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[54] **CORED DIRECT POSITIVE SILVER HALIDE
EMULSION DEVELOPED WITH
POLYHYDROXYBENZENE**
14 Claims, No Drawings

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107, 101

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ABSTRACT: Processing exposed, direct-positive, high-contrast photographic elements with a polyhydroxybenzene developing agent wherein the silver halide emulsion of the element contains silver halide grains comprising internal centers which promote the deposition of photolytic silver and an outer region comprising a fogged silver halide that develops to silver without exposure. Certain halogen-conducting compounds and electron-accepting compounds can also be added to the element to increase speed.

CORED DIRECT POSITIVE SILVER HALIDE EMULSION DEVELOPED WITH POLYHYDROXYBENZENE

This invention relates to photographic materials, their preparation and use. In one of its aspects, this invention relates to processing direct-positive, high-contrast, lithographic elements.

In the graphic arts field, where it is desired to make photographic reproductions of line and halftone material, it is customary to employ silver halide emulsions having extreme contrast. For this purpose, photographic silver chlorobromide emulsions are generally employed, the silver chloride content of the emulsions being at least about 50-mole percent. After exposure of the emulsions in the conventional way, either to a halftone negative or to an original through a vacuum contact screen, the emulsions are processed in a polyhydroxybenzene photographic developer having very low free sulfite content. Development is believed to proceed catalytically, and such development is commonly referred to in the graphic arts field as "infectious development." In order to control the amount of free sulfite in the developer, it is customary to employ compounds, such as sodium formaldehyde bisulfite, in the developer which releases small amounts of sulfite to at least partially stabilize the developing solutions for short periods of time.

In reproducing continuous tone material, it is customary to make a halftone photographic intermediate, usually a film negative, in which the gradations in tone are represented by differing sizes of dots of uniform density. The shape, density and uniformity of the halftone dots are closely correlated to the quality of the resulting picture.

Photographic films used in the graphic arts field for making halftone or line images should be capable of producing extremely high contrast and good image sharpness.

A disadvantage of the lithographic films which are currently available is that they are all negative-working. In present systems, it is necessary to use a negative material in the camera, prepare a positive transparency from the negative print and then prepare the printing plate from the positive transparency. If a direct-positive, high-contrast material could be made with projection speed, it could be used in a camera to make direct-positive halftone reproductions which could then be used directly to prepare printing plates. If a direct-positive camera speed film were available, therefore, it would eliminate a costly step in the prior art process.

It is also desirable to provide a direct-positive lithographic material which will form a good image record with blue light. This would eliminate the need for filters and light sources for systems which require exposure with radiation from only selected regions of the spectrum.

According to this invention, I have now found a system for providing improved direct-positive lithographic film records. This objective has been accomplished by a process which comprises developing exposed, direct-positive, high-contrast photographic elements in a photographic developer wherein the developing agent consists essentially of a polyhydroxybenzene compound. The direct-positive emulsion utilized in the process comprises silver halide grains containing internal centers which promote the deposition of photolytic silver and an outer region comprising a fogged silver halide that develops to silver without exposure, said halide being at least 50-mole percent chloride. Direct-positive emulsions of this type generally provide a reversal image when imaged exposed to light in the blue region of the visible spectrum and processed according to this invention.

In one preferred embodiment of this invention, the developer contains low concentrations of a sulfite to provide "infectious" development.

According to another embodiment of the invention, the direct-positive emulsion has adsorbed to the fogged grains a halogen-conducting compound having an anodic polarographic half-wave potential less than 0.85 and a cathodic polarographic half-wave potential which is more negative than -1.0. These emulsions have an unusually high sensitivity or photographic speed. If the halogen-conducting compound

does not have the polarographic halfwave potential set forth above, the emulsions containing the compound will not have an unusually high sensitivity.

In another embodiment of the invention, electron-accepting compounds can be used in combination with halogen-conducting compounds in the silver halide emulsions to further improve photographic properties such as speed and the like.

In another embodiment of the invention, certain high-molecular-weight organic compounds, particularly sulfonated compounds as described hereinafter, can be used in combination with halogen-conducting compounds to effect an even greater increase in photographic speed or sensitivity.

It has been found that through the above embodiments a lithographic system has been provided which yields relatively high photographic speed, high-contrast, blue-sensitive-direct-positive, lithographic records.

The photographic developer employed in my invention contains a silver halide developing agent consisting essentially of a polyhydroxybenzene compound. Examples of polyhydroxybenzene compounds are hydroquinone, catechol, pyrogallol, isopropyl-hydroquinone, methylhydroquinone, 2,5-dimethylhydroquinone, o-chlorohydroquinone, o-bromohydroquinone, 4-phenyl catechol, 4-phenethyl catechol, 4-phenylpropyl catechol, 4-t-butyl catechol, 4-n-butylpyrogallol, 4,5-dibromocatechol, etc. Esters of such compounds, e.g., formates and acetates, can also be employed. The developer can be contained in the element in the solution or can be supplied from a layer on a separate support. In one preferred embodiment of this invention, the developing agent consists essentially of 1,4-dihydroxybenzene compounds.

The developing agent can be employed in any concentration effective for the intended purpose. Generally, good results are obtained when the developer contains from about 12 to about 20 grams of developing agent per liter of developer.

The developer can contain conventional addenda such as antioxidants, e.g., sodium sulfite; alkaline material to produce pH of at least about 9.0, e.g., sodium carbonate, sodium hydroxide, etc.; restrainer, e.g., potassium bromide, sodium bromide; sequestering agents, etc. The use of a developer containing a carbonyl bisulfite-amine condensation product, with at least about 0.075 mole of excess free amine per liter of developer composition and a dihydroxybenzene developing agent, as described in Belgian Pat. No. 704,595 published Nov. 14, 1967 of my coworker Masseth, is also quite useful in my invention.

In a preferred embodiment of this invention, the developers contain (1) sodium formaldehyde bisulfite or a carbonyl bisulfite amine and (2) from about 0.01 to about 0.05 molar of sulfite ion. Generally this developer has a pH of at least 9.0. The sodium formaldehydebisulfite can generally be used in the developer in concentrations of about 40 grams to 80 grams per a liter and is preferably used with an alkali metal sulfite; it can also be formed in situ by employing a mixture of formaldehyde (or paraformaldehyde) and sodium sulfite in the developer.

Alkylenes can also be utilized in one embodiment of this invention. Typical useful compounds include polyethylene glycol, polyethylene glycol oleyl ether, polyethylene glycol cetyl ether, polyethylene oxide derivatives, block copolymers such as those comprising blocks of polyoxypropylene, polyoxyethylene and the like, water-soluble organosilicone polyalkyleneoxide polymers and the like.

The silver halide emulsions of this invention contain silver halide grains which comprise centers which promote the deposition of photolytic silver and an outer shell or region of a fogged or spontaneously developable silver halide. Silver halide grains containing such fogged shells or regions develop to silver without further exposure to light.

In one preferred embodiment, the silver halide emulsion comprises silver halide grains comprising a central core of a silver halide containing centers which promote the deposition of photolytic silver and an outer shell or covering for said core

of a fogged or spontaneously developable silver halide. The core emulsion of this embodiment can be chemically or physically treated by methods described in the art to produce centers which promote the deposition of photolytic silver; the core can then be covered with a fogged silver halide.

In another preferred embodiment, the silver halide emulsion comprises silver halide grains having centers which promote the deposition of photolytic silver which are either sufficiently small or sufficiently buried within the crystal as to be inaccessible to initiate development. The grains contain an outer region comprising a fogged silver halide that develops to silver without exposure.

The centers which promote the deposition of photolytic silver can be obtained by various techniques as described herein. Chemical sensitization techniques of the type described by Antoine Hautot and Henri Saubenier in *Science et Industries Photographiques*, Volume XXVIII, Jan. 1957, pages 57-65, are particularly useful. Such chemical sensitization includes three major classes, namely, gold or noble metal sensitization, sulfur sensitization, such as by a labile sulfur compound, and reduction sensitization, i.e., treatment of the silver halide with a strong reducing agent which introduces small specks of metallic silver into the silver halide crystal or grain.

When the emulsion is chemically sensitized, it is preferably sensitized so that when examined according to normal photographic testing techniques by coating a test portion of the emulsion on a transparent support, exposing to a light intensity scale for a fixed time between 0.01 and 1 second and development for 6 minutes at 68° F. in Developer A, as hereinafter defined, it has a sensitivity greater than the sensitivity of an identical test portion of the same emulsion (measured at a density of 0.1 above fog), which has been exposed in the same way, bleached 5 minutes in an aqueous 0.3 percent potassium ferricyanide solution at 65° F., and developed for 5 minutes at 65° F., in Developer B, as hereinafter defined. Developer A is the usual type of surface image developer and Developer B is an internal developer having high silver halide solvent activity.

Developer A

N-methyl-p-aminophenol sulfate	2.5 grams
Ascorbic acid	10.0 grams
Potassium metaborate	35.0 grams
Potassium bromide	1.0 gram
Water to	1 liter
pH of	9.6

Developer B

N-methyl-p-aminophenol sulfate	2.0 grams
Sodium sulfite, desiccated	90.0 grams
Hydroquinone	8.0 grams
Sodium carbonate, monohydrate	52.5 grams
Potassium bromide	5.0 grams
Sodium thiosulfate	10.0 grams
Water to	1 liter

The emulsions can be chemically sensitized by any method suitable for this purpose. For example, the emulsions can be digested with naturally active gelatin, or sulfur compounds can be added, such as those described in Sheppard U.S. Pat. No. 1,574,944 issued Mar. 2, 1926; Sheppard et al., U.S. Pat. No. 1,623,499 issued Apr. 5, 1927; and Sheppard et al., U.S. Pat. No. 2,410,689 issued Nov. 5, 1946.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al., U.S. Pat. No. 2,399,083 issued Apr. 23, 1946, and Damschroder et al., U.S. Pat. No. 2,642,361 issued June 16, 1953. Suitable compounds are potassium chloroaurate, 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. Pat. No. 2,487,850 issued Nov. 15, 1949), polyamines, such as

diethylene triamine (Lowe and Jones U.S. Pat. No. 2,518,698 issued Aug. 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Pat. No. 2,521,925 issued Sept. 12, 1950), or bis(beta-aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Pat. No. 2,521,926 issued Sept. 12, 1950).

The emulsions can also be treated during or after the formation of the silver halide with salts of polyvalent metals such as bismuth, the noble metals and/or the metals of Group VIII of the Periodic Table, such as ruthenium, rhodium, palladium, iridium, osmium, platinum and the like. Representative compounds are ammonium chloropalladate, potassium chloropalladate, sodium chloropalladate and the like.

The emulsions can also be subjected to fogging by exposure to light either to low- or high-intensity light, to produce centers which promote the deposition of photolytic silver prior to forming the outer region or shell thereon.

The emulsions employed in practicing this invention can also contain spectral sensitizers such as the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls and hemicyanines. Particularly good spectral sensitizers which can be used are the merocyanines disclosed in Brooker et al., U.S. Pat. Nos. 2,493,747 and 2,493,748 issued Jan. 10, 1950, such as carboxy-substituted merocyanines, sulfosubstituted merocyanines and rhodanine-merocyanine dyes.

The grains of the emulsions of this invention can be sensitized to provide internal centers which promote the deposition of photolytic silver by several procedures. In one embodiment the sensitizing agent is added to the precipitation medium before precipitation occurs or immediately after silver halide crystals begin to form. The concentration of the sensitizing agent is lowered significantly by occlusion of the agent in the grains so that continued precipitation would result in lowered concentrations of the resultant centers for promoting deposition of photolytic silver in the outer region of each grain. In a preferred embodiment, the centers which promote the deposition of photolytic silver are sufficiently small as not to be developable to provide visible silver images after the exposure necessary to obtain a good reversal image with the emulsion. A direct-positive emulsion according to this embodiment can be reversed with blue light exposure with twice the normal exposure period without a substantial increase in D_{min} of the image record when developed in the internal developer, Developer B.

In another embodiment of the invention, the core of the grains in the emulsion layer is a coarse grained silver halide and silver halide from a finer grained silver salt is deposited thereon by Ostwald ripening to form the shell. Also, coarse grained silver halides can be used to form a shell over a finer grained core when the shell-forming silver halide is more water-soluble than the core silver halide. In another embodiment of the invention, the silver halide shell or outer region is formed immediately after formation of the core without interrupting the precipitation. Generally, about 2 to 8 molar equivalents of shell silver halide per molar equivalent of core silver halide can be used in the grains of this embodiment. The shell or outer region is of sufficient thickness to prevent access of the developer used in processing the emulsions of this embodiment to the core.

The silver halide outer regions or shells of the grains are surface fogged to make it developable to metallic silver with conventional surface image developing compositions. Substantially all of the silver halide grains in an emulsion are fogged prior to exposure and/or processing i.e., such emulsions are uniformly fogged. Such fogging can be effected by chemically sensitizing to fog with the sensitizing agents described for chemically sensitizing the core emulsion, high-intensity light and like fogging means well known to those skilled in the art. While the core need not be sensitized to fog, the shell or outer region is fogged, for example, reduction fogged with a reducing agent such as stannous chloride. Fogging by means of a reduction sensitizer, a noble metal salt such as gold salt plus a reduction sensitizer, high pH and low pAg silver halide precipitating conditions, and the like, can be suitably utilized.

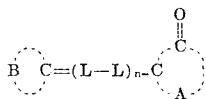
The silver halide grains employed in the practice of this invention are fogged sufficiently to give a density of at least 0.5 when developed without exposure for 5 minutes in Developer A, described hereinbefore, when a direct-positive emulsion layer containing such grains is coated at a coverage of about 50 to about 1000 milligrams of silver per square foot of support.

The emulsions used in this invention preferably contain grains which are substantially uniform in grain-size distribution as contrasted with conventional emulsions having wide size distributions. Typical emulsions of this invention have an average grain size of about 0.05 to 10 microns in diameter and are generally coated at silver coverages in the range of about 100 to about 1,000-milligrams silver per square foot, preferably about 200 to about 600-milligrams silver per square foot.

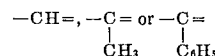
The silver halide emulsions employed in the practice of this invention comprise at least 50-mole percent chloride. Preferably, the silver halide emulsions comprise at least 70-mole percent chloride, less than 5-mole percent iodide, and the balance bromide. Silver halide emulsions comprising 100-mole percent chloride have also been found to be quite useful. Emulsions of this type can be exposed on a sensitometer and developed for 2 minutes in Kodak D-85 Developer at 20° C. to provide a γ of at least 4 measured between a density of 0.3 and 3.0.

The halogen-conducting compounds employed in practicing one embodiment of this invention referred to above are adsorbed to the fogged silver halide grains. The halogen-conducting compounds which give particularly good results in the practice of this invention can be characterized in terms of their polarographic halfwave potentials, i.e., their oxidation reduction potentials determined by polarography. Cathodic measurements can be made with a 1×10^{-4} molar solution of the halogen-conducting compounds in a solvent, for example, methanol which is 0.05 molar in lithium chloride using a dropping mercury electrode with the polarographic halfwave potential of the most positive cathodic wave being designated $E_{(c)}$. Anodic measurement can be made with 1×10^{-4} molar aqueous solvent solution, for example, methanolic solutions of the halogen acceptor which are 0.05 molar in sodium acetate and 0.005 molar in acetic acid using a carbon paste or pyrolytic graphite electrode, with the voltammetric half-peak potential for the most negative anodic response being designated $E_{(a)}$. In each measurement, the reference electrode can be an aqueous silver—silver chloride (saturated potassium chloride) electrode at 20° C. Electrochemical measurements of this type are known in the art and are described in *New Instrumental Methods in Electrochemistry*, by Delahay, Interscience Publishers, New York, N.Y., 1954; *Polarography*, by Kolthoff and Lingane, 2nd Edition, Interscience Publishers, New York, N.Y., 1952; *Analytical Chemistry*, 36, 2,426 (1964) by Elving; and *Analytical Chemistry*, 30, 1,576 (1958) by Adams.

Compounds which can be employed as halogen conductors in the practice of this invention include organic or inorganic compounds having an anodic polarographic halfwave potential $E_{(a)}$ less than 0.85 and a cathodic polarographic potential $E_{(c)}$ which is more negative than -1.0 (determined according to the IUPAC Convention). A preferred class of halogen-conducting compounds is characterized by an anodic halfwave potential which is less than 0.62 and a cathodic halfwave potential which is more negative than -1.3. A preferred class of halogen conductors that can be used in the practice of this invention comprises the spectral sensitizing merocyanine dyes having the formula:



where A represents the atoms necessary to complete an acid heterocyclic nucleus, e.g., rhodanine, 2-thiohydantoin and the like, B represents the atoms necessary to complete a basic nitrogen-containing heterocyclic nucleus, e.g., benzothiazole, naphthothiazole, benzoxazole and the like, each L represents a methine linkage, e.g.,



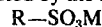
and n is an integer from 0 to 2, i.e., 0, 1 or 2. Specific examples of merocyanine dyes falling within the above formula include:

- 3-carboxymethyl-5-[(3-ethyl-2-benzothiazolinyldiene)-ethylidene]rhodanine;
- 3-ethyl-5-[1-(4-sulfobutyl)-4-(1H)-pyridylidene]rhodanine, sodium salt;
- 3-carboxymethyl-5-[(3-ethyl-2-benzoxazolinyldiene)-ethylidene]-2-thio-2,4-oxazolidinedione;
- 1-carboxymethyl-5-[(3-ethyl-2-benzothiazolinyldiene)ethylidene]-3-phenyl-3-thiohydantoin;
- 4-[(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)-1-methylethylidene]-3-methyl-1-(4-sulfonphenyl)-2-pyrazolin-5-one;
- 4-[(3-ethyl-6-nitro-2-benzothiazolinyldiene)ethylidene]-3-phenyl-2-isoxazolin-5-one; etc.

For a further description of suitable halogen conductors, see Wise, Belgian Pat. No 695,361 granted Sept. 11, 1967. Suitable procedures for preparing merocyanine dyes are described in Brooker et al., U.S. Pat. Nos. 2,493,747 and 2,493,748 issued Jan. 10, 1950.

The halogen-conducting compounds employed in practicing one embodiment of this invention referred to above can be used in widely varying concentrations. However, the halogen-conducting compounds are generally employed at concentrations in the range of about 25 milligrams to about 2.0 grams, preferably about 150 to about 1,000 milligrams per mole of silver halide.

As already indicated, the halogen-conducting compounds described herein can be employed in combination with certain types of high-molecular-weight organic compounds to achieve an even greater increase in the photographic speed of direct-positive emulsions. These compounds are sulfonated and comprise polynuclear aromatic compounds containing at least one sulfo group. The term "polynuclear aromatic" as used herein is intended to mean 2 or more benzene rings fused together (for example, as in naphthalene, pyrene, etc.), or at least 2 benzene rings or aromatic rings directly joined together (for example, as in diphenyl, terphenyl, quaterphenyl, etc.), or through an aliphatic linkage. Such sulfonated derivatives can conveniently be represented by the following general formula:



wherein R represents a polynuclear aromatic group as defined above and M represents a cation such as a hydrogen atoms or a water-soluble cation salt group (e.g., sodium, potassium, ammonium, triethylammonium, triethanolammonium, pyridinium, etc.).

Included among the sulfonated derivatives of the above formula are the following typical examples:

- Calcofluor White-MR—This is the trade name for a bis(s-triazin-2-ylamino)stilbene-2,2'-disulfonic acid, sodium salt.
- Leucophor B—This is the trade name for a bis(s-triazin-2-ylamino)stilbene-2,2'-disulfonic acid, sodium salt.
- Sodium 6-(4-methoxy-3-sulfo-w-phenylacryloyl)-pyrene.
- 3,4-Bis(4-methoxy-3-sulfobenzamido)-dibenzo-thiophene dioxide, sodium salt.
- 4',4''-Bis(2,4-dimethoxy-5-sulfobenzamido)-p-terphenyl, disodium salt.
- Chrysene-6-sulfonic acid, sodium salt.
- 4,4'-Bis[2-phenoxy-4-(2-hydroxyethylamino)-1,3,5-triazin-6-ylamino]stilbene-2,2'-disulfonic acid, disodium salt.

These sulfonated derivatives may be used in any concentration effective for the intended purpose. Good results are generally obtained by employing the compounds in concentrations in the range of about 0.02 to about 10 grams per mole of silver halide.

The halogen-conducting compounds can also be employed in combination with water-soluble halide salts, e.g., bromide salts, as described in Belgian Pat. No. 695,363 granted Sept. 11, 1967.

Electron-accepting compounds are used in combination with the halogen-conducting compounds described above in one preferred embodiment of this invention. Improved photographic properties, such as improved speed, can be obtained with this combination. Suitable electron-accepting compounds include the photoelectron-acceptor compounds or desensitizing dyes often used in photographic reversal systems. Compounds of this type include the known desensitizers which trap electrons, as disclosed in Illingsworth and Spencer, Belgian Pat. No. 695,364 granted Sept. 11, 1967.

The compounds which accept electrons in the direct-positive photographic silver halide emulsions of this invention can be employed in widely varying concentrations. However, such compounds are preferably employed at concentrations in the range of about 100 milligrams to about 2 grams of electron acceptor per mole of silver halide. Typical examples of suitable electron acceptors include nitrosubstituted azoles, nitrosubstituted cyanine and merocyanine dyes, indolocarboxyanine dyes, phenosafranine, pinacryptol yellow, and the like.

The silver halide emulsion of a photographic element useful in this invention can contain conventional addenda such as gelling plasticizers, coating aids, antifoggants such as the azaindines and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis(sodium bisulfite), maleic dialdehyde, aziridines, dioxane derivatives and oxypolysaccharides.

The silver halide emulsion layer of a photographic element which is useful in the instant invention can contain any of the hydrophilic, water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumin, polyvinyl compounds, cellulose derivatives, acrylamide polymers, etc. Mixtures of these binding agents can also be used. The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Pat. No. 3,142,568 of Nottorf issued July 28, 1964; U.S. Pat. No. 3,193,386 of White issued July 6, 1965; U.S. Pat. No. 3,062,674 of Houck, Smith and Yudelsohn issued Nov. 6, 1962; and U.S. Pat. No. 3,220,884 of Houck, Smith and Yudelsohn issued Nov. 30, 1965; and include the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

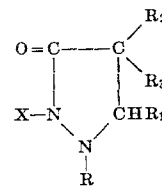
The silver halide emulsion of a photographic element which is useful in the instant invention can be coated on a wide variety of supports. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthalate) film and related films or resinous materials as well as glass, paper, metal and the like. Supports such as paper which are coated with α -olefin polymers, particularly polymers of α -olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers and the like can also be employed.

One of the most convenient ways to develop exposed high-contrast elements of this invention is to process them in a continuous transport processing machine. Such machines are disclosed, for example, in U.S. Pat. No. 3,025,779 of Russell and Kunz issued Mar. 20, 1962; U.S. Pat. No. 3,078,024 of Sardeson issued Feb. 19, 1963; U.S. Pat. No. 3,122,086 of Fitch issued Feb. 25, 1964; U.S. Pat. No. 3,149,551 of Cramer issued Sept. 22, 1964; U.S. Pat. No. 3,156,173 of Meyer issued Nov. 10, 1964; and U.S. Pat. No. 3,224,356 of Fleisher and Hixon issued Feb. 21, 1965. In such machines, the element is processed in one continuous motion by transporting it into

and out of at least one processing solution. The roller-transport-processing machine of the type disclosed in the Russell and Kunz patent mentioned above has been found to be especially useful.

The photographic elements of this invention may also contain certain onium salts, such as quaternary ammonium salts, sulfonium salts and phosphonium salts in order to increase the development rate without adversely affecting contrast. Such compounds are disclosed, for example, in Carroll U.S. Pat. No. 2,271,623 issued Feb. 3, 1942; Beavers et al., U.S. Pat. No. 2,944,898 issued July 12, 1960; Carroll et al., U.S. Pat. Nos. 2,944,900 issued July 12, 1960, 2,288,226 issued June 30, 1942, 2,275,727 issued Mar. 10, 1942, and 2,271,622 issued Feb. 3, 1942; British Pat. No. 1,067,958 published May 10, 1967; and Piper U.S. Pat. No. 2,886,437 issued May 12, 1959. Concentrations ranging from about 0.01 to about 2.0 grams of onium salt per mole of silver in the silver halide emulsion can be used with good results.

The addition of from about 0.005 to about 2.0 grams of a 3-pyrazolidine per mole of silver in the emulsion will also increase the development rate. The pyrazolidones used to advantage include those disclosed in U.S. Pat. No. 2,751,297 of Hood and Crookshank issued June 19, 1956, and represented by the following general formula:



wherein X represents hydrogen or acetyl, R represents a heterocyclic group or an aryl group of the benzene or naphthalene series and R₁ represents hydrogen, an alkyl group or an aryl group of the benzene or naphthalene series, and R₂ and R₃ each represents hydrogen or an alkyl group. Examples within this formula include 1-phenyl-3-pyrazolidone; 5-methyl-3-pyrazolidone; 1-phenyl-5-phenyl-3-pyrazolidone; 1-phenyl-5-methyl-3-pyrazolidone; 1-phenyl-4,4-dimethyl-3-pyrazolidone; 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidone; 4-methyl-1-phenyl-3-pyrazolidone; etc. The above 3-pyrazolidones may also be contained in a contiguous layer instead of the silver halide emulsion if desired.

The invention can be further illustrated by the following examples:

EXAMPLE I

the following emulsions are prepared:

A. Emulsion made with an uninterrupted precipitation + iridium and reduction fogged

A silver chloride emulsion is prepared by adding simultaneously 1 mole of sodium chloride and 1 mole of silver nitrate over a period of 36 minutes at 70° C. to a solution containing 10 grams of gelatin and 40 milligrams of potassium chloroiridate. An additional 40 grams of gelatin are added, the emulsion is cooled to 40° C., 100 grams of a 10 percent gelatin solution are added and the emulsion is chill-set and washed with cold water. The washed emulsion is chemically fogged with 2-milligrams thiourea dioxide per silver mole by heating for 30 minutes at 65° C. until high contrast is obtained and the emulsion develops to maximum density without being exposed.

B. Emulsion made with an interrupted precipitation—core treated with sulfur + gold sensitizers—reduction fogged

A silver chlorobromide emulsion is prepared by simultaneously adding over a period of 5 minutes at 65° C. 0.225 mole of sodium chloride, 0.25 mole of silver nitrate and 0.025 mole of potassium bromide to a solution containing 10 grams of gelatin. Sodium thiosulfate (1.78 milligrams) and potassium chloroaurate (1.72 milligrams) are added and the emulsion held 10 minutes. An additional 0.675 mole of sodium chloride, 0.75 mole of silver nitrate and 0.075 mole of potassium bromide are added over a period of 15 minutes at 65° C. An additional 40 grams of gelatin are added and the emulsion is chill-set, washed and fogged by heating with 0.75 milligrams thiourea dioxide for 40 minutes at 65° C.

C. Emulsion made with an interrupted precipitation—AgCl core—AgClBr shell—reduction and gold fogged

A silver chlorobromide emulsion is prepared by simultaneously adding over a period of 5 minutes at 70° C. 0.25 mole sodium chloride and 0.25 mole silver nitrate to a solution containing 25 grams of gelatin. An additional 0.65 mole of sodium chloride, 0.09 mole of potassium bromide and 0.74 mole of silver nitrate are added over a period of 1 minute at 70° C. An additional 25 grams of gelatin are added and the emulsion is chill-set and washed as in (A). The washed emulsion is chemically fogged by heating with thiourea dioxide (0.3 milligram/Ag mole, 20 minutes at 65° C.), adding potassium chloroaurate (0.2 milligram/Ag mole, 50 minutes at 65° C.) and continuing heating until high-contrast is obtained and the emulsion develops to maximum density without being exposed.

D. Emulsion made with an interrupted precipitation—AgBrI core + iridium—AgCl shell precipitation—reduction and gold fogged

A silver chlorobromiodide emulsion is prepared by simultaneously adding over a period of 35 minutes at 55° C. 0.4875 mole of potassium bromide, 0.0125 mole of potassium iodide and 0.50 mole of silver nitrate to a solution containing 21 grams of gelatin and 52.5 milligrams of potassium chloroiridite. An additional 19 grams of gelatin are added and the emulsion is chill-set and washed with cold water. An additional 61.5 grams of gelatin are added, the emulsion is melted at 60° C. and 4.5 moles of sodium chloride and 4.5 moles of silver nitrate are simultaneously added over a period of 24 minutes at 60° C. An additional 50 grams of gelatin are added and the emulsion is chill-set, washed and chemically fogged as in (C).

The above emulsions are spectrally sensitized with a carboxy-methyl-thiazoline-rhodanine merocyanine dye of the type described in U.S. Pat. No. 2,493,748 of Brooker et al. issued Jan. 10, 1950, and are coated upon a cellulose triacetate film support at the silver and gelatin coverages shown below. The films are then exposed and processed to direct-positive images employing Kodak D-85 Developer for 3½ minutes with the following results:

Emulsion	Coverage (mg./ft. ²)		Relative Speed	D _{max}	D _{min}
	Ag	Gelatin			
A	106	392	257	1.21	0.52
B	99	366	447	0.95	0.04
C	180	416	339	0.93	0.32
D	200	463	1141	1.96	0.08

Kodak D-85 Developer employed in this example has the following composition:

sodium sulfite	30.0 grams
Paraformaldehyde	7.5 grams
Sodium bisulfite	2.2 grams
Boric acid	7.5 grams
Hydroquinone	22.5 grams
Potassium bromide	1.6 grams
Water to make	1 liter
pH	

EXAMPLE 2

The emulsion systems of this invention provide highly improved photographic properties such as speed, contrast and D_{min} compared to a conventional Herschel reversal emulsion.

Emulsion E: A Herschel reversal emulsion similar to that of example 2 of U.S. Pat. No. 2,541,472 is prepared with the provision that 4-nitro-6-chlorobenzotriazole is used as the desensitizer. The emulsion is coated on a cellulose acetate film support.

Emulsion F: A silver chloride emulsion is prepared by simultaneously adding over a 20-minute period at 70° C., one-half mole of silver nitrate and one-half mole of sodium chloride to a solution containing 10 g. of gelatin. The emulsion is cooled to 40° C., 50 mg. of potassium chloroiridite is added and held 10 minutes. The temperature is then raised to 70° C. and another one-half mole each of silver nitrate and sodium chloride is added over 20 minutes. The emulsion is cooled to 40° C., an additional 70 g. of gelatin is added and the whole is chill-set and washed with cold water for 2 hours. The washed emulsion is fogged by heating with thiourea dioxide (0.3 mg./Ag mole, 20 minutes at 60° C.), adding potassium chloroaurate (0.2 mg./Ag mole, 50 minutes at 65° C.) and continued heating until high-contrast is obtained and the emulsion developed to maximum density without being exposed. The emulsion is then coated on a cellulose acetate film support.

The respective samples are exposed to a tungsten source, unmodulated, and modulated by a Kodak Wratten Filter No. 4 (yellow). The coatings are processed for 2 minutes in Kodak Developer D-85 with the following results:

Emulsion	White light exposure				Yellow light exposure			
	Rel. speed	γ	D _{max}	D _{min} , speed	Rel.	γ	D _{max}	D _{min}
E	46	1.98	(1)		100	9.5	1.96	.04
F	1,910	7.8	2.70	.16	110	10.3	2.70	.24

¹ Too solw.

EXAMPLE 3

Halogen-conducting dyes can be effectively used to improve the photographic properties of the system.

Emulsion G: To a portion of Emulsion F is added 350 mg. of a halogen-accepting dye, 3-carboxymethyl-5-[3-methyl-2(3)-thiazolynylidene]-isopropylidene]rhodanine, per mole of silver. The emulsion is coated on a cellulose acetate film support.

Samples of Emulsions F and G are exposed to a white light and processed for 1¾ minutes in Kodak Developer D-85. The results are as follows:

	Rel. Speed	γ	D _{max}	D _{min}
Emulsion F	100	7.8	2.42	0.20
Emulsion G	26,900	15.5	2.24	0.08

EXAMPLE 4

A lithographic developer containing a free amine can advantageously be used to process the emulsions of the invention.

Samples of Emulsion F and G are exposed to white light and then processed for 1½ minutes in an amine developer having the following composition:

Sodium-bis-(2-hydroxyethyl) aminomethane sulfonate*	82.0 grams
Sodium sulfite	3.0 grams
Boric acid	7.5 grams
Hydroquinone	22.5 grams
Potassium bromide	1.6 grams
2,2'-iminodiethanol	39.0 grams
Water to make	1.0 liter
pH of	9.5

*Sodium formaldehyde bisulfite and 2,2'-iminodiethanol can be used to form this compound in situ.

Additional samples are given a 365 μ line exposure to show the inherent emulsion sensitivity of each coating and then processed for 2¼ minutes in the amine developer. The results are as follows:

	White Light				365 μ Exp.
	Rel. Speed	γ	D_{max}	D_{min}	Rel. Speed
Emulsion F	100	8.3	3.0	0.09	200
Emulsion G	42,700	9.5	2.25	0.08	33,900

Similar results are obtained when the emulsions are exposed to light of other wave lengths in the 350 to 500-millimicron wave-length regions.

EXAMPLE 5

Direct-positive emulsions comprising a halogen conductor in combination with an electron acceptor provide improved systems according to this invention.

Emulsion H: To a portion of Emulsion F is added 200 mg. of 3-carboxymethyl-5[(3-methyl-2(3)-thiazolinyldene)-isopropylidene]rhodanine per mole of silver as a halogen-conducting compound. This emulsion is coated on a cellulose acetate support.

Emulsion I: To a sample of Emulsion H is added 100 mg. per mole of silver of the electron acceptor, 1,1'-diethyl-2,2'-cyanine chloride which has been treated with N-bromosuccinimide. This emulsion is coated on a cellulose acetate film support.

The respective emulsion samples are exposed and then developed for 1½ minutes in Kodak Developer D-85. The results are as follows:

	Rel. Speed	γ	D_{max}	D_{min}
Emulsion H	100	2.90	1.56	0.08
Emulsion I	159	1.88	1.42	0.08

EXAMPLE 6

Other types of electron-acceptor dyes can also be used to provide improved photographic properties.

Emulsion J: To a portion of Emulsion H is added 200 mg. per mole of silver of a phenyl imidazo-quinoxaline-indole carbocyanine dye as an electron acceptor. The emulsion is coated on a cellulose acetate support.

Samples of Emulsion H and J are exposed and developed for 3¼ minutes in Kodak Developer D-85. The results are as follows:

	Rel. Speed	γ	D_{max}	D_{min}
Emulsion H	100	2.55	1.21	0.08
Emulsion J	91	3.30	1.41	0.08

Emulsion J provided higher D_{max} , higher contrast and a sharper toe compared to Emulsion H which contained the halogen-acceptor dye alone.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and in the appended claims.

I claim:

1. A process comprising developing an exposed, direct-positive, high-contrast photographic element in a photographic developer comprising a silver halide developing agent consisting essentially of a polyhydroxybenzene compound, said photographic element comprising a support coated with a direct-positive silver halide emulsion comprising silver halide grains containing internal centers which promote the deposition of photolytic silver and an outer region comprising fogged silver halide that develops to silver without exposure, said halide being at least 50-mole percent chloride.

2. A process according to claim 1 wherein said direct-positive silver halide emulsion comprises silver halide grains comprising a central core of silver halide containing centers which promote the deposition of photolytic silver and an outer shell covering said core comprising fogged silver halide that develops to silver without exposure.

3. A process according to claim 2 wherein said centers which promote the deposition of photolytic silver are formed by a chemical treatment of the central core.

4. The process of claim 1 wherein said centers which promote the deposition of photolytic silver are obtained from an iridium salt.

5. The process of claim 1 wherein said halide comprises at least 70-mole percent chloride.

6. The process of claim 1 wherein said direct-positive emulsion has adsorbed to said fogged grains a halogen-accepting compound having an anodic polarographic halfwave potential less than 0.85 and a cathodic polarographic halfwave potential which is more negative than -1.0.

7. The process of claim 6 wherein said halogen-accepting compound is a merocyanine dye.

8. The process of claim 6 wherein said direct-positive emulsion also contains a sulfonated compound having the following formula:



wherein R represents a polynuclear group and M represents a cation.

9. The process of claim 1 wherein said polyhydroxybenzene compound is hydroquinone.

10. The process of claim 9 wherein said developer also contains a carbonyl bisulfite-amine condensation product.

11. The process of claim 9 wherein said developer contains excess free amine.

12. The process of claim 1 wherein said element also contains a 3-pyrazolidone.

13. The process of claim 1 wherein said direct-positive silver halide emulsion comprises an electron-accepting compound having an anodic and polarographic halfwave potential sum which is positive.

14. A process as in claim 1 wherein said developer also contains a carbonyl bisulfite-amine condensation product and contains at least 0.075 mole of excess free amine per liter of said developer.

* * * * *

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70

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