation were found to have occurred in the negative. In another test in which the negative did not contain barium carbonate, no development occurred at all.

The processing in the experiment just cited was limited by the amount of processing solution absorbed by the web, owing to the reduced swelling in the presence of the sodium sulfate. Increased development and fixation could be obtained if the processing chemicals and the sodium sulfate were coated in the gelatin of the web and the web were merely wet quickly with water.

The following examples illustrate a system in which the negative material and a processing sheet together contain all the processing chemicals, requiring only water for activation.

EXAMPLE 22

On a white-pigmented cellulose acetate support, there was first coated an aqueous mixture containing the following compounds:

	Mg./ft.^{2}
Gelatin	320
Sodium thiosulfate	50
Sodium sulfite	100
4,4-dimethyl-1-phenyl-3-pyrazolidone	5
N-(p-hydroxyphenyl)glycine	50
Sodium carbonate	50
(Ethylenedinitrilo)tetraacetic acid tetrasodium salt	300
Bis(2,3-epoxypropoxyethyl)ether	6

A nucleated layer was next coated over this pad comprising:

	Mg./ft.^{2}
Gelatin	40
Nickel sulfide nuclei	0.46
5-methyloxazoline-2-thiol	0.25
7,13-dithia-nonadecane - 1,19 - bis - (pyridinium-p-toluene sulfonate)	4.0
3-mercapto-1,2,4-triazole	0.5
Bis(2,3-epoxypropoxyethyl)ether	2

EXAMPLE 23

For the negative material an underlayer was first coated on a cellulose-acetate support comprising, per square foot, 500 mg. zinc hydroxide in 250 mg. gelatin. On top of this layer was coated a silver bromoiodide emulsion consisting of 60 mg. silver in 550 mg. gelatin. Typical optical sensitizers, antifoggants, hardeners, and coating aids were present in the emulsion.

The exposed negative material was soaked in water at room temperature for 6 seconds and then brought in contact with the dry receiving sheet of Example 22. After remaining in contact for 2 minutes, the sheets were stripped apart to reveal a substantially neutral, high-density image in the receiving sheet. It was estimated that about 5 milliliters of water were held by the sandwich. Most of the water absorption took place on the receiver as the sheets were rolled together, the soaked negative sheet not being squeegeed prior to making contact. Test tube experiments indicated that the pH in the sandwich may have been initially close to 12.

EXAMPLE 24

A receiver was prepared by coating a layer on a white pigmented cellulose acetate support which was comprised of:

	Mg./ft.^{2}
Gelatin	360
Sodium sulfite, anhydrous	25
Sodium thiosulfate, pentahydrate	50
4,4-dimethyl-1-phenyl-3-pyrazolidone	10
(Ethylenedinitrilo)tetraacetic acid, tetrasodium salt	100
(Ethylenedinitrilo)tetraacetic acid, trisodium salt	200
Nickel sulfide nuclei	0.18
5-methyloxazoline-2-thiol	0.4
7,13-dithianonadecane - 1,19 - bis - (pyradinium-p-toluene sulfonate)	10

Solution coated at pH 8.3.

The composition of the negative may be summarized as follows.

Support:

Cellulose acetate film with antihalation pelloid backing.

	Mg./ft.^{2}
Coat 1:	
Gelatin	250
Zinc hydroxide	500
Coat 2:	
Gelatin	550
Silver bromoiodide (as silver)	60
4,4-dimethyl-1-phenyl-3-pyrazolidone	5
Hydroquinone-sulfur dioxide clathrate (assumed 3HQ/SO_2)	33.3
Coat 3: Gelatin	90

The exposed negative was soaked in water for two seconds, and immediately rolled in contact with the dry receiver. After two minutes the sheets were separated to reveal an image of good density, tone and contrast on the receiver. The receiver was finally rinsed in water for 15 seconds and dried.

EXAMPLE 25

A negative element was coated on a cellulose acetate support. The first or underlayer contained in each square foot 250 mg. of gelatin, 500 mg. of zinc hydroxide, 240 mg. of hydroquinone-sulfur dioxide clathrate, 8 mg. of 4-methyl-1-phenyl-3-pyrazolidone, and 4 mg. of n-decyldimethyl hydrazinium perchlorate. A second layer was coated that contained a high speed silver bromoiodide emulsion layer containing in each square foot 60 mg. of silver, 550 mg. of gelatin, 33 mg. of hydroquinone-sulfur dioxide clathrate, 1.1 mg. of 4-methyl-1-phenyl-3-pyrazolidone, and 0.55 mg. of n-decyldimethyl hydrazinium perchlorate. The second layer was overcoated with a layer containing 146 mg. of gelatin per square foot.

A receiving sheet was prepared by coating a white pigmented cellulose acetate support with a layer containing in each square foot approximately 0.5 mg. of nickel sulfide, 182.5 mg. of gelatin, 40 mg. sodium thiosulfate, 0.25 mg. of 5-methyl-oxazoline-2-thiol, 0.5 mg. of 3-mercapto-1,2,4-triazole, and 3.5 mg. of dithianonadecane-1,19-bis-(pyridinium-p-toluene sulfonate).

A sample of the negative material was exposed to an image then brought into intimate contact with the coated side of the receiving sheet which had been presoaked for five seconds in an activator solution having the composition:

Sodium sulfite (anhydrous)	g..	60
0.5% carboxymethyl cellulose solution	cc..	1000
Potassium citrate	g..	50

After five minutes the negative and receiving sheet were separated, exposing a negative silver image in the negative and a positive silver in image in the receiving sheet.

EXAMPLE 26

A negative element was prepared by coating on a cellulose acetate support a first layer containing in each square foot 250 mg. of gelatin and 500 mg. of zinc hydroxide. Over this was coated a high-speed silver bromoiodide emulsion layer containing in each square foot 60 mg. of silver, 550 mg. of gelatin, 33 mg. of hydroquinone-sulfur dioxide clathrate, 5.0 mg. of 4,4-dimethyl-1-phenyl-3-pyrazolidone, and 0.55 mg. n-decyldimethyl hydrazinium perchlorate, and finally over this was coated a layer containing 90 mg. of gelatin per square foot.

Receiving sheet A was prepared by coating on a white pigmented cellulose acetate support a layer containing in each square foot 82.5 mg. of gelatin, approximately 0.5 mg. nickel sulfide, 0.56 mg. of 3-mercapto-1,2,4-triazole, 0.28 mg. of 1-methyl-1,2,3,6-tetrahydro-1,3,5-triazine-4-thiol, and 3.9 mg. of 3,8-dithiadecane-1,10-bis(N-methylpiperidinium-p-toluene sulfonate).

Receiving sheet B was made by overcoating a sample of receiving sheet A with a layer 0.006 inch thick. The coating solution had the following composition:

0.5% solution of carboxymethyl cellulose	cc..	1000
Sodium citrate	g..	50
Sodium sulfite (anhydrous)	g..	10
Sodium thiosulfate	g..	12

Two samples of the negative material were given identical exposures to an image. The samples were soaked for five seconds in distilled water, and then one of them was squeegeed into contact with receiving sheet A and the other squeegeed into contact with receiving sheet B so that in each instance the coated side of the negative material was in contact with the coated side of the receiving sheet. After allowing five minutes for processing to occur, the negatives and receiving sheets were separated. No image was formed when receiving sheet A was used, however, a useful silver negative image was produced in the negative material contacted with receiving sheet B along with a useful silver positive image in receiving sheet B.

Another alkali-releasing reagent is 2-dimethylaminoethanol-SO_2 which may be used in the process of our invention with lead hydroxide as the alkali-releasing agent. Apparently, in this system lead sulfite was formed and the pH was raised by the release of hydroxyl ions from the lead hydroxide and the hydrolysis of the free amine.

The contacting of a processing web and the photographic element to be processed may be accomplished by any of the means used in the prior art. For example, this may be done in a batchwise manner to strips of film and web by contacting the moist surface of the web to the emulsion layer of the photographic element at one end and then rolling the two together on a spool. After the required processing time has elapsed, the web and film sandwich are unrolled and the web is stripped from the processed element. For continuous processing the web and film are advantageously brought together by passing them between wringer rollers and allowed to remain in contact for the required processing time while traveling to a second pair of rollers when the elements are separated.

The accompanying drawing, FIGS. 1 and 2, will further illustrate the use of our photographic element low alkali developer process as embodied in a web type of process. Both figures show greatly enlarged cross sectional views of the photographic element and the processing web.

FIG. 1 shows the web consisting of support **10** and gelatin layer **11** incorporating zinc hydroxide, and colloidal silver that has been moistened with a water solution of hydroquinone and hypo, with layer **11** contacting latent image **13** bearing gelatino silver chlorobromide emulsion layer **12** which incorporates sodium citrate as an alkali-releasing reagent, with layer **12** coated on film support **14**.

FIG. 2 shows the web support **10** bearing gelatin layer **15** containing zinc hydroxide, zinc citrate, oxidized hydroquinone and silver being separated from silver image **16** bearing processed emulsion layer **17** on support **14**.

The novel light-sensitive photographic emulsion-developer combination of our invention is characterized by utilizing a system in which the alkali needed for developing agent activation is generated in the area where development is to take place, making it possible to use a low alkali inactive developer solution or a processing web moistened with such a developer solution. For this system a light-sensitive photographic element is used that incorporates in the light-sensitive layer or an adjacent layer an alkali-releasing agent comprising a slightly water-soluble metal hydroxide, the element being developed with a low alkali developer solution containing an alkali-releasing reagent which reacts with the metal hydroxide to form a substantially less dissociated compound and release the hydroxyl ions needed to activate the development reaction. This system is particularly well adapted to use in a web process in which the photographic emulsion layer is developed by contacting it with the developer solution incorporating hydrophilic layer of a processing web. After development, the web is stripped from the developed layer. By incorporating a silver nucleating agent and a silver halide solvent in such a web, a developed and fixed negative is produced in the photographic emulsion layer and a positive image is produced in the web. Alternatively, in such web processing systems as these, the metal Z in one of said layers and (3) the incorporaporated in the hydrophilic layer of the web and the alkali-releasing reagent incorporated in the light-sensitive layer or an adjacent layer in a photographic element. The novel process of our invention utilizes low pH inactive developer solutions which have longer storage life after use and exposure to air than do prior art developer solutions. Processing webs containing our novel processing solutions have keeping lives that are from two to four times longer than the keeping lives of prior art webs.

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 as described hereinabove and as defined in the appended claims.

We claim:

1. In a solvent transfer process for forming a silver negative image in a latent image bearing light-sensitive silver halide emulsion layer, and for simultaneously forming a silver positive image in a processing element containing a hydrophilic colloid layer that incorporates a silver halide solvent and a silver nucleating agent, the improvement comprising (1) the incorporation of a silver halide developing agent in at least one of said layers, (2) the incorporation of a compound having the formula $Z(OH)_n$ wherein Z represents a metal selected from the class consisting of cadmium, aluminum, zinc, titanium and lead, and *n* represents an integer of from 2 to 4 which has the same numerical value as the valence of the metal Z in one of said layers and (3) the incorporation of a compound having the formula XY, wherein X represents a metal selected from the class consisting of sodium and potassium, and Y represents a group selected from the class consisting of the citrate radical, the ferrocyanide radical, the fluorine atom, the tartrate radical, an ethylenedinitrilo tetraacetate radical, a 1,3-diamino-2-propanol tetraacetate radical, a trimethylaminetricarboxylate radical, a di-ω,ω′-methylaminodiethylaminedicarboxylate radical, and a di-ω,ω′-methylaminodiethylaminetetracarboxylate radical, in the other said layer not containing the compound of the formula $Z(OH)_n$, so that the said silver image is developed by contacting the said emulsion layer with said hydrophilic colloid layer in the presence of water.

2. In a solvent transfer process for producing a silver negative image in a light-sensitive photographic element bearing a silver halide emulsion layer with a latent image, and for simultaneously producing a corresponding silver positive image in a receiving sheet bearing a hydrophilic colloid layer containing a silver halide solvent and a silver nucleating agent, at least one of said layers incorporating a silver halide developing agent, the improvement comprising the use of a photographic element in which a slightly water-soluble multivalent metal hydroxide having the formula $Z(OH)_n$ wherein Z represents a metal selected from the class consisting of cadmium, aluminum, zinc, titanium and lead, and *n* represents an integer of from 2 to 4 which has the same numerical value as the valence of the metal Z is incorporated contiguously with said silver halide and the use of a receiving sheet which incorporates a compound having the formula XY wherein X represents a metal selected from the class consisting of sodium and potassium, and Y represents a group selected from the class consisting of the citrate radical, the ferrocyanide radical, the fluorine atom, the tartrate radical, an ethylenedinitrilo tetraacetate radical, a 1,3-diamino-2-propanol tetraacetate radical, a trimethylaminetricarboxylate radical, a di-ω,ω′-methylaminodiethylaminedicarboxylate radical, and a di-ω,ω′-dimethylaminodiethylaminetetracarboxylate radical so that said silver images are produced by contacting the said emulsion layer with the said hydrophilic colloid layer in the presence of water.

3. In a solvent transfer process for producing a silver negative image in a light-sensitive photographic element bearing a silver halide emulsion layer with a latent image, and for simultaneously producing a corresponding silver positive image in a receiving sheet bearing a hydrophilic colloid layer containing a silver halide solvent, and a silver nucleating agent, at least one of said layers incorporating a silver halide developing agent, the improvement comprising the use of a photographic element in which a compound having the formula XY wherein X represents a metal selected from the class consisting of sodium and potassium, and Y represents a group selected from the class consisting of the citrate radical, the ferrocyanide radical, the fluorine atom, the tartrate radical, an ethylenedinitrilo tetraacetate radical, a 1,3-diamino-2-propanol tetraacetate radical, a trimethylaminetricarboxylate radical, a di-ω,ω′-methylaminodiethylaminedicarboxylate radical, and a di-ω,ω′-dimethylaminodiethylaminetetracarboxylate radical is incorporated contiguously with said silver halide and the use of a receiving sheet in which a slightly water-soluble multivalent metal hydroxide having the formula $Z(OH)_n$ wherein Z represents a metal selected from the class consisting of cadmium, aluminum, zinc, titanium and lead, and *n* represents an integer of from 2 to 4 which has the same numerical value as the valence of the metal Z is incorporated contiguously to the silver halide developing agent so that said silver images are produced by contacting the said emulsion layer of the photographic element with the said hydrophilic colloid layer of the receiving sheet in the presence of water.

4. A process of claim **2** in which an alkali metal salt of ethylenedinitrilo tetraacetic acid is used as the alkali-releasing reagent.

5. A process for forming a silver image in a latent image bearing light-sensitive silver halide emulsion layer containing a very slightly water-soluble metal hydroxide having the formula $Z(OH)_n$ wherein Z represents a metal selected from the class consisting of cadmium, aluminum, zinc, titanium and lead, and *n* represents an integer of from 2 to 4 which has the same numerical value as the valence of the metal Z comprising the steps of (1) contacting the said emulsion layer with the water-moistened, hydrophilic colloid layer of a processing element, the said hydrophilic colloid layer incorporating a compound having the formula XY wherein X represents a metal selected from the class consisting of sodium and potassium, and Y represents a group selected from the class consisting of the citrate radical, the ferrocyanide radical, the fluorine atom, the tartrate radical, an ethylenedinitrilo tetraacetate radical, a 1,3-diamino-2-propanol tetraacetate radical, a trimethylaminetricarboxylate radical, a di-ω,ω′-methylaminodiethylaminedicarboxylate radical, and a di-ω,ω′-dimethylaminodiethylaminetetracarboxylate radical and a developing agent, and (2) stripping said processing element from the said developed emulsion layer leaving therein a silver image.

6. A process for producing a photographic image comprising developing a negative silver image in a photo-exposed photographic silver halide emulsion of a photographic element by chemical development of said emulsion in an alkaline medium, transferring imagewise, the unexposed silver halide into a receiving sheet nucleated with a silver precipitating agent wherein said unexposed silver halide is reduced and converted to a positive silver image, the said alkaline medium for said chemical development being provided by the reaction of a slightly water-soluble multivalent metal hydroxide having the formula $Z(OH)_n$ wherein Z represents a metal selected from the class consisting of cadmium, aluminum, zinc, titanium and lead, and *n* represents an integer of from 2 to 4 which has the same numerical value as the valence of the metal Z with a compound having the formula XY wherein X represents a metal selected from the class consisting of sodium and potassium, and Y represents a group selected from the class consisting of the citrate radical, the ferrocyanide radical, the fluorine atom, the tartrate radical, an ethylenedinitrilo tetraacetate radical, a 1,3-diamino-2-propanol tetraacetate radical, a trimethylaminetricarboxylate radical, a di-ω,ω′-methylaminodiethylaminedicarboxylate radical, and a di-ω,ω′-dimethylaminodiethylaminetetracarboxylate radical, one of said reactants being present in said photographic element and the other being present in said receiving sheet.

7. A process of developing a silver image in a photographic silver halide emulsion layer containing a latent image, said process comprising the step of developing the grains of silver halide in said layer in the presence of

(1) a compound having the formula $Z(OH)_n$ wherein Z represents a metal selected from the class consisting of cadmium, aluminum, zinc, titanium and lead, and *n* represents an integer of from 2 to 4 which has the same numerical value as the valence of the metal Z and

(2) a compound having the formula XY wherein X represents a metal selected from the class consisting of sodium and potassium, and Y represents a group selected from the class consisting of the citrate radical, the ferrocyanide radical, the fluorine atom, the tartrate radical, an ethylenedinitrilo tetraacetate radical, a 1,3-diamino-2-propanol tetraacetate radical, a trimethylaminetricarboxylate radical, a di-ω,ω′-methylaminodiethylaminedicarboxylate radical, and a di-ω,ω′-dimethylaminodiethylaminetetracarboxylate radical.

8. A process for forming a silver image in a latent image bearing light-sensitive silver halide emulsion layer containing in contiguous relationship to the grains of silver halide in said layer, a compound having the formula $Z(OH)_n$ wherein Z represents a metal selected from the class consisting of cadmium, aluminum, zinc, titanium and lead, and *n* represents an integer of from 2 to 4 which has the same numerical value as the valence of the metal Z, comprising the treatment of said emulsion layer in a water solution containing a developing agent and a compound having the formula XY wherein X represents a metal selected from the class consisting of sodium and potassium, and Y represents a group selected from the class consisting of the citrate radical, the ferrocyanide radical, the fluorine atom, the tartrate radical, an ethylenedinitrilo tetraacetate radical, a 1,3-diamino-2-propanol tetraacetate radical, a trimethylaminetricarboxylate radical, a di-ω,ω′-methylaminodiethylaminedicarboxylate radical, and a di-ω,ω′-dimethylaminodiethylaminetetracarboxylate radical.

References Cited by the Examiner

UNITED STATES PATENTS

1,207,042	12/1916	Hochstetter	96—61
1,503,595	8/1924	Mees	96—48
2,558,857	7/1951	Land	96—29
2,584,030	1/1952	Land	96—110
2,607,685	8/1952	Land	96—29
2,618,556	11/1952	Hewitson et al.	96—108
2,656,273	10/1953	Henn et al.	96—76
2,662,822	12/1953	Land	96—29
2,698,236	12/1954	Land	96—29
2,747,999	5/1956	Yutzy et al.	96—29
2,768,958	10/1956	Stewart et al.	96—94
2,882,151	4/1959	Yutzy	96—29
2,910,359	10/1959	Maffet	96—108
2,953,455	9/1960	Maffet	96—110
2,992,102	7/1961	Land	96—29
3,017,270	1/1962	Tregillus	96—29
3,186,842	1/1965	De Haes et al.	96—29

FOREIGN PATENTS

221,880	5/1959	Australia.

OTHER REFERENCES

Photographic Engineering, vol. 4, No. 3, pages 157–161 (1953).

Photo Methods for Industry, February 1959, pages 32–35 and 72, 73.

Photo Science and Engineering, vol. 5, No. 1, January-February 1961, page 48–54.

Photo Science and Engineering, vol. 4, No. 5, September-October 1960, pages 298–299.

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