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3,846,136

CERTAIN ACTIVATOR-TONERS IN PHOTSENSITIVE AND THERMOSENSITIVE ELEMENTS, COMPOSITIONS AND PROCESSES

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22 Claims

ABSTRACT OF THE DISCLOSURE

In a photosensitive and thermosensitive element, composition or process employing such an element, an oxidation-reduction image forming combination comprising an oxidizing agent, such as silver behenate, with a reducing agent, a binder and an activator-toner agent, improved tone results when an activator-toner agent is employed which is (a) a 2-pyrazolin-5-one, (b) a cyclic imide, such as succinimide and/or certain of its metal salts, and/or (c) a quinazolinone. Preferably a catalyst for the image forming combination, especially photographic silver halide is also employed. A high dielectric, polar solvent, such as tetrahydrothiophene-1,1-dioxide can also be employed. These elements and compositions are useful in so-called dry processing with heat. The element can be an image reproduction sheet in which a radiation sensitive heavy metal salt can be reduced to free metal and form the image components in an oxidation-reduction reaction combination by producing a visible color change with an organic silver salt.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to photosensitive and thermosensitive elements, compositions and processes for developing a latent image employing improved activator-toner agents. In one of its aspects it relates to a photosensitive and thermosensitive element employing (a) an oxidation-reduction image forming combination of an oxidizing agent, especially a silver salt oxidizing agent, with a reducing agent, (b) a binder, (c) the described activator-toner agents, (d) and preferably a catalyst for the oxidation-reduction image forming combination, especially photographic silver halide. In another of its aspects it relates to a photosensitive and thermosensitive composition employing such activator-toner agents. A further aspect relates to a process of developing a latent image in a photosensitive and thermosensitive element or composition, as described, employing so-called dry processing with heat.

Description of the State of the Art

It is known to develop a latent image in a photographic silver halide element using a silver halide developing agent in so-called dry processing with heat. The photographic element can contain a silver halide developing agent as well as other components to produce a developed, stable image. After exposure the resulting latent image can be developed and stabilized by heating the photographic element. Such a process is described, for example, in U.S. Pat. 3,301,678 of Humphlett et al. issued Jan. 31, 1967.

Other methods and elements for so-called dry processing with heat are described, for example, in U.S. Pat. 3,152,904 of Sorensen et al. issued Oct. 13, 1964; French Pat. 1,441,619; U.S. Pat. 3,392,020 of Yutzy and Yackel issued July 9, 1968; Belgian Pat. 705,872; and U.S. Pat. 2,910,377 of Owen issued Oct. 27, 1959.

Many photosensitive and thermosensitive elements have been proposed employing, on a support, (a) an oxidation-

reduction image forming combination, e.g. a combination of an oxidizing agent, such as silver behenate, with a reducing agent, especially a phenolic reducing agent, (b) a so-called catalyst for the oxidation-reduction image forming combination, e.g. photographic silver halide, (c) a binder, such as polyvinyl butyral, and (d) a toner. These have been employed for so-called dry processing with heat, and are described, for instance, in the noted references. In many cases these have not provided a desired black tone or developed image. This is demonstrated in following comparative Example 20.

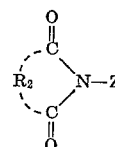
Many so-called toners have been proposed in elements which are thermosensitive, i.e. elements in which an image is developed with imagewise heating. One of the toners proposed for such elements is phthalazinone, as set out, for example, in U.S. Pat. 3,080,254 of Grant issued Mar. 5, 1963 and U.S. Pat. 3,107,174 of Wartman issued Oct. 15, 1963.

However, there has been a continuing need to provide photosensitive and thermosensitive elements which contain the described components with a so-called activator-toner agent, other than phthalazinone, which provide a desired developed image and improved black tone. As demonstrated in the following Example 1, in the absence of the activator-toner agents of the invention, surprisingly no image is developed upon heating the element.

SUMMARY OF THE INVENTION

It has been found, according to the invention, that in a photosensitive and thermosensitive element also referred to herein as a photothermographic element, employing (i) an oxidation-reduction image forming combination comprising an oxidizing agent, especially a silver salt oxidizing agent, with a reducing agent, (ii) a binder, and preferably (iii) a catalyst for the oxidation-reduction image forming combination, especially a catalyst from photographic silver halide, an activator-toner agent which is

- (a) a 2-pyrazolin-5-one,
- (b) a cyclic imide of the formula:



wherein R₂ represents atoms completing a succinimido, 4-cyclohexane-1,2-dicarbonylimido, glutarimido, or 2,4-thiazolidinedione nucleus; Z is hydrogen, hydroxyl, silver, mercury, potassium, sodium, lithium or gold; and/or

- (c) a quinazolinone,

provides a developed image with improved black tone. The above activator-toner agents are also useful in thermographic materials as described herein.

DETAILED DESCRIPTION OF THE INVENTION

A range of 2-pyrazolin-5-one, cyclic imide and/or quinazolinone compounds can be employed according to the invention, as described. A test can be employed to determine the degree of black tone and other properties which a particular compound within the described classes provides in a photosensitive and thermosensitive element. This test is as follows: A dispersion is prepared by ball

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milling the following components together at about 20° C. and atmospheric pressure typically for several hours:

Polyvinyl butyral -----g--	1.25
Behenic acid -----g--	3.50
Silver behenate -----g--	3.90
Sodium bromide -----g--	0.20
Acetone-toluene mixture (1:1 parts by volume) -----ml--	50.00

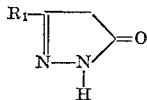
This is designated as Dispersion A. The following composition is then prepared employing Dispersion A by mixing the following components:

Dispersion A -----Ml.	3.76
Acetone containing 5% by weight/volume 2,2'-methylene-bis(4-methyl-6-tertiarybutylphenol) -----	3.76
Acetone containing 0.01% by weight benzoxazolyldinethiohydantoin sensitizing dye -----	0.70
Acetone containing 10.0% by weight/volume tetrahydrothiophene-1,1-dioxide -----	1.20
Acetone-toluene mixture (1:1 parts by volume) -----	2.38
Volatile, organic solvent, preferably methanol, containing 2.0% by weight/volume of activator-toner agent -----	1.88

The resulting composition is coated on a polyethylene coated paper support at a coating thickness of about 0.002 inches. The resulting coating is dried by permitting the resulting element to stand at about 20° C. to about 40° C. and atmospheric pressure until the coating is substantially solid. The element is exposed to tungsten light imagewise for 5 seconds and then heated by placing the element with the side opposite the described coating on a heated metal plate at 100° C. for 5 to 60 seconds. Compounds which are suitable activator-toner agents in the practice of the invention provide a developed image which has a maximum density and tone at least equal to a control element in which quinazolinone is employed as the described activator-toner agent. Employing an arbitrary rating scale of tone and density which corresponds to 0 for very poor or no image to 10 for excellent for a developed image, a preferred activator-toner agent received a rating of 7 to 10. Employing this scale, and the described test, succinimide and phthalimide receive a rating of at least 7 and 3-phenyl-2-pyrazolin-5-one and 3-methyl-2-pyrazolin-5-one receive a rating of at least 8. These are accordingly preferred activator-toner agents. In the absence of an activator-toner agent in the described test little or no developed image is observed.

A range of 2-pyrazolin-5-one activator-toner agents are suitable in the practice of the invention. These include 2-pyrazolin-5-one compounds which satisfy the described test for suitable activator-toner agents. Useful activator-toner agents include, for example, 2-pyrazolin-5-one compounds of the formula:

(II)



wherein R₁ is hydrogen, lower alkyl, e.g. alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl, propyl, or butyl, or aryl, especially aryl containing 6 to 12 carbon atoms, such as phenyl, tolyl, or xylyl. Suitable 2-pyrazolin-5-one compounds include, for instance:

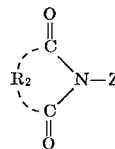
- 3-methyl-2-pyrazolin-5-one,
- 3-ethyl-2-pyrazolin-5-one, and/or
- 3-phenyl-2-pyrazolin-5-one.
- 3-phenyl-2-pyrazolin-5-one and/or 3-methyl-2-pyrazolin-5-one are preferred.

Also a range of cyclic imide activator-toner agents can be employed in the practice of the invention. These include cyclic imides having a succinimido, 4-cyclohexane-1,2-dicarboximido, glutarimido or 2,4-thiazolidinedione nucleus which satisfy the described test for suitable toning

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agents. Cyclic imides which are suitable toning agents in the practice of the invention are compounds of the formula:

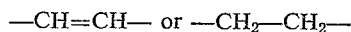
(I)



wherein R₂ represents atoms completing a succinimido, 4-cyclohexane-1,2-dicarboximido, glutarimido or 2,4-thiazolidinedione nucleus. R₂ can preferably be



wherein R''' is aryl, preferably aryl containing 6 to 12 carbon atoms, e.g. phenyl, tolyl and xylyl, and especially a group of the formula:



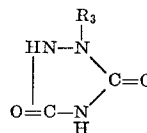
Z is hydrogen, hydroxyl or a metal ion, such as silver, mercury, potassium, sodium, lithium and gold.

Cyclic imides which are suitable activator-toner agents are, for instance:

- 25 N-hydroxysuccinimide
- succinimide
- 4-cyclohexane-1,2-dicarboximide
- glutarimide and
- 2,4-thiazolidinedione.

Urazole toning agents of the formula:

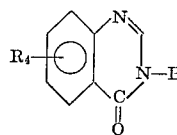
(III)



wherein R₃ is hydrogen or aryl, especially aryl containing 6 to 12 carbon atoms, e.g. phenyl, tolyl and xylyl, such as 1-phenyl urazole or 1-phenyl-2-methylurazole are surprisingly less effective as activator-toner agents than the described 2-pyrazolin-5-one activator-toner agents and succinimide and phthalimide.

A so-called quinazolinone activator-toner agent can be employed in the practice of the invention, although these agents have been found surprisingly less effective than the described 2-pyrazolin-5-one or succinimide or phthalimide. Quinazolinone activator-toner agents which can be employed are compounds of the formula:

(IV)



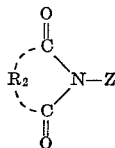
wherein R₄ is hydrogen, alkyl, especially alkyl containing 1 to 5 carbon atoms, e.g. methyl, ethyl, propyl, butyl or pentyl; aryl, especially aryl containing 6 to 12 carbon atoms, e.g. phenyl, tolyl and xylyl.

Photosensitive and thermosensitive elements which are suitable for processing with heat according to the practice of the invention 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 in which the described activator-toner agents are useful are described, for example, in U.S. Pat. 3,429,706 of Shepard et al., issued Feb. 25, 1969 and U.S. Pat. 3,152,904 of Sorensen et al., issued Oct. 13, 1964. In elements, as described, typically a support is provided with a light-stable organic silver salt oxidizing agent, an organic reducing agent, and photographic silver salt, especially silver halide, which provides a photographic and heat-sensitive element, also referred to herein as a photo-thermographic element. A visible image on the photo-sensitive and thermosensitive element can be produced

within a few seconds after exposure by heating the element to moderately elevated temperatures, e.g. about 80° C. to about 250° C.

Accordingly one embodiment of the invention is: in a photosensitive and thermosensitive element, also referred to herein as a photothermographic element, comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photographic silver halide, a binder and an activator-toner agent the improvement comprising an activator-toner agent which is:

- (a) a 2-pyrazolin-5-one,
- (b) a cyclic imide of the formula:



wherein R₂ represents atoms completing a described heterocyclic nucleus; Z is hydrogen, hydroxyl, silver, mercury, potassium, sodium, lithium or gold, or

- (c) a quinazolinone.

An especially suitable photosensitive and thermosensitive element according to the invention is one comprising a support,

- (a) an oxidation-reduction image forming combination comprising (i) silver behenate with (ii) a phenolic reducing agent,
- (b) photographic silver halide,
- (c) polyvinyl butyral, and
- (d) an activator-toner agent which comprises succinimide.

If desired the described photosensitive and thermosensitive elements can contain a so-called high dielectric, polar solvent, such as tetrahydrothiophene-1,1-dioxide. This can provide a denser black image.

A range of concentration of activator-toner agent can be employed in the described photosensitive and thermosensitive elements and compositions. The concentration of activator-toner is typically about 1 to about 3 mols of activator-toner agent per mol of photographic silver halide in the element. This can vary depending upon the particular activator-toner agent, desired image, particular components of the element, processing temperature and the like.

The described elements can comprise a silver salt as an oxidizing agent. The silver salt should be resistant to darkening under illumination to prevent undesired deterioration of a developed image. An especially suitable class of silver salts is the class of silver salts of organic acids, especially 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 phthalazine, silver benzotriazole, silver saccharin, silver-4'-n-octadecyloxydiphenyl-4-carboxylic acid, silver ortho-aminobenzoate, silver acetamidobenzoate, silver furoate, silver camphorate, silver p-phenylbenzoate, silver phenyl acetate, silver salicylate, silver butyrate, silver terephthalate, silver phthalate, silver acetate, silver acid phthalate. Oxidizing agents which are not silver salts can be employed if desired, such as zinc oxide, gold stearate, mercury behenate, gold behenate, and the like. Combinations of oxidizing agents can be employed.

Organic reducing agents are employed in the practice of the invention with the described oxidizing agents to provide a desired developed image. Such reducing agents are typically silver halide developing agents. Suitable silver halide developing agents or organic reducing agents in-

clude, 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; methylhydroxy naphthalene; 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. Pat. 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 Pat. 930,572 published July 3, 1963; hydroxytetronic acid, and hydroxytetronimide developing agents; and the like. Combinations of these reducing agents can be employed if desired.

The described element contains a photographic salt, especially a photographic silver salt. Suitable photographic silver salts include silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide or mixtures thereof. The photographic silver halide can be coarse or fine grain, very fine grain emulsions being particularly useful. The emulsion containing the photographic 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 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 or internal image silver halide emulsions such as those described in U.S. Pat. 2,592,250 of Davey et al. issued Apr. 8, 1952; U.S. Pat. 3,206,313 of Porter et al. issued Sept. 14, 1965; U.S. Pat. 3,367,778 of Berriman et al. issued Feb. 6, 1968; and U.S. Pat. 3,447,927 of Bacon et al. issued June 3, 1969. If desired, mixtures of surface and internal image silver halide emulsions can be used as described in U.S. Pat. 2,996,382 of Luckey et al. issued Apr. 15, 1961. Negative type emulsions can be used or direct positive silver halide emulsions such as those described in U.S. Pat. 2,184,013 of Leermakers issued Dec. 19, 1939; U.S. Pat. 2,541,472 of Kendall et al. issued Feb. 13, 1951; U.S. Pat. 3,367,778 of Berriman et al. issued Feb. 6, 1968; British Pat. 723,019; French Pat. 1,520,821; U.S. Pat. 2,563,785 of Ives issued Aug. 7, 1951; U.S. Pat. 2,456,953 of Knott et al. issued Dec. 21, 1968; and U.S. Pat. 2,861,885 of Land issued Nov. 25, 1958. The silver halide emulsion can be a regular grain emulsion such as described in Klein and Moisar, *Journal of Photographic Science*, vol. 12, No. 5, September-October (1964), pp. 242-251.

The silver halide emulsion 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; silver, 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.

Photographic silver halide 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 Alen 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 Triveli 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 composition described and used in the practice of the invention can contain various colloids alone or in combination as vehicles or 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 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, 1965; 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, e.g., those ethylene oxide polymers having an average molecular weight of about 1,000 to about 3,000,000 or more.

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(vinylacetate) 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, carbodimides, 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 Trevooy issued Feb. 18, 1969. The photographic 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 Baldisieffen 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. Pat. 2,992,101 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 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 dispersions of brighteners can be used 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 and filter 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 Russel issued Sept. 4, 1956 and British Pat. 837,095.

If desired, the photographic 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 photographic 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.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the elements 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 Pat. 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 are described, for example, in U.S. Pat. 2,526,632 of Brooker et al. issued Oct. 24, 1950; U.S. Pat. 2,503,776 of Sprague issued Apr. 11, 1950; U.S. Pat. 2,493,748 of Brooker et al. issued Jan. 10, 1950; and U.S. Pat. 3,394,486 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 or the methine or polymethine chain.

The merocyanine dyes can contain the basic nuclei described as well as acid nuclei such as thiohydantoin, 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 can be included such as, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in U.S. Pat. 2,933,390 of McFall et al. issued Apr. 19, 1960 and U.S. Pat. 2,937,089 of Jones et al. issued May 17, 1960.

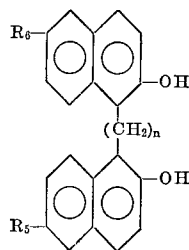
The sensitizing dyes and other addenda used in the practice of the invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including, for example, those described in U.S. Pat. 2,912,343 of Collins et al. issued Nov. 10, 1959; U.S. Pat. 3,432,605 of McCrossen et al. issued Sept. 19, 1967; U.S. Pat. 2,996,287 of Audran issued Aug. 15, 1961; and U.S. Pat. 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 condition and the like. Typically a concentration of the described sensitizing dye is about 0.05 to about 1 milli-

gram per square foot of the described photographic and thermosensitive element, usually about 0.1 milligram per square foot of dye being employed.

Other so-called activator-toner agents can be employed in the described photosensitive and thermosensitive elements according to the invention in combination with the other described components. Various activator-toner agents 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. Pat. 3,080,254 of Grant issued Mar. 5, 1963. Suitable toners include, for example, phthalazine, phthalic anhydride, 2-acetyl phthalazinone, and 2-phthalyl phthalazinone. Other suitable toners are described, for example in U.S. Pat. 3,446,648 of Workman issued May 27, 1969.

A reducing agent which is a bis-naphthol is especially suitable in a photosensitive and thermosensitive element, composition and/or process of the invention. These include bis-naphthol reducing agents of the formula:



wherein R_5 and R_6 are each hydrogen, alkoxy, e.g., alkoxy containing 1 to 3 carbon atoms, including methoxy, ethoxy, or propoxy, alkyl containing 1 to 3 carbon atoms, e.g. methyl, ethyl, or propyl, nitro, amino or azonium, i.e. $-M+=N$, groups, n is 0 or 1. Suitable bis-naphthol reducing agents include, for instance:

6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthol
6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthol
bis-2-hydroxynaphthyl-1-methane
2,2'-dihydroxy-1,1'-binaphthol.

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

- (a) an oxidation-reduction image forming combination comprising (i) a silver salt oxidizing agent with (ii) a reducing agent,
- (b) photographic silver halide,
- (c) a binder, and
- (d) an activator-toner agent comprising
 - (i) a 2-pyrazolin-5-one,
 - (ii) a cyclic imide of Formula I, as described, and/or
 - (iii) a quinazolinone, as described.

In the described photosensitive and thermosensitive elements and compositions, the photographic silver halide is believed to catalyze the image forming reaction which takes place upon heating the silver salt oxidizing agent with the reducing agent, as described. The concentration of photographic silver halide which is suitable in the practice of the invention can vary depending upon the desired image, the particular silver salt oxidizing agent and reducing agents employed, the time and intensity of exposure of the element, the particular components of the element, and the like. Typically, a concentration of about 0.01 to about 10 mol percent of photographic silver halide relative to the described silver salt oxidizing agent is suitable.

The concentration of reducing agent which is suitable can also vary depending upon the particular silver salt

oxidizing agent, the particular reducing agent, other components of the element, desired image, and the like. Usually about a stoichiometric concentration of reducing agent is suitable with regard to the silver salt oxidizing agent. The reducing agent and oxidizing agent are typically employed in about a 1:1 molar ratio. The concentration of reducing agent and oxidizing agent are typically each about 5 to about 100 milligrams per square foot of support of the described element.

An especially suitable photosensitive and thermosensitive composition comprises

- (a) an oxidation-reduction image forming combination comprising (i) silver behenate with (ii) a phenolic reducing agent,
- (b) photographic silver halide,
- (c) polyvinyl butyral, and
- (d) succinimide and/or 3-phenyl-2-pyrazolin-5-one and/or 3-methyl-2-pyrazolin-5-one.

The described composition can be prepared by mixing the described components with a suitable mixing means. The photographic silver halide is preferably prepared *in situ* in the described composition by mixing a source of halide ions with the described silver salt oxidizing agent. This method is described in U.S. Pat. 3,457,075 of Morgan et al. issued July 22, 1969.

A latent image in the described photosensitive and thermosensitive element after exposure to actinic radiation can be developed merely by heating the element. Accordingly another embodiment of the invention is a process of developing a latent image in an exposed photosensitive and thermosensitive element, as described, by heating the element to about 70° C. to about 250° C. until a desired image is developed.

A temperature range of about 70° C. to about 250° C. is suitable, typically about 80° C. to about 150° C. By increasing or decreasing the time of heating, a higher or lower temperature within the described range can be employed. A developed and stable image usually results within about 1 second to about 60 seconds, e.g. about 1 second to about 30 seconds.

Processing is usually carried out under ambient conditions of pressure and humidity. Pressures 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 catalyst, i.e. photographic silver halide, can be in one layer and other components in other layers of the element. For example, an element according to the invention can comprise a support, a layer containing photographic silver halide and a layer contiguous to the silver halide containing the described oxidation-reduction image forming composition and a described toning agent.

Various means can be employed in providing the necessary heating. The described element can be brought into contact with a simple hot plate, iron or the like.

Other addenda useful in photosensitive and thermosensitive elements can be employed in elements, compositions and processes according to the practice of the invention. Such elements and addenda are described, for example, 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.

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

EXAMPLE 1

This illustrates the invention.

A Dispersion A is prepared as described. The components of Dispersion A are mixed in a ball mill for 16 hours. The following composition is prepared by mixing the following components:

	MI.
Dispersion A -----	3.76
Acetone containing 5% by weight/volume 2,2'-methyl-6-tertiarybutylphenol) -----	3.76
Acetone containing 0.01% by weight/volume benzoxazolyldine thiohydantoin sensitizing dye -----	0.70
Acetone containing 0.01% by weight volume tetrahydrothiophene-1,1-dioxide -----	1.20
Methanol containing 2.0% by weight/volume 3-phenyl-2-pyrazolin-5-one -----	1.88
Acetone-toluene mixture (1:1 parts by volume) ---	2.38

The resulting composition is coated on a polyethylene coated paper support at about 20° C. at a wet coating thickness of 0.002 inches. The resulting coating is permitted to dry under atmospheric conditions to provide a photosensitive and thermosensitive element.

This element is then sensitometrically exposed to tungsten light for 5 seconds. It is then contacted with a metal plate at a temperature of 100° C. for 30 seconds. A developed, neutral tone (black) image is developed.

Employing the described rating scale of tone and density which corresponds to 0 for very poor or no image to 10 for excellent for a developed image, the developed image receives a rating of 8.

A control element is prepared, exposed and processed in the same manner with the exception that 3-phenyl-2-pyrazolin-5-one is omitted. The resulting control element receives a rating of 0 since no image is developed.

EXAMPLE 2

The procedure set out in Example 1 is repeated with the exception that 3-methyl-2-pyrazolin-5-one is employed in place of 3-phenyl-2-pyrazolin-5-one. The resulting element upon processing receives a rating of 8.

EXAMPLE 3

The procedure set out in Example 1 is repeated with the exception that succinimide is employed in place of 3-phenyl-2-pyrazolin-5-one. The resulting element upon processing receives a rating of 7.

EXAMPLE 4

The procedure set out in Example 1 is repeated with the exception that phthalimide is employed in place of 3-phenyl-2-pyrazolin-5-one. The resulting element upon processing receives a rating of 7.

EXAMPLE 5

The procedure set out in Example 1 is repeated with the exception that 2,4-thiazolidinedione is employed in place of 3-phenyl-2-pyrazolin-5-one. The resulting element upon processing receives a rating of 7.

EXAMPLE 6

The procedure set out in Example 1 is repeated with the exception that quinazoline is employed in place of 3-phenyl-2-pyrazolin-5-one. The resulting element upon processing receives a rating of 4.

EXAMPLE 7

The procedure set out in Example 1 is repeated with the exception that 1-phenylurazole is employed in place of 3-phenyl-2-pyrazolin-5-one. The resulting element upon processing receives a rating of 3.

EXAMPLE 8

The procedure set out in Example 1 is repeated with the exception that 1-phenyl-2-methylurazole is employed in place of 3-phenyl-2-pyrazolin-5-one. The resulting element upon processing receives a rating of 3.

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EXAMPLE 9

A dispersion is prepared by mixing the following components:

Silver behenate	g--	23.3
Behenic acid	g--	26.0
Polyvinyl butyral	g--	1.25
Sodium bromide	g--	1.31
Acetone-toluene (1:1 parts by volume)	ml--	500.0

This mixture is ball-milled for 18 hours and the resulting dispersion is designated as Dispersion B.

A composition is prepared by thoroughly mixing the following components:

Dispersion B, as described	ml.	2.0
4,4'-isopropylidene diphenol (5% by weight in acetone)		2.0
Phthalimide (1% by weight in acetone)		2.0
Sensitizing dye I ¹ (0.01% by weight in acetone)		0.5

¹ 3-ethyl-5-(3-ethyl-2(3H)-benzothiazylidene-isopropylidene)-2-thio-2,4(3,5)-oxazolidione.

The resulting composition is coated on a resin treated paper support at a wet thickness of 0.004 inches. The resulting coating is permitted to dry under atmospheric conditions to provide a photosensitive and thermosensitive element. This is then sensitometrically exposed with a step wedge to tungsten light for 0.5 second (in a contact printer and then contacted with a hot metal block for about 10 seconds at about 135° C. A visible line image results having 8 visible, developed steps. The image has a gray-black tone.

EXAMPLE 10

A composition is prepared by thoroughly mixing the following components:

Dispersion B, as described in Example 9	ml.	225
2,2'-methylene-bis(4-ethyl-6- <i>t</i> -butyl-phenol) (5% by weight in acetone)		58
Succinimide (1% by weight in acetone)		45
Sensitizing dye I, as described in Example 9 (0.01% by weight in acetone)		3.8
Acetone-toluene (1:1 parts by volume)		68

The resulting composition is coated on a resin treated paper support at a wet thickness of 0.004 inches. The resulting coating is permitted to dry under atmospheric conditions to provide a photosensitive and thermosensitive element. This is then sensitometrically exposed with a step wedge to tungsten light for 0.5 second (in a contact printer) and then contacted with a hot metal block for about 10 seconds at about 135° C. A visible line image is developed having 10 visible steps. The image tone is a brown-gray on a tan background.

EXAMPLE 11

A composition is prepared by thoroughly mixing the following components:

Dispersion B, as described in Example 9	ml.	225
2,2'-methylene-bis-(4-methyl-6- <i>t</i> -butyl-phenol) (5% by weight in acetone)		58
Succinimide (1% by weight in acetone)		45
Sensitizing dye I as described in Example 9 (0.01% by weight in acetone)		3.8
Acetone-toluene (1:1 parts by volume)		68

The resulting composition is coated on a resin treated paper support at a wet thickness of 0.004 inches. The resulting coating is permitted to dry under atmospheric conditions to provide a photosensitive and thermosensitive element. This is sensitometrically exposed with a step wedge to tungsten light for 0.5 second (in a contact printer) and then contacted with a hot metal block for about 10 seconds at about 135° C. A visible line image is developed

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having 10 visible steps. The image tone is dark brown on a tan background.

EXAMPLE 12

A composition is prepared by thoroughly mixing the following components:

Dispersion B, as described in Example 9	ml.	2.0
2,2'-thiobis-(4-methyl-6- <i>t</i> -butyl-phenol) (5% by weight in acetone)		2.0
Phthalimide (1% by weight in acetone)		2.0
Sensitizing dye II ¹ (0.01% by weight in methanol)		0.5

¹ 3-carboxymethyl-5-[(3-methyl-2(3)-thiabolinylidene)-isopropylidene]rhodanine.

The resulting composition is coated on a resin treated paper support at a wet thickness of 0.004 inches. The resulting coating is permitted to dry under atmospheric conditions to provide a photosensitive and thermosensitive element. This is then sensitometrically exposed with a step wedge to tungsten light for 0.5 second (in a contact printer) and then contacted with a hot metal block for about 10 seconds at about 135° C. A visible line image results having 9 visible steps. The image has a green-brown tone on a gray-green background.

EXAMPLE 13

A composition is prepared by thoroughly mixing the following components:

Dispersion B, as described in Example 9	ml.	2.0
4,4'-dihydroxy-3,3'-dimethyl biphenyl (5% by weight in acetone)		2.0
Succinimide (1% by weight in acetone)		2.0
Sensitizing dye I, as described in Example 9 (0.01% by weight in acetone)		0.5

The resulting composition is coated on a resin coated paper support at a wet thickness of 0.004 inches. The resulting coating is permitted to dry under atmospheric conditions to provide a photosensitive and thermosensitive element. This is then sensitometrically exposed with a step wedge to tungsten light for 0.5 seconds (in a contact printer) and then contacted with a hot metal block for about 10 seconds at about 135° C. A visible line image results.

EXAMPLE 14

The procedure set out in Example 13 is repeated with the exception that 4,4'-dihydroxybiphenyl is employed in place of 4,4'-dihydroxy-3,3'-dimethylbiphenyl. Similar results are obtained.

EXAMPLE 15

The procedure set out in Example 1 is repeated with the exception that tetrahydrothiophene-1,1-dioxide is omitted from the described composition. Exposure and processing is carried out as described in Example 1 resulting in a neutral tone (black) image having slightly lower density than that which is obtained in Example 1.

EXAMPLE 16

This illustrates the invention. A thermographic element is prepared without the use of photographic silver halide.

A dispersion is prepared by ball milling the following components together at about 20° C. and atmospheric pressure for 16 hours:

Polyvinyl butyral	g--	1.25
Behenic acid	g--	3.50
Silver behenate	g--	3.90
Acetone-toluene mixture (1:1 parts by volume)	m--	50.0

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The following composition is then prepared employing this dispersion by mixing the following components:

	ML.
Dispersion -----	4.0
2,2'-methylene-bis(4-methyl-6- <i>t</i> -butyl phenyl) (5% by weight in acetone) -----	3.8
3-phenyl-2-pyrazolin-5-one (2% by weight in methanol) -----	1.9

The resulting composition is coated on a polyethylene coated paper support at a coating thickness of about 0.002 inches. The resulting coating is dried by permitting the resulting element to stand at about 40° C. and atmospheric pressure until the coating is substantially solid. The element is then heated by placing the element with the side opposite the described coating on a heated metal plate at 160° C. for 20 seconds. The resulting density has a warm black tone and a maximum density of 1.38.

EXAMPLE 17

This is a comparative example.

The procedure set out in Example 16 is repeated with the exception that 1.9 ml. of acetone is employed in place of 1.9 ml. of a methanol containing 2% by weight of 3-phenyl-2-pyrazolin-5-one.

A warm black tone results which has a density of 0.79.

EXAMPLE 18

The procedure set out in Example 16 is repeated with the exception that the element described is heated for 15 seconds at 140° C.

A warm, black tone having a density of 1.05 is produced.

EXAMPLE 19

This is a comparative example.

The procedure set out in Example 17 is repeated with the exception that the element is heated for 15 seconds at 140° C.

The resulting developed warm, black tone has a density of 0.23.

EXAMPLE 20

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that N-methyl phthalazinone is employed in place of 3-phenyl-2-pyrazolin-5-one.

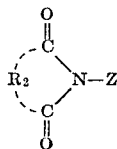
Exposure and processing as described in Example 1 produces no visible image.

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. In a photothermographic element comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photosensitive silver salt, a binder and an activator-toner agent, the improvement wherein said activator-toner agent is

- (a) a 2-pyrazolin-5-one,
- (b) a cyclic imide of the formula



wherein R₂ represents atoms completing a succinimido, 4-cyclohexane - 1,2 - dicarboximido, glutarimido or 2,4-thiazolidinedione nucleus; Z is hydrogen, hydroxy, silver mercury, potassium, sodium, lithium or gold, or

- (c) a quinazolinone,

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2. A photothermographic element as in claim 1 wherein said photosensitive silver salt is photographic silver halide.

3. A photothermographic element as in claim 1 wherein said photosensitive silver salt is photographic silver halide and said element comprises about 1 to about 3 moles of said activator-toner agent per mole of said photographic silver halide.

4. A photothermographic element comprising a support, (a) an oxidation-reduction image forming combination comprising (i) silver behenate with (ii) a phenolic reducing agent,

(b) photographic silver halide,

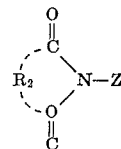
(c) polyvinyl butyral, and

(d) an activator-toner which comprises succinimide.

5. A photothermographic composition comprising (a) an oxidation-reduction image forming combination comprising (i) a silver salt oxidizing agent with (ii) a reducing agent, (b) photographic silver halide, (c) a binder, and (d) an activator-tone agent comprising

(i) a 2-pyrazolin-5-one,

(ii) a cyclic imide of the formula



wherein R₂ represents atoms completing a succinimido, 4-cyclohexane-1,2-dicarboximido, glutarimido or 2,4-thiazolidinedione nucleus; Z is hydrogen, hydroxyl, silver, mercury, potassium, sodium, lithium or gold, or

(iii) a quinazolinone.

6. A photothermographic composition comprising

(a) an oxidation-reduction image forming combination comprising

(i) silver behenate with (ii) a phenolic reducing agent,

(b) photographic silver halide,

(c) polyvinyl butyral, and

(d) succinimide.

7. A photothermographic composition comprising

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

(b) photographic silver halide,

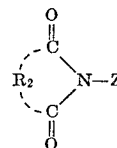
(c) polyvinyl butyral, and

(d) 3-phenyl - 2 - pyrazolin-5-one or 3-methyl-2-pyrazolin-5-one.

8. A process of developing a latent image in an exposed photothermographic element comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photosensitive silver salt, a binder, and an activator-toner agent comprising

(a) a 2-pyrazolin-5-one,

(b) a cyclic imide of the formula



wherein R₂ represents atoms completing a succinimido, 4-cyclohexane - 1,2 - dicarboximido, glutarimido or 2,4-thiazolidinedione nucleus; Z is hydrogen, hydroxy, silver, mercury, potassium, sodium, lithium or gold, or

(c) a quinazolinone,

comprising heating said element to a temperature within the range of about 70° C. to about 250° C.

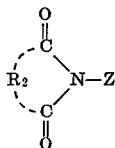
9. A process as in claim 8 wherein said photosensitive silver salt is photographic silver halide.

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10. A process of developing a latent image in an exposed photothermographic element as in claim 9 comprising heating said element to a temperature within the range of about 70° C. to about 250° C. for about 1 to about 30 seconds.

11. In a thermographic element comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, a binder and an activator-toner agent, the improvement comprising an activator-toner agent which is

- (a) a 2-pyrazolin-5-one,
(b) a cyclic imide of the formula



wherein R₂ represents atoms completing a succinimido, 4-cyclohexane - 1,2 - dicarboximido, glutarimido or 2,4-thiazolidinedione nucleus; Z is hydrogen, hydroxy, silver, mercury, potassium, sodium, lithium or gold, or

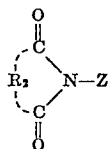
(c) quinazolinone.

12. A thermographic element comprising a support, an oxidation-reduction image forming combination comprising silver behenate with a phenolic reducing agent, a binder and an activator-toner agent which is 3-phenyl-2-pyrazolin-5-one or 3-methyl-2-pyrazolin-5-one.

13. A thermographic element comprising a support, an oxidation-reduction image forming combination comprising silver behenate with a phenolic reducing agent, a binder and an activator-toner agent which is succinimide.

14. A thermographic composition comprising an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a phenolic reducing agent, a binder and an activator-toner agent, the improvement wherein said activator-toner agent is

- (a) a 2-pyrazolin-5-one,
(b) a cyclic imide of the formula



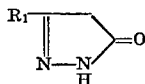
wherein R₂ represents atoms completing a succinimido, 4-cyclohexane - 1,2 - dicarboximido, glutarimido or 2,4-thiazolidinedione nucleus; Z is hydrogen, hydroxy, silver, mercury, potassium, sodium, lithium or gold, or

(c) a quinazolinone.

15. A thermographic composition comprising an oxidation-reduction image forming combination comprising silver behenate with a phenolic reducing agent, a binder and an activator-toner agent which is 3-phenyl-2-pyrazolin-5-one or 3-methyl-2-pyrazolin-5-one.

16. A thermographic composition comprising an oxidation-reduction image forming combination comprising silver behenate with a phenolic reducing agent, a binder and an activator-toner agent which is succinimide.

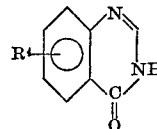
17. In a photothermographic element comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photosensitive silver salt, a binder and an activator-toner agent, the improvement wherein said activator-toner agent is a 2-pyrazolin-5-one of the formula:



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wherein R₁ is hydrogen, alkyl containing 1 to 4 carbon atoms or aryl containing 6 to 12 carbon atoms.

18. In a photothermographic element comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photosensitive silver salt, a binder and an activator-toner agent, the improvement wherein said activator-toner agent is a quinazolinone of the formula:

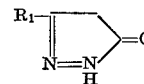


wherein R₄ is hydrogen, alkyl containing 1 to 5 carbon atoms, or aryl containing 6 to 12 carbon atoms.

19. In a photothermographic element comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photosensitive silver salt, a binder and an activator-toner agent, the improvement wherein said activator-toner agent is succinimide.

20. In a photothermographic element comprising a support, an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photosensitive silver salt, a binder and an activator-toner agent, the improvement wherein said activator-toner agent is 3-phenyl-2-pyrazolin-5-one or 3-methyl-2-pyrazolin-5-one.

21. A photothermographic composition comprising an oxidation-reduction image forming combination comprising a silver salt oxidizing agent with a reducing agent, photosensitive silver salt, a binder, and an activator-toner agent which comprises a 2-pyrazolin-5-one of the formula:



wherein R₁ is hydrogen, alkyl containing 1 to 4 carbon atoms or aryl containing 6 to 12 carbon atoms.

22. A process of developing a latent image in an exposed photothermographic element comprising a support, an oxidation-reduction image forming combination comprising (i) silver behenate with (ii) a phenolic reducing agent, (b) photographic silver halide, (c) polyvinyl butyral, and an activator-toner agent which comprises succinimide, comprising heating said element to a temperature within the range of about 70° C. to about 250° C. for about 1 to about 30 seconds.

References Cited

UNITED STATES PATENTS

3,042,517	7/1962	Wainer	250—65.1
3,094,417	6/1963	Workman	96—28
3,149,990	9/1964	Coles	117—36.8
3,322,557	5/1967	Schwab	117—36.8
3,438,776	4/1969	Yudelson	96—95
3,457,075	7/1969	Morgan	96—114.1
3,531,286	9/1970	Renfrew	96—67

FOREIGN PATENTS

1,131,108	10/1968	Great Britain.
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MARY F. KELLEY, Primary Examiner

U.S. Cl. X.R.

96—66 T, 67; 117—36.7, 36.8

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,846,136

DATED : November 5, 1974

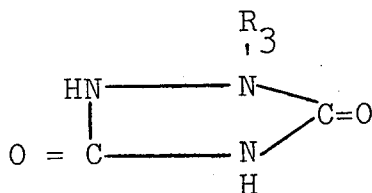
INVENTOR(S) : Michael F. Sullivan

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 24, "demonstarted" should read ---demonstrated---
 . Line 55,
 "dicorboximido" should read ---dicarboximido---. Lines 62-63,
 "thermograhic" should read ---thermographic---.

Column 4, lines 32-36, the formula should read as follows:

(III)



Column 5, line 61, that part of the formula reading
 " octadecycloxydiphenyl " should read ---octadecyloxydiphenyl---.

Column 6, line 3, "exemplifide" should read ---exemplified---.

Column 7, line 4, "Alen" should read ---Allen---. Line 10,
 "Triveli" should read ---Trivelli---. Line 23, "viny" should
 read ---vinyl---. Line 47, "molecuar" should read
 ---molecular---.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,846,136

DATED : November 5, 1974

INVENTOR(S) : Michael F. Sullivan

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

Column 8, line 45, after "used" insert ---such---. Line 65, "Russel" should read ---Russell---.

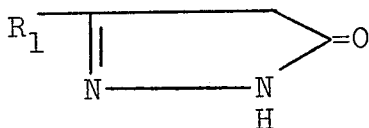
Column 9, line 46, the first occurrence of "or" should be changed to ---on---. Lines 65-66, " 3,432,605 " should read --- 3,342,605 ---.

Column 10, line 41, the formula " -M+=N " should read
 --- -N+=N ---.

Column 15, line 73, a "," should be inserted after ---silver---.

Column 17, line 25, " (c) quinazolinone " should read
 --- (c) a quinazolinone ---. Lines 55-56, "oxidathion-
 reduction" should read ---oxidation-reduction---.

Column 18, lines 37-41, the formula should read as follows:



Signed and Sealed this

ninth Day of December 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks