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3,666,477

ELEMENT, COMPOSITION AND PROCESS

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22 Claims

ABSTRACT OF THE DISCLOSURE

An alkylene oxide polymer, such as polyethylene glycol oleyl ether, and/or a mercaptotetrazole derivative, such as 1-phenyl-5-mercaptotetrazole, in combination with a gelatino silver halide emulsion, a heavy metal salt oxidizing agent 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. A combination of a bis- β -naphthol reducing agent, a gelatino silver halide emulsion, an alkylene oxide polymer and/or a mercaptotetrazole derivative in conjunction with a stable source of silver for physical development is useful in photosensitive elements for dry processing with heat. The element can contain a sensitizing dye and an activator-toning agent. A stable developed image is provided by heating the element. Other suitable photosensitive metal salts can be used in the photosensitive element.

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-naphthol reducing agent, an oxidizing agent, especially a heavy metal salt oxidizing agent and a gelatino, photosensitive silver halide emulsion in conjunction with alkylene oxide polymers and/or mercaptotetrazoles which increase the photosensitivity of the element. In another of its aspects, it relates to a photosensitive composition suitable for dry processing with heat containing a bis-naphthol reducing agent and a combination of a gelatino silver halide emulsion, a hydrophilic alkylene oxide polymer and/or a mercaptotetrazole derivative which increases the sensitivity of the element as described. A further aspect relates to a dry process of developing and increasing the speed, gamma and maximum density of a photosensitive and thermosensitive element containing an oxidation-reduction image forming combination comprising a reducing agent, an oxidizing agent, a gelatino, photographic silver halide emulsion as a source of photographic silver halide, an alkylene oxide polymer and/or a mercaptotetrazole, as described.

Description of the state art

Hydrophilic colloids used in the practice of this invention are known as alkylene oxide polymers, polyoxyalkylene glycols or polyalkylene glycols. They are synthesized by the reaction between alkylene oxides (such as ethylene oxide, propylene oxide, or butylene oxide) and glycols such as ethylene glycol, as described, for example, in Ellis, the Chemistry of Synthetic Resins (1935), pages 990 to 994. An example is polyethylene glycol of the formula:



wherein n is an integer greater than about 10.

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These polymers can be reacted with organic compounds containing an active hydrogen, e.g., aliphatic alcohols such as oleyl alcohol; aliphatic acids, such as lauric and myristic acids, and amino acids such as glycine; amines or amides such as glycine and laurylamide and phenols, as described in U.S. Patent 1,970,578 of Schoeller et al., issued Aug. 21, 1934.

Water soluble block polymers are also known and include those in which the polyoxypropylene and polyoxyethylene units constitute from about 10 to about 70 percent by weight of the block polymer, such as described in Lundsted U.S. Patent 2,674,619, issued Apr. 6, 1964 and Lundsted U.S. Patent 3,022,335, issued Feb. 20, 1962. These block polymers may have an average molecular weight of about 800 to about 3,000, exclusive of the groups which may be used to replace the active hydrogen as in the simple polyalkylene glycols. These block polymers can be condensed with organic compounds containing an active hydrogen and in addition they can react with reagents such as dialkyl siloxanes, such as described in U.S. Patent 2,917,480, of Bailey et al., issued Dec. 15, 1959.

In addition to the above derivatives of polyalkylene glycols and polyalkylene glycol block polymers, phosphate esters of ethylene oxide addition products of alkyl phenols are known, as described in U.S. Patents 3,004,056 of Nunn et al., issued Oct. 10, 1961 and 3,004,057 of Nunn, issued Oct. 10, 1961.

Polyoxyalkylene glycols or polyalkylene glycols and their derivatives have been used for a variety of purposes in the photographic field. For example, the water soluble condensation products derived from the reaction of at least 10 moles of ethylene oxide with one mole of a monohydric alcohol containing at least 10 carbon atoms such as decyl or oleyl alcohol can be used as a suitable non-ionic peptizer or surface active dispersing agent during the preparation of silver halide dispersions suitable for photographic materials, as described in U.S. Patent 2,752,246 of Weaver, issued June 26, 1956. Certain polyalkylene glycols can increase the photosensitivity of a gelatin containing silver halide element, as described, for example, in U.S. Patent 2,423,549 of Blake et al., issued July 8, 1947, and U.S. Patent 2,886,437 of Piper issued May 12, 1959. As described in British Patents 1,057,948-950, published Feb. 8, 1967, certain condensation products resulting from the reaction between polyoxyalkylene glycol with a phosphoric acid amide dihalide or diester are suitable for use as development modifiers, sensitizers, and stabilizers.

Certain di-alkoxypolyoxyalkylene glycols are known plasticizers of gelatin, as described in U.S. Patent 2,860,980 of Milton, issued Nov. 18, 1958. The phosphate esters made from the condensation products resulting from the reaction of ethylene oxide with alkyl phenols are useful as antistatic agents in film coatings as described in U.S. Patent 3,264,108 of Mackey et al., issued Aug. 2, 1966. Simple ethylene glycols and polyethylene glycols are also known antistatic agents, as described in U.S. Patent 1,757,482 of Seel, issued May 6, 1930.

Also, the addition of certain water-soluble organo-silicone block copolymers with polyethylene glycols to "lith-type" chlorobromiodide emulsions increases their speed of development, contrast and halftone quality, as described in U.S. Pat. 3,294,537 of Milton, patented Dec. 27, 1966. In U.S. Pat. 3,347,675 of Henn et al., issued Oct. 17, 1967, alkylene oxide polymers provide a medium for silver halide processing agents upon heating.

Hydrophilic polyethylene glycol polymers are described as being useful as binders in photosensitive elements, such as in U.S. Pat. 3,152,903 of Shepard and Shely, issued Oct. 13, 1964 and U.S. Pat. 3,152,904 of Sorensen and

Shepard, issued Oct. 13, 1964; U.S. Pat. 3,429,706 of Shepard et al., issued Feb. 25, 1965; and British Pat. 1,161,777 for so-called dry processing with heat.

It is also known to employ phenylmercaptotetrazole and mercaptotetrazole compounds in or on photographic materials. For example, it is known to deactivate a photosensitive and thermosensitive element by swabbing a 1% solution of phenylmercaptotetrazole solution onto the surface of the coating prior to, or after exposure of the element as described in U.S. Pat. 3,457,075 of Morgan and Shely, issued July 22, 1969. In addition it is known that certain heterocyclic mercapto azole compounds can be employed as stabilizers and anti-fogging agents for light-sensitive, gelatino, silver halide emulsions as described in British Pat. 1,053,587, published Jan. 4, 1967. Also these same compounds can be used as toners in a chemical transfer process disclosed in British Pat. 1,053,588, published Jan. 4, 1967.

Despite the several references describing the use of polyalkylene glycols and mercaptotetrazole compounds in photographic materials, none describe polyalkylene glycols and/or mercaptotetrazole compounds as addenda which can be used to enhance the photosensitivity of a photosensitive and thermosensitive element.

In photosensitive and thermosensitive elements, such as described in U.S. Pats. 3,152,904, issued Oct. 13, 1964, and in 3,437,075 of Morgan and Shely, published July 22, 1969, photographic silver halide formed in situ has been employed as a so-called light sensitive photocatalyst for the element as described. Pre-formed silver halide, i.e. silver halide formed separately from other components of a photosensitive and thermosensitive element, upon addition to a similar photosensitive and thermosensitive element, as described in these two patents, does not enhance the image-forming capabilities of the element as greatly as silver chloride or bromide formed in situ.

In addition, in some cases these photosensitive and thermosensitive elements suffer from a low degree of photosensitivity, contrast and maximum density. It would be desirable also to employ so-called pre-formed silver halide in such elements to provide better control of silver halide formation and to enable production of silver halide by procedures commonly employed in the photographic art, e.g. procedures employed in preparing gelatino photographic silver halide emulsions.

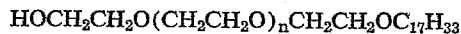
Accordingly, there has been a continuing need for a photosensitive and thermosensitive element suitable for so-called dry processing with heat which has increased photosensitivity, i.e., speed, contrast and image density and one which can utilize so-called pre-formed silver halide.

SUMMARY OF THE INVENTION

It has been found, according to the invention, the described improvements are provided in a photosensitive and thermosensitive element comprising a support, photographic silver halide, an oxidation-reduction image-forming combination comprising an oxidizing agent, e.g. a silver salt oxidizing agent, with a reducing agent, a binder, an alkylene oxide polymer and/or a mercaptotetrazole derivative, as described.

DETAILED DESCRIPTION OF THE INVENTION

A range of alkylene oxide or polyalkylene glycol polymers and their derivatives can be employed in the practice of the invention to cause an increase in photosensitivity, i.e., speed, contrast and maximum density. An especially suitable derivative or condensation product of polyethylene glycol is the oleyl ether of polyethylene glycol of the formula:



and having an average molecular weight of 1540; n is an integer of 10 or more. Other examples of suitable alkylene oxide polymers and their derivatives which can be em-

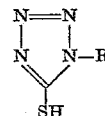
ployed in the practice of the invention include, for example:

polyethylene oxide oleic ester,
polyethylene oxide nonyl phenol ester,
N-methylmyristylamino polyethylene oxide, and/or
N-methyl-n-dodecylamino polyethylene oxide.

The polyalkylene oxides or derivatives of the polyalkylene oxides can be of a wide range of molecular weights; however, in the practice of the invention they are especially suitable in an average molecular weight range of about 300 to about 20,000 or more. These are available under the trade name "Carbowax" from Union Carbide Co., U.S.A.

The described alkylene oxide polymers are suitable in a wide range of concentration depending on the particular components of the element, desired image and the like; but preferably the concentration is about 0.5 gram to about 50 grams of polyalkylene glycol per mole of silver. They are especially suitable at a concentration from about 5 grams to about 25 grams per mole of photographic silver halide or from about 1 gram to about 5 grams per mole of silver salt of organic acid oxidizing agent. This concentration is not sufficient for the described alkylene oxide polymers to function as a binder.

A range of mercaptotetrazole derivatives can be employed in the practice of the invention to cause an increase in photosensitivity, i.e., speed, contrast and maximum density. In addition, in some cases, a synergistic effect is observed when a mercaptotetrazole derivative is employed with an alkylene oxide polymer as practiced by the invention. Suitable mercaptotetrazole derivatives which can be employed in the described combination are of the formula:



wherein R is hydrogen, alkyl with 1 to 3 carbon atoms, such as methyl, ethyl or propyl, aryl such as phenyl or naphthyl. The aryl group can contain substituent groups which do not adversely affect the desired properties of the photosensitive element, e.g. acetamido. Suitable mercaptotetrazoles which can be employed in the practice of the invention include:

5-mercaptotetrazole,
1-phenyl-5-mercaptotetrazole,
1-(3-acetamido)-5-mercaptotetrazole,
1-naphthyl-5-mercaptotetrazole, and/or
1-ethyl-5-mercaptotetrazole.

The described mercaptotetrazoles are suitable in a wide range of concentration depending on the particular compounds of the element, desired image and the like; but preferably the concentration is from about 0.5 gram to about 10 grams per mole of silver salt oxidizing agent. However, they are especially suitable at a concentration from about 2 grams to about 5 grams per mole of silver salt oxidizing agent. In addition, the disulfide derivatives of the mercaptotetrazole compounds can be employed in the practice of the invention.

The described element contains 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 Lippmann emulsions, ammoniacal

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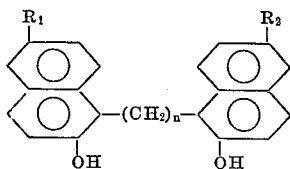
emulsions, thiocyanate or thioether ripened emulsions, such as those described in U.S. Pat. 2,222,264 of Nietz et al., issued Nov. 14, 1940; U.S. Pat. 3,320,069 of illingsworth issued May 15, 1967 and U.S. Pat. 3,271,157 of McBride issued Sept. 6, 1966. Surface image silver halide emulsions can be used if desired, mixtures of surface and internal image silver halide emulsions can be used as described in U.S. Pat. 2,996,332 of Luckey et al. issued Apr. 15, 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) pp. 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.

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



Wherein R_1 and/or R_2 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.

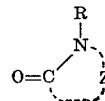
The described reducing agents are suitable in a range of concentration; however, they are especially suitable, at a concentration from about 0.10 to about 0.75 mole of reducing agent per mole of oxidizing agent.

Other reducing agents, which are typically silver halide developing agents, can be used also. These can be used alone, in various combinations, or in conjunction with the above bis-naphthol reducing agents. Suitable silver

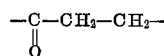
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halide developing agents include for example, polyhydroxybenzenes such as hydroquinone developing agents, e.g., hydroquinone, alkyl-substituted hydroquinones as exemplified by tertiary butylhydroquinone, methylhydroquinone, 2,5-dimethylhydroquinone 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 ketals 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 hydroxytetronamide developing agents; reductone developing agents such as anhydrodihydropyrrolidone nexose reductone; and the like.

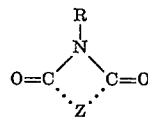
It is desirable to employ an activator-toning agent in the elements, compositions and processes of the invention to obtain a desired image, particularly when phenolic reducing agents are used. A suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen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



where R is hydrogen, hydroxyl, or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z, represents atoms completing a heterocyclic nucleus, especially a 5 or 6 member heterocyclic nucleus. The atoms completing the heterocyclic nucleus can be, for example,

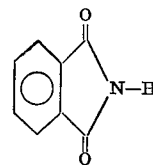


or an alkylene group containing 3 or 4 carbon atoms. The atoms completing the heterocyclic nucleus can contain various substituent groups, such as amino, alkyl amino, e.g. methylamino or ethylamino, hydroxyl, carbamyl and the like. An especially suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom which is preferably a cyclicimide of the formula:



wherein R can be hydrogen, hydroxyl, or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z represents carbon atoms of a series completing a cyclicimide nucleus, typically consisting of from 5 to 6 carbon atoms, e.g. a phthalimide or succinimide nucleus. The atoms of the cyclic imide 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.

An especially suitable activator-toning agent is phthalimide of the formula



Examples of suitable cyclic-imides which can be employed in the practice of the invention include:

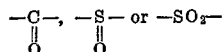
N-hydroxyphthalimide
N-potassium phthalimide
N-silver phthalimide
N-mercury phthalimide
succinimide
N-hydroxysuccinimide.

The described cyclic-imide activator-toning agents are suitable in a range of concentration; however, they are especially suitable at a concentration from about 1.0 to about 3.0 moles of activator-toning agent per mole of silver halide.

The described activator-toning agents are suitable in a range of concentration, such as at a concentration of about 1.0 to about 3.0 moles of activator-toning agent per mole of silver halide; 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 e.g. per mole of silver behenate.

Other so-called activator-toning agents can be employed in the described photosensitive and thermosensitive element in the practice of the invention. Various toners can be employed for this purpose. 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



moiety, in a described photosensitive and thermosensitive element suitable for dry processing with heat can provide improved maximum image densities. Tetrahydrothiophene-1, 1-dioxide; 4-hydroxybutanoic acid lactone and methylsulfinylmethane are examples of such solvents.

The described elements comprise an 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 hydroxystearate, silver caprate, silver myristate and silver palmitate. Other suitable oxidizing agents are silver benzoate, silver phthalazinone, silver benzotriazole, silver saccharin, silver 4'-n-octadecyl-oxydiphenyl-4-carboxylic acid, silver O-aminobenzoate, 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.

A photosensitive and thermosensitive element and compositions, e.g. 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 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 poly-

vinyl compounds like poly(vinyl pyrrolidone), acrylicamide 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 and polyvinyl alcohol.

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 a 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 oxyguarum 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 Serman et al. issued Sept. 14, 1965 or insoluble inorganic salts such as those described in U.S. Pat. 3,428,451 of Trevoay 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 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.

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.

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. Patent 2,922,101 of Jelley et al. issued July 11, 1961 and U.S. Patent 2,761,245 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 Patent 972,067 and U.S. Patent 2,933,390 of McFall et al. issued Apr. 19, 1960 or dispersions of brighteners can be used such as those described in German Patent 1,150,274; U.S. Patent 3,406,070 of Oetiker et al. issued Oct. 15, 1968 and French Patent 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. Patent 3,253,921 of Sawdey issued May 31, 1966; U.S. Patent 2,274,782 of Gaspar issued Mar. 3, 1942; U.S. Patent 2,527,583 of Silberstein et al. issued Oct. 31, 1950; and U.S. Patent 2,956,879 of Van Campen issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in U.S. Patent 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. Patent 2,681,294 of Beguin issued June 15, 1954. If desired, two or more layers can be coated simultaneously such as by procedures described in U.S. Patent 2,761,791 of Russell issued Sept. 4, 1956 and British Patent 837,095.

If desired, the photosensitive silver halide can be, but need not 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. Patent 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. Patent 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 increase 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) 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, alkylamine 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., typically about 120° C. to about 160° C.

Accordingly, one embodiment of the invention is a photosensitive and thermosensitive element comprising

- (a) support,
- (b) photographic silver halide
- (c) an oxidation-reduction image-forming combination comprising
 - (i) a silver salt oxidizing agent and
 - (ii) a reducing agent,
- (d) a binder, and
- (e) about 0.5 gram to about 50 grams of polyethylene glycol per mole of silver and/or about 0.5 gram to about 10 grams of a mercaptotetrazole derivative, as described, per mole of silver salt oxidizing agent.

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

- (a) a support especially a poly(ethylene terephthalate) support
- (b) gelatino silver halide emulsion
- (c) an oxidation-reduction image forming combination comprising
 - (i) silver behenate and
 - (ii) 2,2'-dihydroxy-1,1'-binaphthyl
- (d) gelatin binder
- (e) about 0.5 gram to about 50 grams of polyethylene glycol oleyl ether per mole of silver behenate and/or about 0.5 gram to about 10 grams, typically about 2 to about 5 grams, of 1-phenyl-5-mercaptotetrazole per mole of silver behenate,
- (f) phthalimide and
- (g) a sensitizing dye.

An example of such an element is a multilayer photosensitive and thermosensitive element comprising, respectively,

- (a) a support,
- (b) a photographic silver halide emulsion layer, and
- (c) a layer comprising
 - (i) an oxidation-reduction image-forming combination, as described,
 - (ii) a binder,
 - (iii) about 0.5 gram to about 50 grams of polyethylene glycol oleyl ether per mole of silver and/or about 0.5 gram to about 10.0 grams of a mercaptotetrazole derivative per mole of silver salt of oxidizing agent and
 - (iv) an activator-toning agent.

For instance, the multilayer photosensitive and thermosensitive element, as described, can comprise, respectively:

- (a) a support, especially a poly(ethylene terephthalate) support,
- (b) a photographic silver halide emulsion layer, and
- (c) a layer comprising
 - (i) an oxidation-reduction image-forming combination comprising
 - (A) silver behenate and (B) 2,2-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral,
 - (iii) about 1 gram to about 5 grams of polyethylene glycol oleyl ether per mole of silver behenate and/or from about 2.0 grams to about 5.0 grams-1-phenyl-5-mercaptotetrazole per mole of silver behenate,
 - (iv) phthalimide and
 - (v) a sensitizing dye.

Another embodiment of the invention is a multilayer photosensitive and thermosensitive element comprising, respectively,

- (a) a support,
- (b) a photographic silver halide emulsion layer comprising about 0.5 gram to about 50.0 grams of polyethylene glycol or polyethylene glycol oleyl ether per mole of silver,

- (c) a layer comprising
 - (i) an oxidation-reduction image-forming combination, as described,
 - (ii) a binder,
 - (iii) about 0.5 gram to about 50.0 grams of polyethylene glycol or polyethylene glycol oleyl ether per mole of silver and/or about 0.5 gram to about 10.0 grams of a mercaptotetrazole derivative per mole of silver salt oxidizing agent and
 - (iv) an activator-toning agent.

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

- (a) a support, especially a poly(ethylene terephthalate) support,
- (b) a gelatino photographic silver halide emulsion layer comprising about 5.0 grams to about 25.0 grams of polyethylene glycol oleyl ether per mole of silver halide,
- (c) a layer comprising
 - (i) an oxidation-reduction image-forming combination comprising
 - (A) silver behenate, and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 1 gram to about 5 grams of polyethylene glycol oleyl ether per mole of silver behenate and/or about 2 grams to about 5 grams of 1-phenyl-5-mercaptotetrazole per mole of silver behenate,
 - (iv) phthalimide and
 - (v) a sensitizing dye.

Still another embodiment of the invention is a photosensitive and thermosensitive composition comprising

- (i) an oxidation-reduction image-forming combination comprising
 - (A) a silver salt oxidizing agent, as described, and
 - (B) a reducing agent, as described,
- (ii) about 1 gram to about 5 grams of polyethylene glycol or polyethylene glycol oleyl ether per mole of silver salt oxidizing agent.

For example, the photosensitive and thermosensitive composition can comprise

- (i) an oxidation-reduction image-forming combination comprising
 - (A) silver behenate and
 - (B) 2,2'-dihydroxy-1,1'-binaphthyl,
- (ii) about 1 gram to about 5 grams of polyethylene glycol oleyl ether per mole of silver behenate, and
- (iii) phthalimide; and can also comprise
- (iv) photographic silver halide,
- (v) about 0.5 gram to about 10 grams of 1-phenyl-5-mercaptotetrazole per mole of silver behenate and
- (vi) a sensitizing dye.

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: a method of developing a latent image in an exposed photosensitive and thermosensitive element comprising

- (a) a support,
- (b) photographic silver halide,
- (c) an oxidation-reduction image-forming combination comprising
 - (i) a silver salt oxidizing agent and
 - (ii) a reducing agent,
- (d) a binder, and
- (e) about 0.5 gram to about 50 grams of polyethylene glycol or polyethylene glycol oleyl ether per mole of silver and/or about 0.5 gram to about 10 grams of a mercaptotetrazole derivative, as described, per mole

of silver salt oxidizing agent, comprising heating said element to about 80° C. to about 250° C.

A temperature range of about 120° C. to about 160° 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) a support,
- (b) photographic silver halide,
- (c) an oxidation-reduction image-forming combination comprising
 - (i) silver behenate, and
 - (ii) 2,2'-dihydroxy-1,1'-binaphthyl,
- (d) a binder, such as gelatin,
- (e) phthalimide,
- (f) and about 5 grams to about 25 grams of polyethylene glycol oleyl ether per mole of silver halide and/or about 2 grams to about 5.0 grams of 1-phenyl-5-mercaptopentazole per mole of silver behenate,

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

In addition another embodiment of the invention is: in a method of developing a latent image in an exposed photosensitive and thermosensitive multilayer element comprising, respectively,

- (a) a support,
- (b) a photographic silver halide emulsion layer comprising about 0.5 gram to about 50 grams of polyethylene glycol oleyl ether, and
- (c) a layer comprising
 - (i) an oxidation-reduction image-forming combination comprising
 - (A) silver behenate and
 - (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 1 gram to about 5 grams of polyethylene glycol oleyl ether and/or about 2 grams to about 5 grams of 1-phenyl-5-mercaptopentazole,
 - (iv) phthalimide,
 - (v) sensitizing dye,

comprising heating the above described element to 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 temperature, pressure and humidity. Temperatures, pressures and humidity outside normal atmospheric conditions can be employed if desired; however, normal atmospheric conditions are preferred.

Various methods and means can be employed in providing the necessary heating of the described elements. The heating means can be a simple hot plate, iron or the like.

Other addenda known to be useful in photosensitive and thermosensitive elements of this type, such as described in British Patent 1,161,777 published Aug. 20, 1969 and U.S. Patent 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 illustrates the invention.

A photographic element is prepared as follows:

A coating composition is prepared by mixing the following components:

Silver behenate—168.0 g.
Behenic acid—32.0 g.

Polyvinylbutyral—60.0 g.

Acetone-toluene (1:1)—1600 ml.

After ball-milling for 18 hours, 400 ml. of acetone-toluene (1:1 by volume) is added to the resulting dispersion. This is designated as Dispersion A. A multilayer element is prepared by combining 22.5 milliliters of Dispersion A with the following solutions:

	ML.
10 Acetone containing 6.3% by weight 2,2'-dihydroxy-1,1'-binaphthyl -----	8.4
Acetone containing 5.0% by weight phthalimide ---	7.6
Methanol containing 0.167% by weight 1-phenyl-5-mercaptopentazole and -----	8.0
15 Acetone containing 1% by weight oleyl ether of polyethylene glycol (Atlas 93920, average molecular weight 1540) -----	10.0

and coating the resulting composition on a polyethylene terephthalate film support at a wet thickness of approximately 0.002 inch. A second layer consisting of the following composition is prepared as follows:

Silver bromide gelatin emulsion containing 60.0 g. gelatin per mole of silver bromide and weighing 1.90 kg./mole silver—5.0 g.

25 Water—25.00 ml.

Acetone containing 1% by weight oleyl ether of polyethylene glycol (Atlas 63920, average molecular weight 1540) and—5.00 ml.

30 Water containing 15% by weight saponin—7.20 ml.

and coated upon the above first layer at a wet thickness of approximately 0.002 inch. A sample of this coating is exposed, imagewise, for 3 seconds by a No. 2 photoflood lamp at a distance of 1.5 feet from the sample and heat processed on a curved hot block for 10 seconds at a temperature of 140° C. A visible image results.

Example 2.—This is a comparative example.

The procedure set out in Example 1 is followed with the exception that the second layer containing the gelatino silver halide emulsion is omitted from the element. The element is exposed and heat processed as described in Example 1. No visible image is observed.

Example 3.—This illustrates the invention.

A multilayer element is prepared by coating the gelatino silver halide emulsion composition described in Example 1 on a poly(ethylene terephthalate) film support at a wet thickness of approximately 0.002 inch and then coating a second layer consisting of the following composition over the silver halide emulsion layer:

50 silver behenate-behenic acid Dispersion A described in Example 1—22.5 ml.	
polyvinyl butyral—1.1 g.	
acetone containing 6.3% by weight 2,2'-dihydroxy-1,1'-binaphthyl—8.4 ml.	
55 acetone containing 5% by weight phthalimide—7.6 ml.	
methanol containing 0.167% by weight 1-phenyl-5-mercaptopentazole—8.0 ml.	
acetone containing 1% by weight polyethylene glycol oleyl ether (as described above)—10.0 ml.	
60	

The multilayer element is exposed and heat processed as described in Example 1. A visible jet-black image is observed.

Examples 4A-4G.—This illustrates the invention.

A series of multilayer photosensitive and thermosensitive elements are prepared as follows:

A coating composition is prepared by mixing the following components:

70 silver bromide gelatin emulsion (described in Example 1)—190.0 g.	
acetone containing 1 mg. of 3-carboxymethyl-5-[(3-methyl-2-(3-thiazolinylidene)isopropylidene]rhodanine per ml. of acetone—95.0 ml.	
75 water containing 15% by weight saponin—7.2 ml.	

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The resulting dispersion is coated on a poly(ethylene terephthalate) support at a wet thickness of 4.0 grams of melt per foot square of support. The components are thus coated at the following concentrations: 60 mg. silver/ft.², 33 mg. gelatin/ft.² and 1.0 mg. dye/ft.². The multilayer coating is completed by overcoating the above described layer with a second layer at a wet thickness of 0.004 inch and consisting of the following composition:

Silver behenate Dispersion A (preparation described in Example 1)	22.5
Acetone containing 6.3% by weight 2,2'-dihydroxy-1,1'-binaphthyl	8.4
Acetone containing 5.0% by weight phthalimide	7.6

A sample of this coating is exposed and heat processed for 5 seconds as in Example 1. The resulting image is jet-black with a maximum density of 0.84 and a minimum density of 0.25. The element is assigned a relative speed of 100. A series of multilayer coatings is prepared as described above with the exception that the oleyl ether of polyethylene glycol, (designated as PEGO) average molecular weight 1540, and/or 1-phenyl-5-mercaptotetrazole (designated as PMT) is incorporated into the compositions used in either layer 1 or layer 2. Table I shows the sensitometric data which is obtained from these elements and the format followed for each multilayer coating.

Table I shows that incorporation of PEGO into both layers (Example 4E) of the element caused a marked increase in maximum density, gamma and a substantial increase in relative speed (+101) in comparison to the control coating (4A). Table I also shows that a synergistic effect can be obtained when PEGO and PMT are used together in the top layer. This is noted in comparing Example 4D with 4G. In addition, it is apparent that the selective addition of either PMT or PEGO into the photosensitive and thermosensitive element results in an increase in the photosensitivity of the described element.

TABLE I

Example	Relative speed	Gamma	D _{min}	D _{max}	Layer I, g. PEGO/mole AgBr	Layer II, g. PEGO/mole AgBr	Layer II, g. PMT/mole AgBr
4A	100	0.68	0.25	0.94			
4B	159	0.68	0.36	1.34			3.6
4C	162	1.13	0.33	1.81	10.0		
4D	213	0.57	0.25	1.20		2.7	
4E	201	1.37	0.24	1.81	10.0	2.7	
4F	123	0.60	0.26	1.13	10.0	2.7	3.6
4G	234	0.74	0.33	1.54		2.76	3.6

PEGO=Oleyl ether of polyethylene glycol (Atlas G3920, average molecular weight 1,540).
PMT=1-phenyl-5-mercaptotetrazole.

LAYER II
LAYER I
SUPPORT

Example 5.—This illustrates the invention.

A hydrophilic monolayer photographic element is prepared by mixing the following components:

polyethylene glycol oleyl ether (described in Example 1)—1.0 g.

water—200.0 ml.

After mixing for 15 minutes through the use of an ultrasonic probe, 0.85 gram of the above aqueous dispersion is combined with the following addenda as follows:

silver bromide gelatin emulsion (described in Example 1)—15.0 g.

water containing 10% by weight of gelatin—17.5 g.
acetone containing 1 mg. of 3 - carboxymethyl-5-[(3-methyl - 2 - (3) - thiazolinyldene)isopropylidene]-rhodanine per ml. of acetone—4.5 ml.

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acetone containing 6.3% by weight of 2,2'-dihydroxy-1,1'-binaphthyl—8.4 ml.

acetone containing 5.0% by weight of phthalimide—7.6 ml.

polyethylene glycol, oleyl ether (described in Example 1)—0.100 g.

methanol containing 0.167% by weight 1-phenyl-5-mercaptotetrazole and—8.0 ml.
water—20.0 ml.

The composition is mixed, coated on a polyethylene terephthalate film support at a wet thickness of 0.004 inch and dried. A sample of this coating is exposed for 3 seconds by a No. 2 photoflood at a distance of 1.5 feet and then heat processed on a curved hot block for 3 seconds at a temperature of 140° C. The resulting jet-black image is uniform, shows no mottle and has a maximum density of 1.58 with very little background stain.

This example shows that a hydrophilic coating of a photosensitive element suitable for so-called dry processing with heat can be made using a gelatino silver halide emulsion and still obtain a uniform image of relatively high density.

Example 6.—This illustrates the invention.

The procedure set out in Example 5 is repeated with the exception that polyethylene glycol oleyl ether is omitted from the final dispersion. The composition is coated on a polyethylene terephthalate film support at a wet thickness of 0.004 inch, dried, exposed and heat processed as in Example 5. The resulting jet-black image has a maximum density of 1.38 with very little background stain and a slight amount of mottle.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A photosensitive and thermosensitive element comprising

- a support,
- photographic silver halide,
- an oxidation-reduction image forming combination comprising (i) a silver salt oxidizing agent and (ii) a reducing agent,
- a binder, and
- about 0.5 gram to about 50 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver.

2. A photosensitive and thermosensitive element as in claim 1 also comprising an activator-toning agent.

3. A photosensitive and thermosensitive element as in claim 1 also comprising an activator-toning agent which is phthalimide.

4. A photosensitive and thermosensitive element as in claim 1 wherein said reducing agent is a bis-naphthol reducing agent.

5. A multilayer, photosensitive and thermosensitive element comprising, respectively,
- (a) a support,
 - (b) a photographic silver halide emulsion layer, and
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) a silver salt oxidizing agent and (B) a reducing agent,
 - (ii) a binder,
 - (iii) about 1 to about 5 grams of polyethylene glycol per mole of said silver salt oxidizing agent,
 - (iv) about 0.5 gram to about 10 grams of phenylmercaptotetrazole per mole of silver salt oxidizing agent and,
 - (v) an activator-toning agent.
6. A multilayer, photosensitive and thermosensitive element as in claim 5 comprising, respectively,
- (a) a support,
 - (b) a photographic silver halide emulsion layer,
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 1 to about 5 grams of polyethylene glycol or a polyethylene glycol ether, per mole of silver behenate,
 - (iv) about 0.5 gram to about 10 grams of phenylmercaptotetrazole per mole of silver salt oxidizing agent and,
 - (v) phthalimide.
7. A multilayer, photosensitive and thermosensitive element comprising, respectively,
- (a) a support,
 - (b) a photographic silver halide emulsion layer, and
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 1 to about 5 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver behenate and
 - (iv) phthalimide.
8. A multilayer, photosensitive and thermosensitive element comprising, respectively,
- (a) a support,
 - (b) a photographic silver halide emulsion layer comprising about 0.5 gram to about 50 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver,
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) a silver salt oxidizing agent and (B) a reducing agent,
 - (ii) a binder,
 - (iii) about 1 to about 5 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver salt oxidizing agent and
 - (iv) an activator-toning agent.
9. A multilayer, photosensitive and thermosensitive element, as in claim 8, comprising, respectively,
- (a) a support,
 - (b) a photographic silver halide emulsion layer comprising about 0.5 to about 50 grams of polyethylene glycol or a polyethylene glycol ether, per mole of silver in said photographic silver halide emulsion layer,
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 1 to about 5 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver behenate and,

- (iv) phthalimide.
10. A multilayer, photosensitive and thermosensitive element comprising, respectively,
- (a) a support,
 - (b) a photographic silver halide emulsion layer comprising about 0.5 to about 50 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver in said silver halide emulsion layer,
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder, and
 - (iii) phthalimide.
11. A multilayer photosensitive and thermosensitive element comprising,
- (a) a support,
 - (b) a photographic silver halide emulsion layer, and
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) a silver salt oxidizing agent and (B) a reducing agent,
 - (ii) a binder,
 - (iii) about 0.5 gram to about 10 grams of phenylmercaptotetrazole per mole of said silver salt oxidizing agent, and
 - (iv) an activator-toning agent.
12. A photosensitive and thermosensitive element, as in claim 11, comprising, respectively,
- (a) a support,
 - (b) a photographic silver halide emulsion layer, and
 - (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 0.5 gram to about 10 grams of phenylmercaptotetrazole per mole of silver behenate, and
 - (iv) phthalimide.
13. A multilayer photosensitive and thermosensitive element comprising, respectively,
- (a) support
 - (b) a photographic silver halide emulsion layer comprising about 0.5 g. to about 50 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver in said silver halide emulsion layer, and
 - (c) a layer comprising
 - (i) an oxidation-reduction image-forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 0.5 gram to about 10 grams of phenylmercaptotetrazole per mole of silver behenate,
 - (iv) about 1 gram to about 5 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver behenate, and
 - (v) phthalimide.
14. A photosensitive and thermosensitive element comprising, a support and a layer comprising
- (i) photographic silver halide,
 - (ii) an oxidation-reduction image-forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (iii) polyvinyl butyral binder,
 - (iv) phthalimide,
 - (v) about 0.5 gram to about 10 grams of phenylmercaptotetrazole per mole of silver behenate, and
 - (vi) about 1 gram to about 5 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver behenate.
15. A photosensitive and thermosensitive element as in claim 14 wherein, said photographic silver halide comprises a photographic silver halide gelatin emulsion.

16. A photosensitive and thermosensitive composition comprising
- (i) an oxidation-reduction image forming combination comprising (A) a silver salt oxidizing agent and (B) a reducing agent,
 - (ii) about 1 gram to about 5 grams of polyethylene glycol or a polyethylene glycol ether per mole of said silver salt oxidizing agent,
 - (iii) and photographic silver halide.
17. A photosensitive and thermosensitive composition as in claim 16 also comprising an activator-toning agent.
18. A photosensitive and thermosensitive composition as in claim 16 comprising
- (i) an oxidation-reduction image forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) about 1 gram to about 5 grams of polyethylene glycol or a polyethylene glycol ether per mole of silver behenate, and
 - (iii) phthalimide.
19. A photosensitive and thermosensitive composition as in claim 16 comprising about 0.5 gram to about 10 grams of phenylmercaptotetrazole per mole of said silver salt oxidizing agent.
20. A method of developing a latent image in an exposed photosensitive and thermosensitive element comprising,
- (a) a support,
 - (b) photographic silver halide,
 - (c) an oxidation-reduction image-forming combination comprising (i) a silver salt oxidizing agent and (ii) a reducing agent,
 - (d) a binder, and
 - (e) about 0.5 gram to about 50 grams of polyethylene glycol per mole of silver, comprising heating said element to about 80° C. to about 250° C.
21. A method as in claim 20 wherein said element also comprises an activator-toning agent.
22. A method as in claim 20 of developing a latent

image in an exposed photosensitive and thermosensitive multilayer element, comprising, respectively,

- (a) a support,
- (b) a photographic silver halide emulsion layer comprising about 0.5 gram to about 50 grams of polyethylene glycol, and
- (c) a layer comprising
 - (i) an oxidation-reduction image forming combination comprising (A) silver behenate and (B) 2,2'-dihydroxy-1,1'-binaphthyl,
 - (ii) polyvinyl butyral binder,
 - (iii) about 1 to about 5 grams of polyethylene glycol or a polyethylene glycol ether, per mole of silver behenate,
 - (iv) phthalimide, comprising heating said element to about 120° C. to about 160° C. for about 0.5 to about 60 seconds.

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U.S. Cl. X.R.

117—36.8; 250—65.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,666,477 Dated May 30, 1972

Inventor(s) Charles A. Goffe

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

In Column 15, lines 62-64,

"polyethylene glycol oleyl ether (described in Example
silver behenate — 16.8 g.

1) — 1.0 g."

should read

---silver behenate 16.8 g

polyethylene glycol oleyl ether (described in
Example 1) 1.0 g ---

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents