United States Patent Office 3,679,422 Patented July 25, 1972

3,679,422

PHOTOTHERMIC COMPOSITION CONTAINING ONIUM HALIDE SENSITIZER AND THE USE THEREOF

Richard A. de Mauriac, Rochester, and Gary Lynn Hiller, Hilton, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Filed June 3, 1970, Ser. No. 43,172
Int. Cl. G03c 1/28, 1/72
U.S. Cl. 96—107 21 Claims

ABSTRACT OF THE DISCLOSURE

An onium halide compound, such as 1-phenethyl-2-picolinium bromide or trimethylphenylammonium bromide, with an image-forming combination containing a heavy metal salt oxidizing agent, such as silver behenate, and a reducing agent, such as a bis-naphthol reducing agent, in a photosensitive and thermosensitive element suitable for dry processing with heat, provides increased photosensitivity and in some cases reduced background densities. A combination of a bis-β-naphthol reducing agent and a colorless, speed-increasing, onium halide compound in conjunction with a stable source of silver for physical development is useful in photosensitive elements for dry processing. The element can contain a sensitizing dye and an activator-toning agent. A stable, developed image can be provided by heating the element after exposure. The photosensitive component can be photographic silver halide or other suitable photosensitive metal salts.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photosensitive elements, compositions and processes for developing a latent image using so-called dry processing with heat. In one of its aspects, it relates to photosensitive elements suitable for dry processing with heat containing a reducing agent, especially a bis-naphtol reducing agent, an oxidizing agent, especially a heavy metal salt oxidizing agent, and a substantially colorless speed-increasing onium halide compound, especially one containing a quaternary ammonium halide salt which increases the photosensitivity of the element as described. In another of its aspects, it relates to a photosensitive composition suitable for dry processing with heat containing a bis-naphthol reducing compound and a speed-increasing addendum as described. Still another of its aspects involves a method of increasing the photographic speed of a photosensitive and thermosensitive composition comprising an oxidation-reduction image-forming combination, especially one containing a colorless speed-increasing onium halide compound. A further aspect relates to a dry process of developing and increasing the speed with a reduction of minimum density in some cases in a photosensitive and thermosensitive element containing a reducing agent, an oxidizing agent and a colorless onium halide speed-increasing compound as described.

Description of the state of the art

It is known that, in an element containing a gelatin-peptized silver halide emulsion, tertiary and quaternary onium iodides can be used to inhibit the production of yellow (dichroic) fog which is due to the presence of physically developed silver as described in Dersch et al., U.S. Pat. 2,238,631 and U.S. Pat. 2,238,632 issued Apr. 15, 1941, and Dersch et al., U.S. Pat. 2,288,586 issued June 30, 1942. Some examples are trimethylsulfonium iodide, methyltriphenylphosphonium iodide and methyl-tri-(3-hydroxyphenyl)arsonium iodide. These yellow fog inhibitors are added either to the emulsion before being coated as an element or to the developer.

Carroll in U.S. Pat. 2,271,623 issued Feb. 3, 1942, has shown that cationic surface active ammonium salts, when incorporated in elements containing gelatin-peptized grains, can increase the effective sensitivity of the emulsion and can cause supersensitization when used in connection with certain spectral-sensitizing dyes. Two examples are lauryltriethylammonium perchlorate and ethylene-bis-dioxymethylpyridinium perchlorate. Also, Carroll et al. in U.S. Pat. 2,334,864 issued Nov. 23, 1943, have shown that by incorporating substantially non-surface active cycloammonium salts in photographic silver halide emulsions, such as silver bromide or silver chlorobromide emulsions, the sensitivity of these emulsions is increased measurably and is generally independent of spectral sensitization. Some examples are N-β-phenylethyl-α-picolinium bromide, N-ethylquinaldinium bromide and N-β-hydroxyethyl lepidinium perchlorate.

Quaternary ammonium salts have also been included in an aqueous post-fixation bath for silver halide gelatin-peptized elements as protection against sulfiding, staining, inadequate washing after fixing and image fading as shown in U.S. Pat. 3,093,479 of Olivares et al. published June 11, 1963. Some examples are laurylpyridinium chloride, lauryltrimethylammonium chloride and cetylpyridinium fluoride.

In color diffusion transfer processes, it has been found that image densities are enhanced by carrying out development in the presence of at least one onium compound selected from a group consisting of quaternary ammonium, quaternary phosphonium and tertiary sulfonium compounds. The onium compounds apparently react with dye developers to form salts which increase the solubility and diffusibility of the dye developers from the unexposed areas of a negative and also inhibit the transfer of such developers from exposed areas, thereby improving the highlights as shown in U.S. Pat. 3,173,786 of Green et al. published Mar. 16, 1965, and polaroid British Pat. 938,865 published Oct. 9, 1963. Some examples are 1-(β-phenethyl)-2-methylpyridinium bromide, 1-benzyl-2-methylpyridinium bromide, diethylcarboxymethyl sulfonium bromide and carboxymethyltriphenylphosphonium bromide.

Alkaline solutions of onium compounds are known to expedite the diffusion of dye developers from unexposed areas to the surface of a photographic element and the transfer of the resulting diffused positive image to a dye developer receiving sheet superimposed on the photographic element as described in U.S. Pat. 3,253,915 of Weyerts and Salminen issued May 31, 1966. Some examples of the onium compounds are 1-benzyl-2-picolinium bromide, 1-phenethyl-2-picolinium bromide, anhydro-1-(4-sulfobutyl)-2-picolinium hydroxide, lauryldimethtylsulfonium p-toluene sulfonate and tetraethylphosphonium bromide.

It is known that the addition of mercuric ion, e.g., in the form of mercuric acetate at about 0.005 to about 0.05 mole per mole of silver to a heat-developable photographic printing sheet containing photographic silver halide, an organic silver salt and a reducing agent causes a significant increase in photographic speed as described in German Pat. 1,908,761 issued Feb. 18, 1969, or South African Pat. 903,080 published Feb. 27, 1969.

It is also known that tetrazolium salts such as blue tetrazolium or red tetrazolium can be employed as image-forming compounds and as organic oxidizing agents in the top layer of a photosensitive non-silver halide element comprising zinc oxide as a photocatalyst and sodium oxalate as a reducing agent. The above described ele-

ment is exposed for 20–30 seconds to a commercial sun lamp and fixed by washing away the undeveloped image-forming blue tetrazolium along with the binder. The image consists of insoluble formazan absorbed or adsorbed on the surface of zinc oxide as described in U.S. Pat. 3,152,903 of Shepard et. al. published Oct. 13, 1964, and U.S. Pat. 3,429,706 of Shepard et al. published Feb. 25, 1969.

For photosensitive elements suitable for so-called dry processing with heat, a method of obtaining increased photosensitivity has been to use sensitizing dyes as described in U.S. Pat. 3,152,904 of Sorensen et al. published Oct. 13, 1964, and U.S. Pat. 3,457,075 of Morgan et al. published July 22, 1969, or, more recently, mercuric ion, as described above in German Pat. 1,908,761.

Accordingly, there has been a continuing need for addenda suitable for use in photosensitive and thermosensitive elements which will result in an increase in photosensitivity, e.g., speed, and will not promote any reverse effects such as increased minimum density and/or background stain.

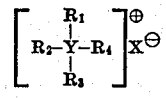
SUMMARY OF THE INVENTION

It has been found, according to the invention, that the described improvements are provided in a photosensitive and thermosensitive element comprising a support, an oxidation-reduction image-forming combination comprising an oxidizing agent with a reducing agent, photographic silver halide, a binder and a substantially colorless, photographic speed-increasing onium halide.

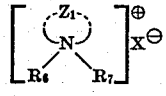
DETAILED DESCRIPTION OF THE INVENTION

A range of colorless onium halides can be employed in the practice of the invention to cause an increase in photosensitity, i.e., speed, and in some cases to obtain a reduction in background density. A suitable speed-increasing onium halide compound is a quaternary onium halide salt or a tertiary sulfonium halide salt of the formulae:

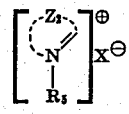
(I)



(II)

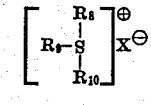


(III)



or

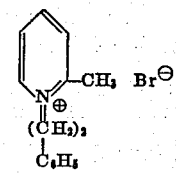
(IV)



wherein X is halide such as chloride, bromide or iodide; R_1 to R_{10} are each alkyl such as alkyl containing 1 to 20 carbon atoms, e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and eicosyl, aryl such as phenyl and naphthyl, arylalkyl such as benzyl, phenethyl and phenylpropyl; Z_1 and Z_2 each represent nonmetallic atoms necessary to complete a heterocyclic ring generally having 5 to 10 atoms in the heterocyclic nucleus such as carbon, nitrogen, oxygen, selenium and sulfur atoms to form such heterocyclic rings as piperidine, pyridine, quinoline, benzoquinoline, benzoxazole, benzoselenazole, thiazole, benzothiazole, naphthothiazole, benzimidazole, naphthimidazole, naphthoxazole, naphthoselenazole, isoquinoline, pyrrole, pyrrolidine and the like; and Y is nitrogen or phosphorus.

The described heterocyclic nucleus or groups can contain substituents which do not adversely affect the desired properties of the compound, such as halogen, lower alkyl and halo lower alkyl.

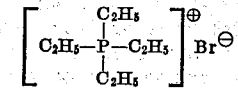
An especially suitable speed-increasing quaternary ammonium compound is 1-phenethyl-2-picolinium bromide of the formula:



Other examples of suitable speed-increasing quaternary ammonium halide compounds which can be employed in the practice of the invention include:

Methapyrilene hydrochloride.
Trimethylphenylammonium bromide.
Tetra-n-propylammonium bromide.
Tetra-n-propylammonium iodide.
ω-Hydroxydecylpyridinium-chloride.
1-benzyl-2-picolinium bromide.
1-γ-phenylpropyl-2-picolinium bromide.
2,4-dimethyl-1-phenethylpyridinium bromide.
2,6-dimethyl-1-phenethylpyridinium bromide.
5-ethyl-2-methyl-1-phenethylpyridinium bromide.
α-Picoline-β-naphtholymethyl bromide.
1-β-phenylcarbamoyloxyethyl-2-picolinium bromide.
2-ethyl-1-phenethylpyridinium bromide.
1-phenethyl-2,4,6-trimethylpyridinium bromide.
1-phenethyl-4-n-propylpyridinium bromide.
4-γ-hydroxypropyl-1-phenethylpyridinium bromide.
1-n-heptyl-2-picolinium bromide.
2-isopropyl-1-phenethylpyridinium bromide.
Tetraphenylammonium bromide.
Tetraethylammonium bromide.
N-ethylpyridinium bromide.
N,N-diethylpiperidinium bromide.
1-phenethyl-3-picolinium bromide.
Cetyltrimethylammonium bromide.
3-methyl-2-ethylisoquinolinium bromide.
1-ethyl-2-methyl-3-phenethylbenzimidazolium bromide.

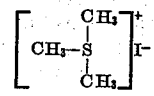
Another suitable speed-increasing onium halide compound is a quaternary phosphonium halide compound, tetraethylphosphonium bromide, of the formula:



Other examples of suitable speed-increasing quaternary phosphonium halide compounds which can be employed in the practice of the invention include:

Ethylene-bis-oxymethylphosphonium bromide.
Tetraphenylphosphonium bromide.
Trimethylphenylphosphonium bromide.

Still another suitable speed-increasing onium halide compound is a tertiary sulfonium halide compound, trimethylsulfonium iodide of the formula:



Other examples of suitable speed-increasing tertiary sulfonium halide compounds which can be employed in the practice of the invention include:

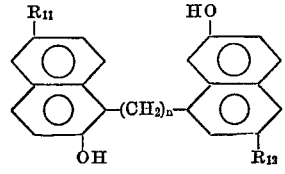
Triethylsulfonium bromide.
Butyldimethylsulfonium bromide.
Phenyldimethylsulfonium bromide.

The described speed-increasing onium compounds are suitable only in the form of a halide salt. The desired concentration of onium halide in an element or composition as described will depend on several factors, such

as the particular image-forming combination, desired image, processing conditions, particular onium compound and the like. A suitable test to determine the speed-increasing capabilities of an onium halide compound is demonstrated in Example 3 wherein the speed-increasing onium compound is added as an addendum at various concentrations to a final coating dispersion. The test element is then coated on a suitable support and compared to an element which does not contain an onium halide compound. If, after exposure and heat processing, the test element does not show a relative speed increase of 10 or more units after testing at several concentration ranges, then the onium halide compound cannot be considered a speed-increasing addendum. The above speed-increasing onium compounds can be used alone or in combination.

Photosensitive and thermosensitive elements, which are suitable for dry processing with heat, can provide a developed image by physical development, such as described in U.S. Pat. No. 3,457,075 of Morgan et al. issued July 22, 1969. Other elements of this type are described, for example, in U.S. Pat. No. 3,429,706 of Shepard et al. issued Feb. 25, 1969, and U.S. Pat. No. 3,152,904 of Sorensen et al. issued Oct. 13, 1964.

Suitable organic reducing agents which can be employed in the described combination include, for example, substituted phenols and naphthols. The bis-naphthol which is preferred is a bis-β-naphthol of the formula:



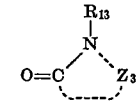
wherein each of R_{11} and/or R_{12} is hydrogen, alkyl with 1 to 3 carbon atoms, alkoxy, e.g., alkoxy containing 1 to 2 carbon atoms such as methoxy or ethoxy, halogen, nitro, amino or a diazonium halide salt, and n is 0 or 1. Suitable bis-β-naphthols which can be employed in the practice of the invention include:

2,2-dihydroxy-1,1'-binaphthyl,
6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl,
6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl, and/or
Bis-(2-hydroxy-1-naphthyl)methane.

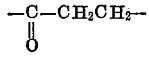
The described reducing agents are suitable in a range of concentration; however, they are especially suitable at a concentration from about 0.10 to about 0.75 mole of reducing agent per mole of oxidizing agent.

Other reducing agents, which are typically silver halide developing agents, can be used alone or in conjunction with the above bis-naphthol reducing agents. Suitable silver halide developing agents include, for example, polyhydroxybenzenes such as hydroquinone developing agents, e.g., hydroquinone, alkyl-substituted hydroquinones as exemplified by tertiary butylhydroquinone, methylhydroquinone, 2,5-dimethylhydroquinone and 2,6-dimethylhydroquinone; catechols and pyrogallol; halo-substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy-substituted hydroquinones such as methoxyhydroquinone or ethoxyhydroquinone; methylhydroxynaphthalene; phenylenediamine developing agents; methylgallate; aminophenol developing agents such as 2,4-diaminophenols and methylaminophenols; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketols and ascorbic acid derivatives such as those described in U.S. Patent 3,337,342 of Green issued Aug. 22, 1967; hydroxylamine developing agents such as N,N'-di(2-ethoxyethyl)hydroxylamine; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone including those described in British Patent 930,572 published July 3, 1963; hydroxytetronic acid and hydroxytetronimide developing agents; reductone developing agents such as anhydrodihydropyrrolidino hexose reductone; and the like.

It is desirable to employ an activator-toning agent in the elements, compositions and processes of the invention to obtain a desired image, particularly when phenolic reducing agents are used. A suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom and of the formula:

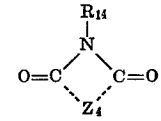


wherein R_{13} is hydrogen, hydroxyl or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z_3 represents atoms completing a heterocyclic nucleus, especially a 5- or 6-member heterocyclic nucleus. The atoms completing the heterocyclic nucleus can be, for example,



or an alkylene group containing 3 or 4 carbon atoms. The atoms completing the heterocyclic nucleus can contain various substituent groups such as amino, alkyl amino, e.g., methylamino or ethylamino, hydroxyl, carbamyl and the like.

An especially suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom which is preferably a cyclic-imide of the formula:



wherein R_{14} is hydrogen, hydroxyl, or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z_4 represents carbon atoms of a series completing a cyclic-imide nucleus, typically consisting of from 5 to 6 carbon atoms, e.g., a phthalimide or succinimide nucleus. The atoms of the cyclicimide nucleus can contain various substituent groups, especially amino, alkyl, such as alkyl containing 1 to 5 carbon atoms, such as methyl, ethyl, propyl, butyl or pentyl or aryl, such as aryl containing 6 to 20 carbon atoms, such as phenyl, tolyl and xylyl. Suitable activator-toning agents which can be employed in the practice of the invention include:

Phthalimide.
N-hydroxyphthalimide.
N-potassium phthalimide.
N-silver phthalimide.
N-mercury phthalimide.
Succinimide.
N-hydroxysuccinimide.

The described activator-toning agents are suitable in a range of concentration; however, they are especially suitable at a concentration from about 0.10 mole to about 1.05 moles of activator-toning agent per mole of oxidizing agent.

Other so-called activator-toning agents can be employed in combination with other components of the described photosensitive and thermosensitive element in the practice of the invention. Typically, a heterocyclic organic toning agent containing at least two hetero atoms in the heterocyclic ring of which at least one is a nitrogen atom is employed. These are described, for example, in U.S. Patent 3,080,254 of Grant issued Mar. 5, 1963. Suitable toners include, for example, phthalazinone, phthalic anhydride, 2-acetylphthalazinone and 2-phthalylphthalazinone. Other suitable toners are described, for example, in U.S. Patent 3,446,648 of Workman issued May 27, 1969.

A non-aqueous, polar, organic solvent, such as a compound containing a

$$-\overset{\overset{O}{\|}}{C}-,\ -\overset{\overset{O}{\|}}{S}-\text{ or }-SO_2-$$

moiety, in a photosensitive and thermosensitive element suitable for dry processing with heat can provide improved maximum image densities, e.g., tetrahydrothiophene-1,1-dioxide, 4-hydroxybutanic acid lactone and methylsulfinylmethane.

The described elements comprise a heavy metal salt oxidizing agent, especially a silver salt of an organic acid. The silver salt of the organic acid should be resistant to darkening under illumination to prevent undesired deterioration of a developed image. An especially suitable class of silver salts of organic acids is represented by the water-insoluble silver salts of long-chain fatty acids which are stable to light. Compounds which are suitable silver salts include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxy-stearate, silver caprate, silver myristate and silver palmitate. Other suitable oxidizing agents are silver benzoate, silver phthalazinone, silver benzotriazole, silver saccharin, silver 4'-n-octadecyloxydiphenyl-4-carboxylic acid, silver ortho-amino-benzoate, silver acetamidobenzoate, silver furoate, silver camphorate, silver p-phenylbenzoate, silver phenylacetate, silver salicylate, silver butyrate, silver terephthalate, silver phthalate, silver acetate and silver acid phthalate. Oxidizing agents which are not silver salts can be employed if desired, such as zinc oxide, gold stearate, mercuric behenate, auric behenate and the like, but silver salts are preferred.

The described element can contain a photosensitive salt, especially a photosensitive silver salt. A typical concentration range of photosensitive silver salt is from about 0.005 to about 0.50 mole of silver salt per mole of silver salt of organic acid, e.g., per mole of silver behenate. Preferred silver salts are photosensitive silver halides, e.g., silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, or mixtures thereof. The photosensitive silver halide can be coarse- or fine-grain, very fine-grain emulsions being especially useful. The emulsion containing the photosensitive silver halide can be prepared by any of the well-known procedures in the photographic art, such as single-jet emulsions, double-jet emulsions such as Lippman emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions, such as those described in U.S. Pat. 2,222,264 of Nietz et al., issued Nov. 14, 1940, U.S. Pat. 3,320,069 of Illingsworth, issued May 15, 1967, and U.S. Pat. 3,271,157 of McBride, issued Sept. 6, 1966. Surface-image silver halide emulsions can be used. If desired, mixtures of surface- and internal-image silver halide emulsions can be used as described in U.S. Pat. 2,996,352 of Luckey et al., issued Apr. 16, 1961. Negative-type emulsions can be used. The silver halide emulsion can be a regular-grain emulsion such as described in Klein and Moisar, Journal of Photographic Science, volume 12, No. 5, September-October (1964), pages 242–251.

The silver halide emulsions employed in the practice of the invention can be unwashed or washed to remove soluble salts. In the latter case, the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed.

The silver halide employed in the practice of the invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described, for example, in U.S. Pat. 1,623,499 of Shepard, issued Apr. 5, 1927; U.S. Pat. 2,399,083 of Waller et al., issued Apr. 23, 1946; U.S. Pat. 3,297,447 of McVeigh, issued Jan. 10, 1967; and U.S. Pat. 3,297,446 of Dunn, issued Jan. 10, 1967.

Photosensitive silver halide emulsions employed in the practice of the invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers, e.g., used alone or in combination include, for example, thiazolium salts; azaindenes; mercury salts as described, for example, in U.S. Pat. 2,728,663 of Allen et al., issued Dec. 27, 1955; urazoles; sulfocatechols; oximes described, for example, in British Pat. 623,448; nitron; nitroindazoles; polyvalent metal salts described, for example, in U.S. Pat. 2,839,405 of Jones, issued June 17, 1958; platinum, palladium and gold salts described, for example, in U.S. Pat. 2,566,263 of Trivelli et al., issued Aug. 28, 1951, and U.S. Pat. 2,597,915 of Yutzy et al., issued May 27, 1952.

A photosensitive and thermosensitive element and emulsions described and used in the practice of the invention can contain various colloids alone or in combination as vehicles, binding agents and in various layers. Suitable materials are typically hydrophobic, but hydrophilic materials can be also be employed. They are transparent or translucent and include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinyl pyrrolidone), acrylamide polymers and the like. Other synthetic polymeric compounds which can be employed include dispersed vinyl compounds such as in latex form and particularly those which increase dimensional stability of photographic materials. Suitable synthetic polymers include those described in U.S. Pat. 3,142,586 of Nottorf, issued July 28, 1964; U.S. Pat. 3,193,386 of White, issued July 6, 1955; U.S. Pat. 3,062,674 of Houck et al., issued Nov. 6, 1962; U.S. Pat. 3,220,844 of Houck et al., issued Nov. 30, 1965; U.S. Pat. 3,287,289 of Ream et al., issued Nov. 22, 1966; and U.S. Pat. 3,411,911 of Dykstra, issued Nov. 19, 1968. Effective polymers include water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, and those which have cross-linking sites which facilitate hardening or curing, as well as those having recurring sulfobetaine units as described in Canadian Pat. 774,054. Preferred high-molecular-weight materials and resins include polyvinyl butyral, cellulose acetate butyrate, polymethyl methacrylate, poly(vinyl pyrrolidone), ethyl cellulose, polystyrene, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid, polyvinyl alcohol, and high-molecular-weight ethylene oxide polymers.

The photosensitive and thermosensitive layers and other layers of an element employed in the practice of the invention and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinylacetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

The photosensitive and thermosensitive and other hardenable layers of an element used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed-function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The photosensitive and thermosensitive elements used

in the practice of the invention can contain antistatic or conducting layers. Such layers can comprise soluble salts such as chlorides, nitrates and the like, evaporated metal layers, ionic polymers such as those described in U.S. Pat. 2,861,056 of Minsk issued Nov. 18, 1958, and U.S. Pat. 3,206,312 of Sterman et al. issued Sept. 14, 1965, or insoluble inorganic salts such as those described in U.S. Pat. 3,428,451 of Trevoy issued Feb. 18, 1969. The photosensitive and thermosensitive elements can also contain antihalation materials and antihalation dyes.

The photosensitive and thermosensitive layers or other layers employed in the practice of the invention can contain surfactants such as saponin; anionic compounds such as alkyl aryl sulfonates described, for example, in U.S. Pat. 2,600,831 of Baldsiefen issued June 17, 1962; amphoteric compounds such as those described in U.S. Pat. 3,133,816 of Ben-Ezra issued May 19, 1964; and adducts of glycidol and an alkyl phenol such as those described in British Pat. 1,022,878.

The photosensitive and thermosensitive layers or other layers employed in the practice of the invention can contain plasticizers and lubricants. Suitable plasticizers and lubricants include, for example, polyalcohols such as glycerin and diols described, for example, in U.S. Pat. 2,960,404 of Milton et al. issued Nov. 1, 1966; fatty acids or esters such as those described in U.S. Pat. 2,588,765 of Robijns issued Mar. 11, 1952; U.S. Pat. 3,121,060 of Duane issued Feb. 11, 1964; and silicone resins such as those described in British Pat. 955,061.

If desired, the photosensitive and thermosensitive elements employed in the practice of the invention can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads described, for example in U.S. Pat. 2,922,101 of Jelley et al. issued July 11, 1961, and U.S. Pat. 2,701,245 of Lynn issued Feb. 1, 1955.

The photosensitive and thermosensitive elements employed in the practice of the invention can contain brightening agents including stilbenes, triazines, oxazoles and coumarin brightening agents. Water-soluble brightening agents can be used such as those described in German Pat. 972,067 and U.S. Pat. 2,933,390 of McFall et al. issued Apr. 19, 1960, or dispersion of brighteners can be used such as those described in German Pat. 1,150,274, U.S. Pat. 3,406,070 of Oetiker et al. issued Oct. 15, 1968, and French Pat. 1,530,244.

The various layers including the photosensitive and thermosensitive layers of an element employed in the practice of the invention can contain light-absorbing materials, filter dyes, antihalation dyes and absorbing dyes, such as those described in U.S. Pat. 3,253,921 of Sawdey issued May 31, 1966; U.S. Pat. 2,274,782 of Gaspar issued Mar. 3, 1942; U.S. Pat. 2,527,583 of Silberstein et al. issued Oct. 31, 1950; and U.S. Pat. 2,956,879 of Van-Campen issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in U.S. Pat. 3, 282,699 of Jones et al. issued Nov. 1, 1966.

The photosensitive and thermosensitive layers used in the practice of the invention can be coated by various coating procedures including dip coating, airknife coating, curtain coating or extrusion coating using hoppers such as described in U.S. Pat. 2,681,294 of Beguin issued June 15, 1954. If desired, two or more layers can be coated simultaneously such as by the procedures described in U.S. Pat. 2,761,791 of Russell issued Sept. 4, 1956, and British Pat. 837,095.

If desired, the photosensitive silver halide can be prepared in situ in the photosensitive and thermosensitive coatings of an element employed in the practice of the invention. Such a method is described, for example, in U.S. Pat. 3,457,075 of Morgan et al. issued July 22, 1969. For example, a dilute solution of a halogen acid such as hydrochloric acid can be applied to the surface of a thin coating containing an organic silver salt, such as silver behenate, on a suitable substrate followed by removal of the solvent if desired. Silver halide is thus formed in situ throughout the surface of the coating of the organic silver salt.

The photosensitive silver halide can be prepared on the oxidizing agent such as silver behenate or silver stearate or other organic silver salt prior to application of the silver halide on the support employed. This is also described in U.S. Pat. 3,457,075 of Morgan et al. issued July 22, 1969; for example, a halogen acid such as hydrochloric acid or hydrobromic acid can be mixed with an organic silver salt in a suitable reaction medium. A halide salt more soluble than the organic silver salt can be added to a suspension of the organic silver salt to form the silver halide. A suitable reaction medium includes water or other solutions which do not interfere with the reaction.

Stability to print-out from light exposure is increased by employing highly purified materials; for example, freedom from halides and sulfides increases stability to light exposure. The use of highly purified silver behenate can, for example, reduce propensity to print-out in background areas of an element prepared according to the invention.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light-sensitive silver halide employed in the practice of the invention. For instance, additional spectral sensitization can be obtained by treating the silver halide with a solution of a sensitizing dye in an organic solvent or the dye can be added in the form of a dispersion as described in British Patent 1,154,781. For optimum results the dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing silver halide emulsions are described, for example, in U.S. Patent 2,526,632 of Brooker et al. issued Oct. 24, 1950; U.S. Patent 2,503,776 of Sprague issued Apr. 11, 1950; U.S. Patent 2,493,748 of Brooker et al. issued Jan. 10, 1950; and U.S. Patent 3,384,486 of Taber et al. issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (trinuclear or tetranuclear) merocyanines, complex (trinuclear or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines such as enamine, hemicyanines, oxonols and hemioxonols. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups that can be fused to carbocyclic or heterocyclic-ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

The merocyanine dyes can contain the basic nuclei described, as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, supersensitizing addenda which do not absorb visible light may be included such as, for instance, ascorbic acid derivatives, azaindenes, cadmium salts and organic sulfonic acid as described in U.S. Patent 2,933,390 of McFall et al. issued Apr. 19, 1960, and U.S. Patent 2,937,089 of Jones et al. issued May 17, 1960.

The sensitizing dyes and other addenda used in the practice of the invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including, for example, those described in U.S. Patent 2,912,343 of Collins et al. issued Nov. 10, 1959; U.S. Patent 3,342,605 of McCrossen et al. issued Sept. 19, 1967; U.S. Patent 2,996,287 of Audran issued Aug. 15,

1961; and U.S. Patent 3,425,835 of Johnson et al. issued Feb. 4, 1969.

A range of concentration of dye can be employed in the practice of the invention. The desired concentration will be influenced by the desired spectral sensitivity, other components in the system, the desired image, processing conditions and the like. Typically, a concentration of the described sensitizing dye is about 0.05 to about 1 milligram per square foot of the described photographic and thermosensitive element, usually about 0.1 milligram per square foot of dye being employed. In elements, as described, typically a support is provided with a light-stable organic silver salt oxidizing agent, an organic reducing agent and photosensitive silver salt, especially silver halide, which provides a photosensitive and thermosensitive element. A visible image on the photosensitive and thermosensitive element can be produced within a few seconds after exposure by heating the element to moderately elevated temperatures, e.g., about 80° to about 250° C.

Accordingly, one embodiment of the invetnion is: in a photosensitive and thermosensitive element comprising a support, an oxidation-reduction image-forming combination comprising an oxidizing agent with a reducing agent, photographic silver halide and a binder; the improvement comprising a colorless, photographic, speed-increasing onium halide.

For example, the photosensitive and thermosensitive element, as described, can comprise:

(a) polyvinyl butyral binder,
(b) silver behenate,
(c) 2,2'-dihydroxy-1,1'-binaphthyl,
(d) photosensitive silver halide,
(e) a sensitizing dye,
(f) phthalimide activator-toning agent and
(g) a speed-increasing onium halide, 1-phenethyl-2-picolinium bromide or trimethylphenylammonium bromide.

Another embodiment of the invention is a photosensitive and thermosensitive composition comprising:

(a) an oxidation-reduction image-forming combination comprising:
  (i) an oxidizing agent with
  (ii) a reducing agent,
(b) photosensitive silver halide,
(c) a binder and
(d) a colorless, photographic speed-increasing onium halide.

For example, the photosensitive and thermosensitive composition can comprise:

(a) about 0.10 to about 0.30 mole of 1-phenethyl-2-picolinium bromide or about 0.20 to about 0.50 mole of trimethylphenylammonium bromide per mole of silver halide,
(b) about 0.10 to about 0.75 mole of 2,2'-dihydroxy-1,1'-binaphthyl per mole of silver behenate oxidizing agent,
(c) about 0.005 to about 0.50 mole of photosensitive silver halide per mole of silver behenate oxidizing agent and
(d) about 0.10 mole to about 1.05 moles of phthalimide activator-toning agent per mole of oxidizing agent.

Another embodiment of the invention is a method of increasing the photographic speed of a photosensitive and thermosensitive composition comprising:

(a) an oxidation-reduction image-forming combination comprising:
  (i) an oxidizing agent with
  (ii) a reducing agent,
(b) photographic silver halide,
(c) a binder and
(d) an activator-toning agent, comprising adding to the described composition a colorless, photographic speed-increasing onium halide.

For example, the photosensitive and thermosensitive element as described can comprise:

(a) polyvinyl butyral binder,
(b) photographic silver halide,
(c) phthalimide,
(d) silver behenate,
(e) 2,2'-dihydroxy-1,1'-binaphthyl and
(f) 1-phenethyl-2-picolinium bromide or trimethylphenyl ammonium bromide.

After exposure of the described photosensitive and thermosensitive element, the resulting latent image is developed merely by heating the element. Accordingly, another embodiment of the invention is: in a process of developing a latent image in an exposed photosensitive and thermosensitive element comprising a support, an oxidation-reduction image-forming combination comprising an oxidizing agent with a reducing agent, photographic silver halide, a binder, an activator-toning agent and a colorless, photographic speed-increasing onium halide, comprising heating the described element from about 80° C. to about 250° C.

A temperature range of about 125° C. to about 140° C. is usually suitable for developing and stabilizing a desired image. By increasing or decreasing the length of time of heating, a higher or lower temperature within the described range can be employed. A developed image is typically produced within a few seconds, such as about 0.5 second to about 60 seconds.

The photographic process can comprise, for example, exposing to actinic radiation a photosensitive and thermosensitive element comprising a support,

(a) an oxidation-reduction image-forming combination comprising:
  (i) silver behenate with
  (ii) a bis-naphthol reducing agent,
(b) photographic silver halide,
(c) polyvinyl butyral,
(d) an activator-toning agent which comprises phthalimide or succinimide and
(e) an alkyl ammonium halide,

and heating the described element from about 80° C. to about 250° C. for about 0.5 second to about 60 seconds.

Processing is usually carried out under ambient conditions of pressure and humidity. A temperature, pressure and humidity outside normal atmospheric conditions can be employed if desired; however, normal atmospheric conditions are preferred.

In some cases, if desired, an element can be prepared wherein the described silver halide can be in one layer and other components in other layers. For example, an element according to the invention can comprise a support, a layer containing photographic silver halide and a layer comprising a so-called processing composition comprising:

(a) a silver salt of an organic acid,
(b) a reducing agent, as described,
(c) an activator-toning agent, as described, and
(d) a speed-increasing onium halide, as described.

A processing composition of this type is a photographic processing composition comprising:
(a) silver behenate,
(b) 2,2'-dihydroxy-1,1'-binaphthyl,
(c) phthalimide or N-hydroxyphthalimide and
(d) trimethylphenylammonium bromide.

Typically, a polyvinyl butyral binder is employed with this processing composition.

As another example, it is sometimes advantageous to incorporate the bis-β-naphthol reducing agent and/or the

trimethylphenylammonium bromide or 1-phenethyl-2-picolinium bromide speed-increasing onium halide in a polyvinylbutyral or cellulose ester binder and coat the resulting composition as an antiabrasion overcoat on the element as described.

Other addenda known to be useful in photosensitive and thermosensitive elements of this type, such as described in British Pat. 1,161,777 published Aug. 20, 1969, and U.S. Pat. 3,152,904 of Sorensen et al. issued Oct. 13, 1964, can be employed in the practice of the invention.

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

EXAMPLE 1

This is a comparative example.

A photographic element is prepared as follows:

A coating composition is prepared by mixing the following components:

Silver behenate—3.50 g.
Behenic acid—3.90 g.
Polyvinylbutyral—1.25 g.
Sodium bromide (reacts with silver behenate to form silver bromide in situ—0.20 g.
Acetone-toluene (1:1)—75.00 ml.

After ball-mixing for about 18 hours, 2.0 milliliters of the above dispersion is combined with the following solutions:

	Ml.
Acetone containing 5.0% by weight 2,2'-dihydroxy-1,1'-binaphthyl	2.00
Acetone containing 1.0% by weight phthalimide	2.00
Acetone containing 0.01% by weight 3-ethyl-5-(3-ethyl-2(3H)-benzothiazylideneisopropylidene)-2-thio-2,4(3,5)-oxazolidenedione	0.50
Acetone-toluene (1:1 by volume) to a total volume of	8.00

The above final dispersion is coated on a paper support at a wet thickness of about 0.004 inch, dried, exposed for 1 second to tungsten light and developed by heating on a curved hot block for 10 seconds at a temperature of 140° C. The resulting jet-black image has a maximum density of 1.26 with a minimum density of 0.15 and is assigned a relative speed of 100.

EXAMPLE 2

This illustrates the invention.

The procedure set out in Example 1 is repeated with the exception that a methanol solution containing 2.5% by weight of methapyrilene hydrochloride is added to the final dispersion just prior to making the coating. The element is developed as in Example 1; the resulting image is jet-black with a maximum density of 1.20 and a minimum density of 0.09; the relative speed is 182.

EXAMPLE 3

This illustrates the invention.

A series of photographic elements is prepared as follows:

A coating composition is prepared by mixing the following components:

	G.
Silver behenate	42.00
Behenic acid	32.00
Polyvinyl butyral	15.00
Sodium bromide	2.50
Phthalimide	8.50

Acetone-toluene (1:1 by volume) to 500.00 ml.

After ball-mixing for about 18 hours, 2.0 ml. of the above dispersion is combined with the following solutions:

	Ml.
Acetone containing 3.0% by weight 2,2'-dihydroxy-1,1'-binaphthyl	2.0
Acetone-toluene (1:1 by volume) to a total of	8.00

The resulting dispersion is coated on a paper support at a wet thickness of about 0.004 inch, dried, exposed to tungsten light for 2 seconds and developed by heating on a curved hot block for 15 seconds at 130° C. The resulting jet-black images have an average maximum densit yof 1.01 with a minimum density of 0.18 and a relative speed of 25.

Additional photosensitive and thermosensitive elements are prepared, as described, with the exception that various speed-increasing, onium compounds are introduced as addenda to the final dispersion within a concentration range based on the moles of silver bromide present. Table I gives the relative speed, maximum density and minimum density obtained after coating trimethylphenylammonium bromide (I), ω-hydroxydecylpyridinium chloride (II) and 1-phenethyl-2-picolinium bromide (III) at various concentrations and processing with heat as described above. From Table I, it can be seen that the speed-increasing onium compounds are concentration-dependent and that the most effective onium compound is 1-phenethyl-2-picolinium bromide (III) at a concentration of 0.19 mole per mole of silver bromide.

TABLE I

Example	Onium compound	Relative speed	$D_{min.}$	$D_{max.}$	Concentration of onium compound: Grams/mole AgBr	Concentration of onium compound: Mole/mole AgBr
3 A	Control	25	0.18	1.01		
3 B	I	88	0.20	1.24	5.4	.024
3 C	I	75	0.18	0.78	10.8	.048
3 D	II	88	0.10	0.92	53.5	0.19
3 E	II	88	0.12	0.92	107.0	0.38
3 F	II	75	0.10	1.04	214.0	0.70
3 G	III	100	0.10	1.14	53.5	0.19
3 H	III	75	0.12	1.14	107.0	0.38

NOTE.—I=Trimethylphenylammonium bromide; II=ω-Hydroxydecylpyridinium chloride; III=1-phenethyl-2-picolinium bromide.

No spectral-sensitizing dye.

EXAMPLE 4

This illustrates the invention.

The procedure set out in Example 3 for the preparation of the final dispersion is repeated with the exception that 0.5 ml. of a methanol solution containing 0.01% by weight of the same spectral-sensitizing dye as described in Example 1 is added to the final dispersion. The composition is repeated several times and coated on a paper support at a wet thickness of 0.004 inch, dried and heat-processed as in Example 3. The resulting jet-black images have an average maximum density of 1.10, a minimum density of 0.17 and a relative speed of 100.

Additional spectrally sensitized, photosensitive and thermosensitive elements are prepared as described above with the exception that various speed-increasing onium compounds are introduced as addenda to the final dispersion within a concentration range based on the moles of silver bromide present. Table II gives the relative speed,

maximum density and minimum density obtained after coating, employing the following compounds:

Trimethylphenylammonium bromide (I),
1-phenethyl-2-picolinium bromide (III),
Tetra-n-propylammonium bromide (IV) and
Tetra-n-propylammonium iodide (V).

Various concentrations as set out in Table II and processing as described in Example 3 are employed. From Table II, it can be seen that compound I, trimethylphenylammonium bromide, is the most effective at the lowest concentration, i.e., at 0.024 mole per mole of silver bromide in the presence of a spectral-sensitizing dye.

TABLE II

Example	Onium compound	Relative speed	$D_{min.}$	$D_{max.}$	Concentration of onium compound: Grams/mole AgBr	Concentration of onium compound: Mole/mole AgBr
4 A	Control	100	0.17	1.10		
4 B	I	138	0.20	1.20	5.4	0.024
4 C	I	138	0.16	1.22	10.8	0.048
4 D	I	113	0.16	1.24	16.2	0.072
4 E	III	137	0.16	1.34	53.5	0.19
4 F	III	125	0.18	1.36	74.9	0.27
4 G	IV	125	0.20	1.18	107.0	0.40
4 H	IV	137	0.26	1.16	214.0	0.80
4 I	IV	125	0.18	1.10	320.0	1.20
4 J	V	125	0.18	1.20	107.0	0.34
4 K	V	137	0.16	1.18	214.0	0.68
4 L	V	137	0.18	1.12	428.0	1.36
4 M	V	125	0.18	1.12	642.0	2.02

Sensitizing dye: 3 - ethyl-5-(3-ethyl-2(3H)-benzothiazylideneisopropylidene)-2-thio-2,4(3,5)-oxazolidenedione.

EXAMPLE 5

Similar results are obtained as in Example 4 also employing tetraethylphosphonium bromide or trimethylsulfonium iodide, as a colorless speed-increasing onium halide compound, in the described element.

EXAMPLE 6

This is a comparative example.

The procedure set out in 4A–4D is repeated with the exception that equimolar amounts of trimethylphenylammonium benzenesulfonate (VI) is substituted for trimethylphenylammonium bromide (I) in the final dispersion. The composition is coated on a paper support at a wet thickness of 0.004 inch, dried and heat-processed as in Example 3. No speed increase is observed. This example shows that the speed-increasing onium salt must be in the halide form.

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.

We claim:

1. In a photosensitive and thermosensitive element comprising a support having thereon an oxidation-reduction image-forming combination comprising a heavy metal salt oxidizing agent with a reducing agent, photographic silver halide and a binder; the improvement comprising a substantially colorless, photographic speed-increasing, onium halide.

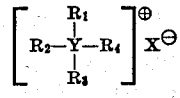
2. A photosensitive and thermosensitive element as in claim 1 also comprising an activator-toning agent comprising phthalazinone, phthalimide or succinimide.

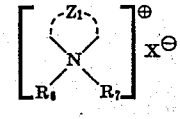
3. A photosensitive and thermosensitive element as in claim 1 wherein said onium halide is an alkylquaternary ammonium halide.

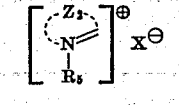
4. A photosensitive and thermosensitive element as in claim 1 wherein said onium halide is a quaternary phosphonium halide.

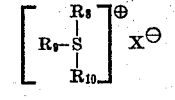
5. A photosensitive and thermosensitive element as in claim 1 wherein said onium halide is a tertiary sulfonium halide.

6. A photosensitive and thermosensitive element as in claim 1 wherein said onium halide is a compound of the formula:

I 

II 

III 

IV 

wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9 and R_{10} are each selected from the group consisting of alkyl containing 1 to 20 carbon atoms, phenyl, naphthyl, benzyl, phenethyl and phenylpropyl; X is a halide ion; Y is nitrogen or phosphorus; Z_1 and Z_2 each represent the atoms necessary to complete a heterocyclic nucleus.

7. A photosensitive and thermosensitive element as in claim 1 wherein said onium halide comprises about 0.10 mole to about 1.00 mole of 1-phenethyl-2-picolinium bromide per mole of said silver halide.

8. A photosensitive and thermosensitive element as in claim 1 wherein said onium halide comprises about 0.01 to about 0.10 mole of trimethylphenylammonium bromide per mole of said silver halide.

9. A photosensitive and thermosensitive element comprising a support, having thereon

(a) an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a bis-naphthol reducing agent,
(b) photographic silver halide,
(c) polyvinyl butyral,
(d) an activator-toning agent which comprises succinimide or phthalimide, and
(e) an alkyl quaternary ammonium halide.

10. A photosensitive and thermosensitive element as in claim 1 comprising a spectral-sensitizing dye.

11. In a photosensitive and thermosensitive composition comprising:

(a) an oxidation-reduction image-forming combination comprising (i) a heavy metal salt oxidizing agent with (ii) a reducing agent,
(b) photosensitive silver halide, and
(c) a binder; the improvement comprising

(d) a colorless, photographic speed-increasing, onium halide.

12. A photosensitive and thermosensitive composition as in claim 11 also comprising an activator-toning agent comprising phthalazinone, phthalimide or succinimide.

13. A photosensitive and thermosensitive composition as in claim 11 wherein said onium halide is an alkyl quaternary ammonium halide.

14. A photosensitive and thermosensitive composition comprising:

(a) an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a bis-naphthol reducing agent,

(b) photographic silver halide,

(c) polyvinyl butyral,

(d) succinimide or phthalimide and

(e) 1-phenethyl-2-picolinium bromide or trimethylphenylammonium bromide.

15. A photosensitive and thermosensitive composition as in claim 11 comprising a spectral-sensitizing dye.

16. A photosensitive and thermosensitive composition as in claim 11 wherein said onium halide comprises about 0.10 mole to about 1.00 mole of 1-phenethyl-2-picolinium bromide per mole of said silver halide.

17. A photosensitive and thermosensitive composition as in claim 11 wherein said onium halide comprises about 0.01 to about 0.10 mole of trimethylphenylammonium bromide per mole of said silver halide.

18. A process of developing a latent image in an exposed photosensitive and thermosensitive element comprising a support, an oxidation-reduction image-forming combination comprising a heavy metal salt oxidizing agent with a reducing agent, photographic silver halide, a binder, an activator-toning agent and a colorless, photographic speed-increasing, onium halide comprising heating said element from about 80° C. to about 250° C. to form a stable, developed image.

19. A process as in claim 18 of developing a latent image comprising heating said element at about 80° C. to about 250° C. for about 0.5 to about 60 seconds.

20. A process as in claim 18 of developing a latent image in said exposed photosensitive and thermosensitive element wherein said onium halide is an alkyl quaternary ammonium halide.

21. A process of developing a latent image in an exposed photosensitive and thermosensitive element comprising a support, having thereon

(a) an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a bisnaphthol reducing agent,

(b) photographic silver halide,

(c) polyvinyl butyral,

(d) an activator-toning agent which comprises succinimide or phthalimide and

(e) an alkyl ammonium halide,

comprising heating said element to about 80° C. to about 250° C. for about 0.5 to about 60 seconds.

References Cited

UNITED STATES PATENTS

3,457,075	7/1969	Morgan et al.	96—114.1 X
2,756,146	7/1956	Levy	96—114.1 X
3,017,271	1/1962	Piper	96—107
3,220,846	11/1965	Tinker et al.	96—114.1 X

NORMAN G. TORCHIN, Primary Examiner

W. H. LOUIE, JR., Assistant Examiner

U.S. Cl. X.R.

96—114.1, 48, 67, 94; 117—36.9, 36.8

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,679,422 Dated July 25, 1972

Inventor(s) Richard A. DeMauriac and Gary L. Hiller

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 40, "polaroid" should read ---Polaroid---. Line 56, "methtylsulfonium" should read ---methylsulfonium---.

Column 3, line 20, "reverse" should read ---adverse---. Line 34, "photosensitity" should read ---photosensitivity---.

Column 4, line 27, "naphtholymethyl" should read ---naphthoylmethyl---.

Column 5, line 44, "2,2-" should read --- 2,2'- ---.

Column 11, line 21, "invetnion" should read ---invention---.

Column 14, line 16, "total of" should read ---total volume of---. Line 22, "densit yof" should read ---density of---.

Column 15, Table II, Line 4 I, "320.0" should read ---321.0---.

Signed and sealed this 29th day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents