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(54) SENSITIVE PHOTOTHERMOGRAPHIC MATERIALS AND NOVEL HETEROCYCLIC SILVER SALTS FOR USE THEREIN

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a sensitive photothermographic material.

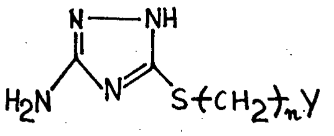
A visible image may be produced with a sensitive photothermographic, or heat-developable, material by imagewise exposure to actinic radiation, normally light, followed by overall heating. The imagewise exposure produces a latent image of centres which catalyze an image-forming reaction, and a temperature is chosen for the overall heating at which that reaction occurs at a negligible rate in the absence of latent image centres but at an appreciable rate in their presence.

The most commonly used silver salts in such heat developable photographic materials are silver salts of long-chain fatty acids, such as silver behenate which generally require hydrophobic binders. It has been desirable to replace these silver salts of long-chain fatty acids to enable use of aqueous or hydrophilic compositions which further enable the use of conventional silver halide emulsion technology in heat developable photographic materials. Use of silver behenate as a source of silver in such heat developable materials is not particularly compatible with aqueous formulations of photosensitive silver halide materials. Other silver complexes or salts have been proposed for use, in heat developable materials including the silver salts of nitrogen acids described in "Research Disclosure", Vol. 150, 15026, October 1976.

A problem encountered with many heat developable photographic materials is instability of the image caused by darkening of the background areas, often termed 'print-up', which occurs on prolonged exposure to light following processing. An image stabilizer, or stabilizer precursor, is sometimes incorporated in the material to improve the post-processing stability. Suitable stabilizer precursors are described in, for example, U.K. Patent Specification 1,346,252 and U.S. Patent 3,839,041.

There has been a continuing need for improved photothermographic materials which enable improved post-processing image stability in the absence of a separate image stabilizer precursor. It has also been desirable to provide a heat developable photographic material as described in which silver development efficiency is improved, such as above about 50%.

According to the present invention there is provided a sensitive photothermographic material which comprises a support and incorporated in a layer or layers coated on one side thereof (a) a photosensitive silver halide, (b) an image-forming combination comprising (i) a silver salt of a triazole derivative of the formula:



wherein Y is an aryl group of 6 to 12 carbon atoms which may contain an alkyl, alkoxy or halogen substituent, and n is 0, 1 or 2 and (ii) a silver halide developing agent or a precursor thereof and (c) a polymeric binder.

Preferred photothermographic materials of the invention are those wherein Y of Formula I is phenyl, *p*-chlorophenyl or *p*-methoxy phenyl.

The silver salts of the compounds of Formula I are believed to be novel compounds and are claimed *per se* in accordance with the invention. An especially useful silver salt of the invention is one wherein the molar ratio of ligand to silver ion has a value within the range of 0.5 to 3.0. The new silver salts can be prepared by reacting a source of silver ions, such as silver nitrate or silver trifluoroacetate, with the appropriate 1,2,4-triazole derivative. The term 'salt' is used herein to cover both neutral and non-neutral complexes. The exact form of bonding in the salts is not known.

An especially preferred silver salt for a photothermographic material of the invention is the silver salt of 3-amino-5-benzylthio-1H-1,2,4-triazole. A mixture of silver sallts of the invention may be used if desired.

The 1,2,4-triazole derivatives from which the silver salts of the invention may be prepared can be made by procedures known in the art. For example, 3-amino-5-benzylthio-1H-1,2,4-triazole may be made as described in the *Journal of the Chemical Society,* 3437 (1960) by L. Godfrey and F. Kurzer. The following is an example of a preparation according to this method. Benzylchloride (139 grams, 1.1 mole) is added dropwise to a mixture of 5-mercapto-3-amino-1H-1,2,4-triazole (116 grams, 1 mole) with 1600 millilitres of ethanol, sodium hydroxide (44 grams, 1.1 mole) and 900 millilitres of water. The reaction mixture is heated at reflux for 6 hours. At the end of this time the ethanol is removed by distillation under reduced pressure; 1000 millilitres of water is added, and the solution is cooled to 5°C. The resulting oil is separated and the desired product crystallized upon cooling. A solid results which is collected and dried in a desiccator. The resulting product can be purified using methods known in the art such as by recrystallization from a suitable solvent such as a benzene methanol mixture. The resulting 3-amino-5-benzylthio-1,2,4-triazole has a melting point of 108—109°C.

A silver salt of the invention may be prepared by mixing a source of silver ions, such as silver trifluoroacetate or silver nitrate, with the appropriate 1,2,4-triazole compound and allowing time for the reaction to come to completion. Heat may be required to cause the ligand to dissolve unless dilute solutions are used. The product can be separated by filtration and washing or other known separation techniques. The preparation of the silver salt of 3-amino-5-benzylthio-1H-1,2,4-triazole is illustrative of the preparation of silver salts according to the invention. In this preparation the silver salt was prepared in the form of a dispersion in an aqueous gelatin solution. 6.18 grams (0.03 mole) of 3-amino-5-benzylthio-1,2,4-triazole and 4.0 grams of deionized, photographic gelatin were dissolved with heat at 50°C in 30 millilitres of a mixture of ethanol and methanol (95:5 parts by volume ethanol:methanol) and 140 millilitres of distilled water. The resulting solution was placed in a suitable reaction vessel equipped with a rapid mixing means and then a solution of 3.4 grams (0.02 moles) of silver nitrate in 30 millilitres of distilled water was added rapidly at 50°C while the solution was rapidly mixed. The reactants were mixed rapidly for 40 minutes followed by cooling to about 19°C. The resulting desired dispersion was diluted to 200 grams (10 kilograms per silver mole) with distilled water. The end dispersion had a pH of 2.8 and a pAg of 4.6.

It is possible to prepare a silver salt of the invention in a liquid medium containing a vehicle other than gelatin, for example poly(vinyl alcohol), or in a medium containing no vehicle. The liquid of the medium may contain organic solvents or aqueous solutions. The silver salt can be separated pure and stored prior to use. However, for photographic purposes it is usually convenient to prepare the silver salt as a dispersion.

The reactants in the described preparation can be mixed in stoichiometric concentrations. However, it is often desirable to use an excess of one reactant to obtain the desired degree of reaction. For example, the reactants may be mixed to provide a molar ratio of ligand to silver ion of about 1.5:1. The reaction can be carried out at a temperature within the range of 40°C to 80°C, and preferably within the range of 50°C to 60°C.

It is not recommended, when preparing a silver salt of the invention for use in a photothermographic material of the invention, to prepare the salt in the presence of other components of the material because doing so makes the preparation less easy to control.

A typical concentration of the photosensitive silver halide in a photothermographic material according to the invention is within the range 0.05 to 1.0 (and especially 0.1 to 0.5) mole per mole of the silver salt of the 1,2,4-triazole derivative. Other photosensitive materials can be useful in combination with the described photosensitive silver halide if desired, for example, the silver dye complexes described in U.S. Patent 3,647,439. Preferred Photosensitive silver halides are silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. Silver iodide may be used, but is more difficult to stabilize after processing at desired levels than silver bromide. Very fine-grain photosensitive silver halide is preferred. The photosensitive silver halide can be prepared by any of the procedures known in the photographic art, especially those procedures which involve the preparation of photographic silver halide gelation emulsions. Useful procedures and forms of photosensitive silver halide for purposes of the invention are described, for example, in the *Product Licensing Index,* Volume 92, December 1971, Publication No. 9232 on page 107. Cubic grain silver bromoiodide, such as silver bromoiodide containing 2.5 mole per cent iodide can be particularly useful. The photographic silver halide as described can be washed or unwashed, can be chemically sensitized, and can be protected against the production of fog and stabilized against loss of sensitivity during keeping as described in the above *Product Licensing Index* publication.

The described photothermographic materials can contain a variety of silver halide developing agents, especially organic silver halide developing agents.

Selection of a suitable reducing agent will be influenced by the grain size and other properties of the particular silver halide grains. For instance, hydroquinone reducing agents are preferred with fine (but not coarse) grain silver halides.

Combinations of organic silver halide developing agents can be especially useful. For example, a combination of a 3-pyrazolidone developing agent with an ascorbic acid developing agent can be useful. Especially useful developing agents are those which are hydroquinone, ascorbic acid, pyrogallol, gallic acid ester and phenylenediamine silver halide developing agents and combinations of these developing agents.

Instead of a free silver halide developing agent a developing agent precursor may be used with releases the developing agent upon a change of conditions occurring in the photothermographic material when it is heated.

A useful concentration of the developing agent in the photothermographic material is from 0.1 to 3 (preferably 0.5 to 1.5) moles per mole of the silver salt of the 1,2,4-triazole derivative.

A photothermographic material of the invention can contain a variety of colloids and polymers alone or in combination as vehicles, binding agents in the layer or layers present. Hydrophilic materials especially gelatin, are preferred although some hydrophobic materials can be useful.

A polymer or colloid overcoat layer or layers may be provided on the photothermographic material increase its resistance to abrasion marks.

A base-release agent (base precursor) may be incorporated in the photothermographic material to provide improved and more effective image development. Examples of useful base-release agents are guanidinium compounds, such as guanidinium trichloroacetate.

A useful concentration range of base-release agent is from 0.5 to 1.5 moles per mole of silver in the photothermographic material.

The photothermographic materials according to the invention can contain an image toner to provide a more neutral or black tone image upon processing. A simple screening test can be used to select an image toning agent suitable for use with the chosen mercaptotriazole derivative. Such testing may be carried out using the procedure described in the following Example 5. The effectiveness of a toning agent may be assessed from ratio of (a) visible maximum density to (b) blue light maximum density. When this ratio exceeds a value of about 0.9, the developed image appears neutral (black). Some toning agents are also found to have other desired effects in the photothermographic material, such as providing development acceleration. Useful toning agents include, for example, 6-methyl-2-thiouracil and 1-phenyl-2-tetraazoline-5-thione. Mixtures of toning agents can be used if desired.

A typically useful concentration of toning agent is from 0.005 to 0.05 mole per mole of silver in the photothermographic material.

A photothermographic material of the invention does not require the presence of a 'melt-forming compound' in order to provide an improved developed image. Such a compound provides at the chosen processing temperature a medium in which the image-forming combination can more readily react and so form a better image.

Spectral sensitizing dyes can be used in photothermographic materials of the invention to confer additional sensitivity on them. Useful sensitizing dyes are described, for example, in the *Product Licensing Index*, Volume 92, December 1971, Publication No. 9232, pages 107—110, paragraph XV.

The preferred dyes are cyanines and merocyanines and their mixtures. Especially useful dyes include:

thiacarbocyanine dyes,
merocyanine dyes containing a rhodanine moiety,
solubilized oxacarbocyanine dyes,
oxacarbocyanine dyes, and
merocyanine dyes containing a 2-thio-2,4-oxazolidinedione moiety.

Typically, the spectral sensitizing dye concentration is within the range of 0.5 to 2.0 grams of dye per mole of silver halide.

The optimum concentration of the various components of a photothermographic material according to the invention depends upon a variety of factors. A preferred material comprises, for each mole of photosensitive silver halide, 2.0 to 8.0 moles of the silver salt of the 1,2,4-mercaptotriazole derivative, and 5.0 to 10.0 moles of silver halide developing agent and/or precursor.

As noted above the silver salt of the 1,2,4-mercaptotriazole derivative can contain a range of ratios of the 1,2,4-mercaptotriazole (ligand) moiety to the silver ion. The molar ratio of the 1,2,4-mercaptotriazole to silver as silver ion in the salt is usefully within the range of 0.5 to 3.0, and is preferably 1.5:1.

The photothermographic materials of the invention also can contain a range of silver ion concentrations (pAg). The pAg can conveniently be measured using conventional calomel and silver-silver chloride electrodes, connected to a commercial digital pH meter. The typical pAg in a dispersion containing the described components according to the invention is within the range 2.5 to 7.5, with a preferred range being 4.0 to 5.0.

A dispersion containing the described components according to the invention typically has a pH in the range 1.5 to 5.0. An especially useful pH for the dispersion is the range of 2.0 to 4.0 with the preferred range being 2.5 to 3.5.

A post-processing image stabilizer or stabilizer precursor is not essential in all photothermographic materials of the invention. If such a compound is employed suitable compounds include sulphur compounds which upon heating of the photothermographic material during processing form a stable silver mercaptide. Less preferred are photolytically activated polyhalogenated compounds.

The photothermographic materials according to the invention can contain other addenda such as development modifiers that function as speed-increasing compounds, hardeners, plasticizers and lubricants, coating aids, brighteners, absorbing and filter dyes, and antistatic materials or layers. These are described, for example, in the *Product Licensing Index*, Volume 92, December 1971, Publication 9232, pages 107—110.

A photothermographic material of the invention can comprise any support which can withstand the processing temperature to be employed. Typical supports include cellulose ester film, poly(vinyl acetal) film, poly(ethylene terephthalate) film, polycarbonate film and polyester film supports.

The photothermographic materials according to the invention can be coated on the chosen supports by single or multilayer coating procedures known in the photographic art.

The components of a photothermographic material according to the invention can be in any location which allows image formation to occur on heating. Thus one or more of the components can be in one or more layers. It can be desirable to include certain percentages of the silver halide developing agent, silver salt of the 1,2,4-triazole derivative and/or other addenda in a protective layer over the photothermographic layer.

Other heat developable photographic compositions or photothermographic compositions can be used in combination with photothermographic compositions according to the invention. For example, a photothermographic material of the invention can comprise a support having thereon a heat-developable photographic layer comprising photosensitive silver halide in reactive association with an image-forming combination comprising (i) a silver salt of a 3-amino-1H-1,2,4-triazole derivative of Formula (I) with (ii) a silver halide developing agent and a separate layer containing a different photothermographic composition also containing a photosensitive silver halide with, for instance, a silver salt of a heterocyclic thione (e.g. as described in U.S. Patent 3,893,860) and an organic reducing agent.

A variety of imagewise exposure means can be used with photothermographic materials of the invention. These materials are typically sensitive to the ultraviolet and blue regions of the spectrum but if a spectral sensitizing dye is present, the sensitivity is acordingly extended. Thus exposure may usually be effected with a visible light source, such as a tungsten lamp, although other sources of radiation such as lasers, electron beams, and X-ray sources may be used.

A visible image can be developed in a photothermographic material of the invention, in many cases within several seconds, merely by heating the material uniformly to a moderately elevated temperature e.g. within the range of 125 to 200°C, and preferably 150 to 180°C. Heating is carried out until a desired image is developed, typically within from 1 to 60 seconds and usually in less than 30 seconds. At the lower processing temperatures, such as at about 125°C, development of an image is slower, and when the temperature is below about 140°C, post-processing stabilization may not occur with silver salts which give such stabilization at higher temperatures.

Although it is often undesirable, due to the lack of control possible in the preparation, the described photosensitive silver halide can be prepared *in situ* in a sensitive material according to the invention. Such a method of preparation of photosensitive silver halide *in situ* in a photothermographic material is described, for example, in U.S. Patent 3,457,075.

A variety of means can be employed to provide the heating necessary in processing a photothermographic material of the invention, including a hot plate, iron or roller.

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

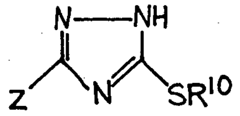
Example 1.

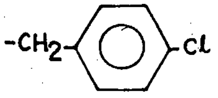
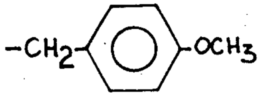
A. Preparation of 3-amino-5-benzylthio-1,2,4-triazole

A. Benzyl chloride (139 grams, 1.1 mole) was added dropwise to a mixture of 5-mercapto-3-amino-1,2,4-triazole (116 grams, 1 mole), 1600 millilitres of ethanol, sodium hydroxide (44 grams, 1.1 mole) and 900 millilitres of water. The reaction mixture was then heated at reflux for 6 hours. At the end of this time the ethanol was removed by distillation under reduced pressure, 1000 millilitres of water was added, and the solution was cooled to 5°C. The resulting oil which separated crystallized upon cooling. The resulting solid was collected, dried in a dessicator and recrystallized from 1200 millilitres of benzene with enough methanol to effect solution. The desired white solid product was obtained having a melting point of 108—109°C. The desired product was also identified through mass spectrum analysis and nuclear magnetic resonance analysis.

The following 1,2,4-triazole derivatives were also prepared using a technique similar to that described above for preparation of 3-amino-5-benzylthio-1H-1,2,4-triazole:

(II)



Z	R^{10}
$-NH_2$	
$-NH_2$	

B. Preparation of 3-amino-5-phenylthio-1,2,4-triazole

Diphenyliodonium bromide (120 g., 0.33 mole) was added to a solution of 3-amino-5-mercapto-1,2,4-triazole (38.2 g., 0.33 mole) and sodium methoxide (17.8 g., 0.33 mole) in 700 ml of methanol. The resulting mixture was stirred at reflux for five days. The reaction mixture was then evaporated to dryness. The residue was taken up in water and extracted twice with ethoxy acetate. The combined organic extracts were dried over magnesium sulphate, filtered and evaporated to dryness. The residue was slurried in chloroform and filtered. The crude product was adsorbed on a silica dry column with ethoxy acetate as solvent. The product band was excised and extracted with ethanol. The extract was evaporated to dryness and the residue slurried in chloroform and filtered. The product was then recrystallized from a mixture of ethoxy acetate and chloroform to provide a white solid having a melting point of 144—146°C. The product was identified by mass spectroscopy and nuclear magnetic resonance.

C. Preparation of silver salts of 1,2,4-triazole derivatives

6.18 grams (0.03 moles) of 3-amino-5-benzylthio-1,2,4-triazole (also referred to herein as ABT) and 4.0 grams of deionized, photographic gelatin were dissolved with heating into 30 millilitres of a solvent consisting of 95 parts by volume ethanol and 5 parts by volume methanol and 140 millilitres of distilled water. To this solution in a water jacketed, stainless steel mixer, held at about 50°C, was rapidly added a solution of 3.4 grams (0.02 moles) of silver nitrate in 30 millilitres of distilled water while rapidly mixing the compositon. The mixing speed was quickly increased and the composition was thoroughly mixed for a period of 40 minutes. The composition was then cooled to about 19°C. The final desired dispersion contained the silver salt of 3-amino-5-benzylthio-1,2,4-triazole and was adjusted to 200 grams by addition of distilled water. The composition weight was 10 kilograms per silver mole. The resulting dispersion had a pH of 2.8 and a pAg of 4.6.

Silver salts of the above 1,2,4-triazole derivatives listed in 1A were prepared in a similar manner.

Example 2.

Photothermographic material containing the silver salt of
3-amino-5-benzylthio-1,2,4-triazole

A photothermographic composition was prepared by mixing the following components:

silver salt dispersion containing the silver salt of 3-amino-5-benzylthio-1,2,4-triazole (ABT) as described from Example 1C	4.0 ml
silver bromoiodide gelatino emulsion (2.5 mole percent iodide, 0.06 micron size, diluted 1:4 with distilled water). (The emulsion was diluted to provide about 13 mg. of Ag per ml.)	0.7 ml
hydroquinone (10% by weight in methanol)	0.7 ml
surfactant ('Surfactant 10G' which is a para-isononylphenoxy-polygylcidol surfactant available from the Olin Co., U.S.A.) (10% by weight in distilled water)	0.2 ml
distilled water	2.4 ml

The resulting composition after mixing was coated on a polyethylene coated paper support at a wet coating thickness of 4 mils. The coating was prepared using a coating apparatus at a temperature of about 45°C. The resulting photothermographic material was permitted to dry with the aid of a source of warm air. The material was imagewise exposed with a flash exposure to light through a 0.3 density increment step tablet. The resulting latent image was developed by heating the material on a metal block at 175°C for 30 seconds. A brown-black tone image was developed having 6 process steps with a white background. The resulting developed image had a visual reflection maximum density of 1.11 and a minimum density of 0.06.

The image and background areas of the photothermographic material were stable to light when exposed for 24 hours at 120 foot candles of exposure.

Example 3.

The silver salts of the following compounds were compared in a composition like that described in Example 2:

3-amino-1,2,4-triazole($3NH_2$);
5-benzylthio-1,2,4-triazole (BTT);
and 3-amino-5-benzylthio-1H-1,2,4-triazole (ABT).

A dispersion with each of the above compounds was prepared as described in Example 1C with a ligand to silver ion molar ratio in each instance of 1.5:1. The dispersion weight was 10 kilograms per silver mole and contained 200 grams of gelatin per silver mole. The dispersion containing the $3NH_2$ silver salt had a pH of 3.4 and a pAg of 4.3. The dispersion containing the silver salt of the BTT compound had a pH of 1.9 and a pAg of 2.9. The dispersion containing the silver salt of the ABT compound had a pH of 2.8 and a pAg of 4.6.

Photothermographic compositions individually containing the three silver salts were prepared having the following composition.

silver salt dispersion as described (5.5 milligrams of silver per square decimetre)	4.0 ml
silver bromoiodide gelatino emulsion (the same emulsion as in Example 2) (1.2 milligrams of silver per square decimetre)	0.7 ml
hydroquinone (10% by weight in distilled water) (8.9 milligrams per square decimetre)	0.7 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.2 ml
distilled water	2.4 ml

The compositions were coated at 4 mil wet thickness on paper and permitted to dry. The resulting sensitive materials were identically exposed to provide developable latent images using a commercially sensitometer. Each exposed material was then heated on a metal block at temperatures within the range of 145°C to 200°C for 30 seconds. The maximum and minimum densities of the developed images were measured with blue light using a commercial reflection densitometer and then placed in a container and exposed to light for 24 hours at 130 foot candles of illumination. After this period of time the minimum densities were again measured. The results are listed in the following Table I, which includes the increase in minimum density $\triangle\ d_{min}$ (the 'print up') caused by the prolonged light exposure.

TABLE I

	Process Temperature (°C)					
Ligand	145	155	165	175	185	200
$3NH_2$ D_{max}	1.00	1.01	1.03	1.05	1.05	1.05
D_{min}	0.27	0.27	0.29	0.24	0.30	0.34
D_{min} (print-up)	0.75	0.80	0.51	0.38	0.37	0.42
ΔD_{min}	0.48	0.53	0.22	0.14	0.07	0.08
BTT D_{max}	0.49	0.48	0.52	0.59	0.58	0.60
D_{min}	0.23	0.23	0.19	0.16	0.17	0.18
D_{min} (print-up)	0.80	0.79	0.73	0.31	0.33	0.26
ΔD_{min}	0.57	0.56	0.54	0.15	0.16	0.08
ABT D_{max}	1.38	1.35	1.41	1.38	1.33	1.18
D_{min}	0.14	0.13	0.13	0.11	0.12	0.17
D_{min} (print-up)	0.89	0.66	0.67	0.17	0.15	0.21
ΔD_{min}	0.75	0.53	0.54	0.06	0.03	0.04

The data in Table I illustrate that the photothermographic element containing the silver salt of ABT provided higher maximum density, lower minimum density and at temperatures of processing over 175°C, less increase in minimum image density than did the compounds not in accordance with Formula I.

Example 4.

Addition of image toner

A dispersion was prepared as described in Example 1C with the silver salt of ABT with the exception that the silver salt contained a ligand to silver ion molar ratio of 1.0. A photothermographic composition was prepared as described in Example 2 with the exception that an equal molar concentration of tertiary-butylhydroqinone was used instead of hydroquinone as the silver halide developing agent. The photothermographic composition was coated as described in Example 2, imagewise exposed and the resulting latent image developed as described in Example 2. A brown-black developed image with a visual to blue light maximum reflection density ratio of 0.73 was obtained. The developed image had a maximum visual reflection density of 0.89 and a reflection maximum density to blue light of 1.21. A perfectly neutral image is considered to have a visual to blue light maximum reflection density ratio of 1.0.

The described procedure was repeated with the exception that 0.6 millilitres of a 0.125 per cent by weight solution of 6-methyl-2-thiouracil in methanol was added as an image-toning agent. The resulting developed image had a visual to blue light maximum reflection density ratio of 0.81 (1.06 maximum density to visual light and 1.31 maximum density to blue light). The developed image appeared gray-black.

This illustrates that image tone was improved by the use of the described toning agent. No significant adverse affects on the stability of the processed material were observed.

Example 5.

Use of 1-phenyl-2-tetraazoline-5-thione as a toning agent

A dispersion was prepared as described in Example 1C with the silver salt of ABT with the exception that the ligand to silver ion molar ratio in this silver salt was 1.6:1. A photothermographic composition was prepared using the coating composition described in Example 2 with the exception that an equal molar amount of tertiary-butylhydroquinone was used instead of hydroquinone as the silver halide developing agent. The photothermographic composition was coated on a paper support as described in Example 2. The resulting photothermographic material was exposed and processed as described in Example 2 to provide a developed image. The resulting developed image had a visual to blue light maximum reflection density ratio of 0.73 (maximum density of 0.83 to visual light and a maximum density of 1.13 to blue light).

The procedure was repeated with the exception that 0.33 millilitres of a 0.25% by weight solution of 1-phenyl-2-tetraazoline-5-thione in ethanol was added as an image-toning agent. The resulting developed image provided a visual to blue light maximum reflection density ratio of 0.91 (a maximum density of 1.12 to visual light and a maximum density of 1.23 to blue light). The developed image appeared neutral (black). Thus both the maximum reflection density and the image tone were improved with the addition of the described toning agent.

Example 6.

Processing temperature latitude with the silver salt of ABT

The dispersion described in Example 1C was used containing the silver salt of ABT. A photothermographic composition was prepared as described in Example 2 with the exception that an equal molar concentration of tertiarybutylhydroquinone was used in place of hydroquinone. The photothermographic composition was coated on a paper support as described in Example 2. The resulting photothermographic material was imagewise exposed and processed also as described in Example 2 with the processing temperature and time as listed in following Table II. The resulting developed image had a maximum and minimum visual reflection density as described in following Table II.

TABLE II

Process Temperature and Time	D_{max}/D_{min}	6th Step Density
155°C/30 sec.	0.92/0.06	0.40
165°C/30 sec.	0.97/0.05	0.49
175°C/30 sec.	0.99/0.06	0.42

The data in Table II shows no significant change in photographic speed or maximum and minimum density over the temperature range of processing concerned.

Example 7.

Chemically sensitized silver halide in photothermographic materials according to the invention

The dispersion described in Example 1C was employed for this example. A photothermographic composition was prepared as described in Example 2 with the exception that an equal molar concentration of tertiary-butylhydroquinone was used in place of hydroquinone as the developing agent.

A photothermographic material was prepared with this composition as described in Example 2. The photothermographic material was imagewise exposed to light and the resulting latent image was developed and stabilized by heating the material on a metal block at 175°C for 30 seconds. The resulting developed image provided 7 developed steps with a visual reflection maximum density of 0.99 and a minimum density of 0.06.

The procedure was repeated with the exception that a silver halide gelatino emulsion of the same grain size was used having sulfur and gold chemical sensitization instead of the silver halide described in Example 2. The resulting developed image had a maximum reflection density of 1.02 and a minimum density of 0.10 with 9 density steps.

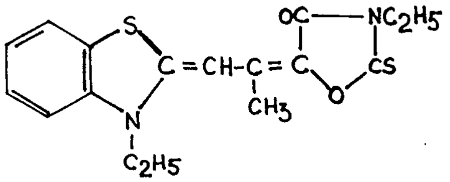
The chemically sensitized emulsion resulted in increased photographic speed.

Example 8.

Spectral sensitization of a photothermographic material containing the silver salt of ABT

The dispersion as described in Example 2 containing the silver salt of ABT was used in this example. A photothermographic composition containing this dispersion was prepared as described in Example 2. This composition was coated on a paper support to provide a photothermographic material as described in Example 2. The resulting material was imagewise exposed and processed as described in Example 7 to provide a developed image having a maximum reflection density to visual light of 0.92 and a minimum density of 0.07 with 7 visible image steps.

The procedure was repeated with the exception that a spectral sensitizing dye (1.5 grams of dye per silver mole) represented by the formula:



was used in the silver halide emulsion. The resulting developed image had a maximum reflection density of 0.97 and a minimum reflection density of 0.08 with 11 developed steps. No evidence was observed of undesirable dye stain in the background areas of the processed material.

Example 9.

Use of higher ligand to silver ion ratios in a photothermographic material

A dispersion containing the silver salt of ABT was used in this example as described in Example 1C except at a ligand to silver ion ratio of 1.2:1 and 100 grams of gelatin per silver mole. The photothermographic composition was prepared by mixing the following components:

silver salt dispersion (prepared as described in Example 1C)	4.0 ml
silver bromoiodide gelatino emulsion (2.5 mole % iodide, 0.06 micron size, diluted 1:4 with distilled water). (The emulsion was diluted to provide about 13 mg. of Ag per ml.)	0.7 ml
hydroquinone (10% by weight in methanol)	0.7 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.2 ml
3-amino-5-benzylthio-1,2,4-triazole (10% by weight in methanol)	0.7 ml
distilled water	1.7 ml

The final ligand to silver ion molar ratio in the photothermographic composition was 2.0. The composition was coated at a 4 mil wet coating thickness on a paper support. The photothermographic layer was permitted to dry and then was imagewise exposed as described in Example 4. The exposed material was then heated by contacting it with a metal block at 145°C for 30 seconds. A red-brown developed image was produced having 6 density steps with a maximum visual reflection density of 0.70 and a minimum density of 0.08. In addition, the background density (minimum density) of the processed material increased only 0.01 density unit upon re-exposure to light for 24 hours at 130 foot candles.

This indicated that increasing the ligand to silver ion ratio from 1.5 to 2.0 provided increased post-processing light stability with about 30°C lower processing temperature.

Example 10.

Use of base-release agent or base precursor

The dispersion containing the silver salt of ABT as described in Example 1C was used in this example. A photothermographic composition was prepared as described in Example 2. The photothermographic composition contained the following components:

silver salt dispersion containing the silver salt of ABT (prepared as described in Example 1C)	4.0 ml
silver bromoiodide emulsion (2.5 mole % iodide, 0.06 micron particle size, diluted 1:4 wtih distilled water). (The emulsion was diluted to provide about 13 mg. of Ag per ml.)	0.7 ml
hydroquinone (10% by weight in methanol)	0.7 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.2 ml
guanidinium trichloroacetate (5% by weight in distilled water)	1.0 ml
distilled water	1.4 ml

The photothermographic composition was coated on a paper support at a 4 mil wet coating thickness to provide a photothermographic material. The photothermographic layer was permitted to dry and then imagewise exposed as described in Example 6. The resulting latent image was developed by heating the photothermographic material on a metal block at a temperature of 165°C for 15 seconds. The developed image had a brown tone. The image had 5 visible developed steps with a maximum visual reflection density of 0.91 and a minimum density of 0.10. The minimum density areas (background areas) of the developed material were stable to light. No measurable increase in density was observed after exposure of the processed element for 24 hours at 120 foot candles of illumination.

Example 11.

Use of acrylamide polymer overcoat

A dispersion containing the silver salt of ABT prepared as described in Example 1C was used in this example. A photothermographic composition was prepared as described in Example 2 with the following components:

silver salt dispersion containing the silver salt of ABT (prepared as described in Example 1C)	4.0 ml
silver bromoiodide gelatino emulsion (2.5 mole % iodide, 0.06 micron particle size, diluted 1:4 with distilled water). (The emulsion was diluted to provide about 13 mg. of Ag per ml.)	0.7 ml
tertiary-butylhydroquinone (10% by weight in methanol)	0.35 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.2 ml
distilled water	2.8 ml

The resulting photothermographic composition was coated at a 4 mil wet thickness on a paper support. The resulting photothermographic layer was permitted to dry and then overcoated at a 4 mil wet coating thickness with the following composition:

poly(acrylamide-co-1-vinylimidazole) (weight ratio 90:10) (5% by weight solids in distilled water)	4.0 ml
tertiary-butylhydroquinone (10% by weight in methanol)	0.35 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.2 ml
distilled water	3.5 ml

The resulting coating was permitted to dry to provide the desired photothermographic material. The material was imagewise exposed as described in Example 7 and the resulting latent image was developed and stabilized by heating the material on a metal block at 155°C for 30 seconds. The resulting developed image had a brown-black tone with 6 visible developed steps and a visual maximum reflection density of 1.00 and a minimum density of 0.37. The image was exposed after processing to 120 foot candles of light for 24 hours. This produced an increase in minimum density of only 0.03 density units.

This illustrated that in addition to providing such advantages as resistance to abrasion marks, the described acrylamide polymer overcoat substantially lowers the processing conditions required to produce essentially complete stabilization to post-processing print-out.

Example 12.

Use of the silver salt of 3-amino-5-(p-methoxy) benzylthio-1,2,4-triazole in a photothermographic material

A silver salt dispersion was prepared as follows:

4.74 grams (0.02 mole) of 3-amino-5-(*p*-methoxy) benzylthio-1,2,4-triazole (referred to herein as AMBT) and 4.0 grams of deionized photographic gelatin were dissolved with heating in 30 millilitres of ethanol and 130 millilitres of distilled water. To this solution in a water jacketed mixing container, maintained at 55°C, was rapidly added a solution of 3.4 grams (0.02 mole) of silver nitrate in 40 millilitres of distilled water while mixing the composition rapidly. The mixing speed was increased and blending was continued for 40 minutes followed by cooling the composition to about 19°C. The final dispersion was adjusted to 233 grams (11.6 kilograms per silver mole) with distilled water. The silver salt dispersion had a pH of 2.1 and a pAg of 4.9.

A photothermographic composition was prepared by mixing the following components:

silver salt dispersion containing the silver salt of AMBT (prepared as described above)	4.0 ml
silver bromoiodide gelatino emulsion (2.5 mole % iodide, 0.06 micron particle size, diluted 1:4 with distilled water). (The emulsion was diluted to provide about 13 mg. of Ag per ml.)	0.7 ml
ascorbic acid (10% by weight in distilled water)	0.7 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.2 ml
3-amino-5-(*p*-methoxy)benzylthio-1H-1,2,4-triazole (5% by weight in methanol)	0.8 ml
distilled water	1.6 ml

The final photothermographic composition contained a ligand to silver ion molar ratio of 1.4:1. The composition was coated at a 4 mil wet coating thickness on a paper support. The resulting layer was permitted to dry to provide the desired photothermographic material. The material was then imagewise exposed as described in Example 7 and the resulting latent image was developed by heating the material on a metal block at 155°C for 30 seconds. The resulting devloped image had a brown tone and 7 developed density steps with a visual maximum reflection density of 0.91 and a minimum density of 0.09.

The developed image was exposed for 24 hours to 120 foot candles of illumination. The $^{\mathrm{D}}$min area had only 0.03 density unit increase after this illumination.

The procedure was repeated with the exception that the latent image was developed bv heating the material at a temperature of 175°C for 10 seconds. A similar image was developed and had similar image stability to light after processing.

This illustrated that the silver salt of AMBT provided stabilization at either lower processing temperatures or shorter processing times than those required with compositions containing the silver salt of ABT.

Example 13.

Use of the silver salt of 3-amino-5-(p-chloro) benzylthio-1,2,4-triazole in a photothermographic material

A. Preparation of silver salt of 3-amino-5-(*p*-chloro) benzylthio-1,2,4-triazole

The procedure described in Example 1C was repeated with the exception that 7.21 g. (0.03 mole) of 3-amino-5-(*p*-chloro)benzylthio-1H-1,2,4-triazole (referred to herein as ACBT) was used in place of 6.18 g. (0.03 mole) of ABT. The desired silver salt dispersion containing the silver salt of ACBT resulted from this preparation.

B. Photothermographic material containing the silver salt of 3-amino-5-(p-chloro) benzylthio-1,2,4-triazole

A photothermographic composition was prepared by mixing the following components:

silver salt dispersion containing the silver salt of ACBT, prepared as described above	8.0 ml
silver bromoiodide gelatino emulsion (2.5% iodide, 0.06 micron particle size, diluted with water to provide about 13 mg. Ag/ml.)	1.5 ml
t-butylhydroquinone (10% by weight in ethanol)	1.5 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.2 ml
distilled water	1.0 ml

The resulting composition was coated at 45°C at a 6 mil wet coating thickness on a gelatin subbed poly(ethylene terephthalate) film support. The resulting photothermographic material was permitted to dry at ambient temperature and pressure. The material was then imagewise exposed to light as described in Example 2 to provide a developable latent image. The exposed material was then overall heated by contacting it with a metal block at 155°C for 30 seconds. An image was developed having a purple tone with 5 visible steps and a visual diffuse maximum transmission density of 1.68 and a minimum density of 0.09.

The developed image was exposed to light (cool white fluorescent light) for 120 hours at 140 foot candles. An increase of only 0.07 in minimum density was observed.

Example 14.

Photothermographic film

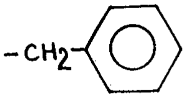
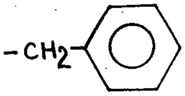
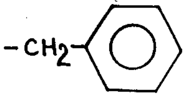
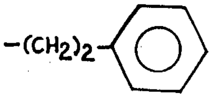
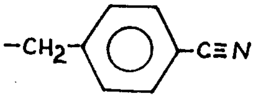
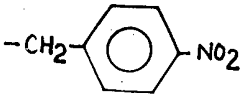
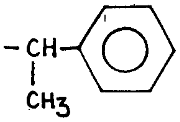
A silver salt dispersion was prepared containing the silver salt of ABT as described in Example 1C. A photothermographic composition was prepared by mixing the following components:

silver salt dispersion containing the silver salt of ABT (prepared as described in Example 1C)	8.0 ml
silver bromoiodide gelatino emulsion (2.5 mole % iodide, 0.06 micron particle size, diluted 1:4 with distilled water). (The emulsion was diluted to provide about 13 mg. of Ag per ml.)	1.4 ml
tertiary-butylhydroquinone (10% by weight in methanol)	1.5 ml
surfactant ('Surfactant 10G', 10% by weight in distilled water)	0.3 ml
distilled water	0.8 ml

The resulting photothermographic composition was coated at a 6 mil wet coating thickness on a gelatin coated poly(ethylene terephthalate) film support at about 45°C. The photothermographic layer was permitted to dry. The resulting photothermographic material was then imagewise exposed as described in Example 2 to provide a developable latent image in the material. The latent image was developed and stabilized by heating the photothermographic film on a metal block at 175°C for 30 seconds. A developed image resulted having a purple tone and 7 density steps. The developed image had a visual diffuse maximum density of 2.36 and a minimum density of 0.06. The clarity of the resulting photothermographic material was excellent, that is the non-image areas were completely transparent.

Example 15.

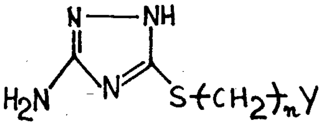
Silver salts of the following 1,2,4-triazole derivatives were tested in a photothermographic material and process substantially as described in Example 2, processing being for 30 seconds at 155°C. In each case image development with no post-processing image stabilization was observed: (Z and R^{10} are groups as defined in Formula II.

Z	R^{10}	Image developed	D_{max}	D_{min}
H		(weak image)	–	–
$-CH_3$		(weak image)	0.50	0.17
$-C_6H_{13}$		(weak image)	0.46	0.18
$-NH_2$	$-C_4H_9-n$	(no image discrimination)	–	–
$-NH_2$		(good image)	1.21	0.10
$-NH_2$		(weak image)	–	–
$-NH_2$		(fair image)	–	–
$-NH_2$		(no image discrimination)	–	–

WHAT WE CLAIM IS:—

1. A sensitive photothermographic material which comprises a support and incorporated in a layer or layers coated on one side thereof (a) a photosensitive silver halide, (b) an image-forming combination comprising (i) a silver salt of a triazole derivative of the formula:

I



wherein Y is an aryl group of 6 to 12 carbon atoms which may contain an alkyl, alkoxy or halogen substituent, and n is 0, 1 or 2 and (ii) a silver halide developing agent or a precursor thereof and (c) a polymeric binder.

2. A material according to Claim 1 wherein the silver halide (a) is present as a gelatino-silver halide emulsion and the binder (c) is hydrophilic.

3. A material according to Claim 1 or 2 wherein the triazole derivative of Formula I is a compound in which n is 1 and Y is a phenyl, *p*-chlorophenyl or *p*-methoxyphenyl group.

4. A material according to any of the preceding Claims wherein an excess of the triazole derivative or of silver is present the molar ratio of the triazole derivative to silver being from 0.5:1 to 3:1.

5. A material according to any of the preceding Claims which contains a base release agent in a layer on the said one side of the support.

6. A material according to Claim 5 wherein the base release agent is a guandinium compound.

7. A material according to any of the preceding Claims which contains an image toner in a layer on the said one side of the support.

8. A material according to Claim 7 wherein the image toner is a 1-phenyl-2-tetrazoline-5-thione.

9. A material according to any of the preceding Claims which contains per mole of the silver halide (a), from 2 to 8 moles of the silver salt (i) and from 5 to 10 moles of the developing agent (ii).

10. A material according to any of the preceding Claims which comprises an overcoat layer coated over the said layer or layers.

11. A material according to Claim 1 substantially as described in any of Examples 2 to 15.

12. A sensitive photothermographic composition which contains (a) a photographic silver halide, (b) an image forming combination comprising (i) a silver salt of a triazole derivative of the Formula I of Claim 1 and (ii) a silver halide developing agent or a precursor thereof, and (c) a polymeric binder.

13. A composition according to Claim 12 wherein the silver halide is present as a gelatino-silver halide emulsion and the polymeric binder is hydrophilic.

14. A composition according to Claim 12 or 13 wherein the triazole derivative of Formula I is a compound in which n is 1 and Y is a phenyl, *p*-chlorophenyl or *p*-methoxyphenyl group.

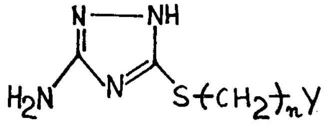
15. A composition according to any of Claims 12 to 14 wherein an excess of the triazole derivative or of sliver is present the molar ratio of the triazole derivative to silver being from 0.5:1 to 3:1.

16. A method of making a sensitive photothermographic material which comprises coating a support with a layer of a composition according to any of Claims 12 to 15.

17. A sensitive photothermographic material made by a method according to Claim 16.

18. A method of making a photographic record which comprises imagewise exposing the sensitive layer of a material according to any of Claims 1 to 11 and 17 to form a latent image therein and heating the material overall to develop the latent image to a visible image.

19. A silver salt of a triazole derivative of the formula:



wherein Y is an aryl group of 6 to 12 carbon atoms which may contain an alkyl, alkoxy or halogen substituent and n is 0, 1 or 2.

20. A silver salt according to Claim 19 for which n is 1 and Y is a phenyl, *p*-chlorophenyl or *p*-methoxyphenyl group.

21. A method of making a silver salt according to Claim 19 or 20 which comprises reacting a source of silver ions with a triazole derivative of the Formula I.

22. A method according to Claim 21 wherein an excess of either the triazole derivative or the source of silver ions is used, the molar ratio of the triazole derivative to the silver ions being from 0.5 : 1 to 3 : 1.

23. A method according to Claim 21 substantially as described in any of Examples 1, 12 and 13 herein.

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