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(54) **Photographic material containing a mesoionic 1,2,4-triazolium-3-thiolate silver halide stabilizing and fixing agent.**

(57) Mesoionic 1,2,4-triazolium-3-thiolate compounds are silver halide stabilizers and fixing agents. They are useful in heat developable and heat stabilizable photographic silver halide materials. After imagewise exposure, developed and stabilized silver images are produced by heating the materials.

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PHOTOGRAPHIC MATERIAL CONTAINING A MESOIONIC 1,2,4-TRIAZOLIUM-3-THIOLATE SILVER HALIDE STABILIZER AND FIXING AGENT

This invention relates to use of mesoionic 1,2,4-triazolium-3-thiolate compounds as silver halide stabilizer and fixing agents in heat developable and heat stabilizable photographic silver halide material.

Although use of stabilizer compounds in heat developable and heat stabilizable photographic materials is known from U.S. Patent 4,012,260, a need exists in the art for water-soluble, organic stabilizers and fixing agents. The problem facing the art is that the known compounds lack sufficient water solubility to permit their effective use in photographic silver halide materials to provide light insensitive silver (I) complexes upon exposure and processing. Such complexes provide light stability to developed images in processed photographic silver halide materials.

The present invention provides a photographic material which contains a silver halide stabilizing and fixing agent which is capable of forming a water soluble, light-insensitive silver (I) complex upon exposure and processing of the photographic silver halide material.

According to the invention, a developed and stabilized silver image is provided in a heat developable and heat stabilizable photographic silver halide material comprising a support having thereon a layer which contains, or adjacent layers which together contain:

(a) photographic silver halide, preferably as a photographic silver halide gelatino emulsion;

(b) a photographic silver halide developing agent;

(c) an activating concentration of a thermal base releasing compound;

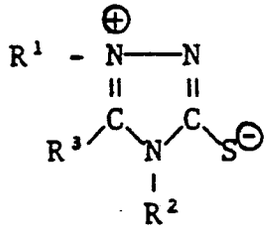
(d) a stabilizing concentration of a mesoionic 1,2,4-triazolium-3-thiolate silver halide compound, and

(e) a binder.

A stabilizer compound according to the invention is also useful in heat activatable photographic silver halide processing compositions comprising a photographic silver halide developing agent, a thermal base releasing compound and a silver halide stabilizing concentration of a stabilizer according to the invention.

A stabilizer compound according to the invention is also useful in a photographic silver halide fixing composition comprising a silver halide fixing concentration of a mesoionic 1,2,4-triazolium-3-thiolate and an organic acid, such as acetic acid. The fixing composition enables fixing of silver halide from an exposed and developed photographic silver halide photothermographic material comprising a hydrophobic binder.

Many mesoionic 1,2,4-triazolium-3-thiolate compounds are useful silver halide stabilizers and fixing agents according to the invention. Combinations of such stabilizers and fixing agents are also useful. Examples of useful mesoionic 1,2,4-triazolium-3- thiolates are represented by the formula:



wherein

R^1 is substituted or unsubstituted alkyl containing 1 to 18 carbon atoms, such a methyl, ethyl, propyl, butyl, decyl and octadecyl; or substituted or unsubstituted aryl containing 6 to 20 carbon atoms, such as phenyl and α-naphthyl or cycloalkyl of from 3 to 12 carbon atoms;

R^2 is NR^4R^5 wherein R^4 and R^5 can be hydrogen, substituted or unsubstituted alkyl of from 1 to 18 carbon atoms or substituted or unsubstituted aryl of from 6 to 20 carbon atoms, with the proviso that when R^4 is alkyl, R^5 is also alkyl; alkenyl containing 3 to 18 carbon atoms, such as allyl, crotonyl or 2-butenyl; substituted or unsubstituted alkyl containing 1 to 18 carbon atoms, such as methyl, methoxymethyl, ethyl, propyl, butyl, pentyl, decyl, benzyl, 2-phenethyl, and octadecyl; substituted or unsubstituted aryl containing 6 to 20 carbon atoms, such as phenyl, 4-tolyl and α-naphthyl; cycloalkyl containing from 3 to 12 carbon atoms such as cyclohexyl and cycloheptyl or alkoxyalkyl containing 2 to 12 carbon atoms, such as 2-methoxyethyl, 3-methoxypropyl and 4-methoxybutyl; and

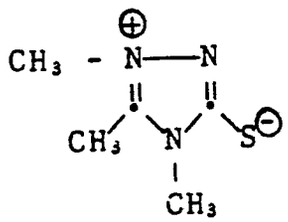
R^3 is substituted or unsubstituted alkyl containing 1 to 9 carbon atoms, such as methyl, ethyl, propyl, butyl and pentyl; or substituted or unsubstituted aryl containing 6 to 12 carbon atoms,

such as phenyl and α-naphthyl.

Examples of substituents which may be included in substituted alkyl groups are methoxy and α,α-dimethoxymethyl groups.

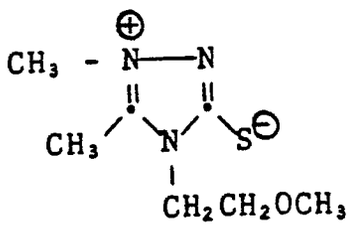
Examples of substituents which may be included in substituted aryl groups are methyl and methoxy groups.

An especially useful 1,2,4-triazolium-3-thiolate is 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate (Compound A) represented by the formula:

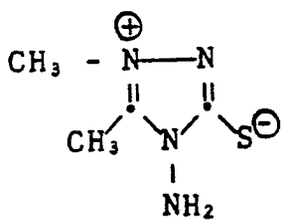


Examples of other useful 1,2,4-triazolium-3-thiolates include:

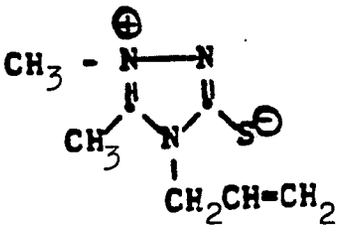
1,5-dimethyl-4-(2-methoxyethyl)-1,2,4-triazolium-3-thiolate (Compound B) represented by the formula:



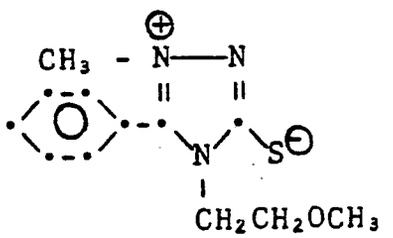
1,5-dimethyl-4-amino-1,2,4-triazolium-3-thiolate (Compound C) represented by the formula:



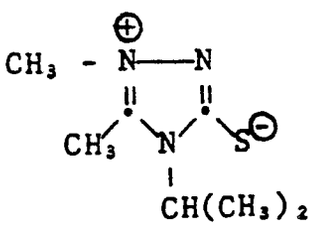
1,5-dimethyl-4-allyl-1,2,4-triazolium-3-thiolate (Compound D) represented by the formula:



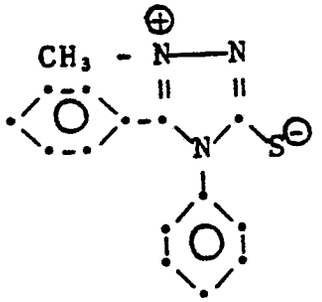
1-methyl-4-(2-methoxyethyl)-5-phenyl-1,2,4-triazolium-3-thiolate (Compound E) represented by the formula:



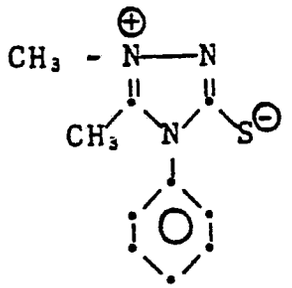
1,5-dimethyl-4-isopropyl-1,2,4-triazolium-3-thiolate (Compound F) represented by the formula:



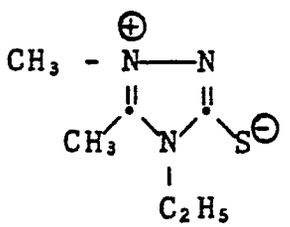
1-methyl-4,5-diphenyl-1,2,4-triazolium-3-thiolate (Compound G) represented by the formula:



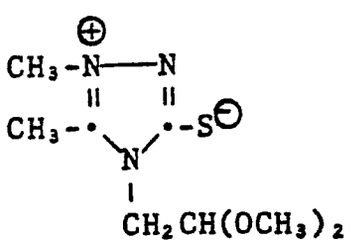
1,5-dimethyl-4-phenyl-1,2,4-triazolium-3-thiolate (Compound H) represented by the formula:



1,5-dimethyl-4-ethyl-1,2,4-triazolium-3-thiolate (Compound I) represented by the formula:



1,5-dimethyl-4-(2,2-dimethoxyethyl)-1,2,4-triazolium-3-thiolate (Compound J) represented by the formula:



The 1,2,4-triazolium-3-thiolate compounds are prepared by methods known in the organic chemical synthesis art. The preparation of 1,4,5-trimethyl-1,2,4-triazolium thiolate illustrates preparation of a 1,2,4-triazolium-3-thiolate:

Acetic anhydride (10.2 g, 0.1 mol) was slowly added to a stirred distilled water (11 g) solution of methyl hydrazine (4.6, 0.1 mol) at 0°C. The resulting solution was stirred at room temperature for one hour and the water was removed under reduced pressure. The residual oily acethydrazide, $CH_3N(COCH_3)NH_2$, was suspended in diethyl ether and to this stirred mixture at room temperature was slowly added a diethylether (25 ml) solution of methyl isothiocyanate (7.3 g, 0.1 mol). The resulting stirred solution was kept at room temperature for 30 minutes and then the solvent was removed under reduced pressure. The residual colorless solid was triturated with diethyl ether to give 4.9 g (30 percent) of the thiosemicarbazide (a white powder); m.p., 180 to 181°C (literature m.p. 175 to 177°C). The thiosemicarbazide (5.0 g, 0.03 mol) was refluxed in a methanol (25 ml) solution for 21 hours. During this reflux period, the thiosemicarbazide completely dissolved in the refluxing methanol and the triazolium thiolate, a colorless solid, then separated (m.p., 258 to 259°C) (m.p. reported in literature, 256 to 257°C).

Another illustrative method is the preparation of 1,5-dimethyl-4-(2-methoxyethyl)-1,2,4-triazolium-3-thiolate as follows: Crude acethydrazide prepared from acetic anhydride (10.2 g, 0.1 mol) and methylhydrazine (4.6 g, 0.1 mol), as described above, was dissolved in diethyl ether (25 ml) and to the resulting stirred translucent solution at room temperature was slowly added a diethyl ether (25 ml) solution of 2-methoxyethyl isothiocyanate

(11.7 g, 0.1 mol). After keeping the stirred solution at ambient temperature for one hour, the ether was removed under reduced pressure. More diethyl ether was added to the residual pale yellow syrup, and the resulting composition was stirred at ambient temperature for 18 hours.

The thiosemicarbazide (2.4 g, 0.012 mol) was heated to its melting point (123°C) and held at this temperature for five hours. After cooling to ambient temperature, the crystalline residue was recrystallized from ethyl acetate/ethanol (1:1 by volume) to yield 1.3 g (59 percent) of pale yellow plates; m.p., 125 to 126°C; mass spectrum M^+ 187.

The structure of the desired product was confirmed by mass spectral analysis and nuclear magnetic resonance.

An illustration of an alternate method of preparation is the synthesis of 1,5-dimethyl-4-(2-methoxyethyl)-1,2,4-triazolium-3-thiolate as follows:

A stirred dichloromethane (40 ml) mixture of 2-methoxyethyl isocyanide dichloride (1.9 g, 0.012 mol) and CH_3-CS-N(CH_3)NH_2 (1.3 g, 0.012 mol) was refluxed for two hours. Solvent was then removed under reduced pressure and the residual orange semi-solid was dissolved in 50 ml of methanol. One-half of this solution was evaporated to dryness and was then dissolved in methylene chloride (50 ml). Ammonia gas was bubbled through this stirred solution at ambient temperature for about 5 minutes. The resulting precipitate (presumably ammonium chloride) was collected, and the filtrate was evaporated to dryness to yield a reddish-brown semi-solid. A stirred ethanol (50 ml) solution of this solid was refluxed for 18 hours. Solvent was removed under reduced pressure to give a slowly separating orange oil. An ethyl acetate solution of this material was treated with decolorizing carbon

and eluted through a diatomaceous SiO_2 absorptive filter aid ('Celite' trade mark). The ethyl acetate elute was concentrated to about 25 ml, and colorless plates began to separate. The desired compound was recovered and had a melting point of 123 to 125°C.

The desired products are purified by procedures known in the chemical art, such as by recrystallization.

One embodiment of the invention is a heat developable and heat stabilizable photographic silver halide material comprising a support having thereon a layer which contains, or adjacent layers which together contain:

(a) photographic silver halide, preferably as a photographic silver halide gelatino emulsion,

(b) a photographic silver halide developing agent,

(c) an activating concentration of a thermal base releasing compound,

(d) a stabilizing concentration of a mesoionic 1,2,4-triazolium-3-thiolate stabilizer compound as defined herein, and

(e) a binder.

The photographic material according to the invention comprises photographic silver halide. Useful photographic silver halides include, for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide and mixtures thereof. The grain size of the silver halide ranges from coarse grain to fine grain. The photographic silver halide is prepared by procedures known in the photographic art, as described in, for example, Research Disclosure, December 1978, Item No. 17643, and Research Disclosure, June 1978, Item No. 17029. The photographic materials according to the invention, if desired, also contain addenda which do

not adversely affect the desired properties of the materials, such as antifoggants, tone modifiers, chemical sensitizers, hardeners, matting agents, brighteners, absorbing and filter dyes, development modifiers, spectral sensitizers and coating aids, as described in these Research Disclosure publications.

The heat developable and heat stabilizable photographic materials according to the invention contain binders and vehicles alone and in combination. Suitable vehicle materials include both naturally occurring substances, such as protein, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextrin or gum arabic; and synthetic polymeric materials such as water-soluble polyvinyl compounds such as poly(vinyl pyrrolidone) or acrylamide polymers. The photographic layers and other layers of the materials of the invention such as overcoat layers, interlayers and subbing layers can also contain, alone or in combination with the described vehicles, other synthetic polymeric vehicle compounds, such as dispersed vinyl compounds, such as in latex from, in particular those which increase the dimensional stability of the photographic materials. Useful binders are also described in the above Research Disclosure publications. Selection of an optimum binder depends upon such factors as the processing conditions, the particular components of the photographic material and the desired image.

Many supports are useful for a photographic material according to the invention. Typical supports include those which are resistant to adverse changes in structure and do not adversely affect the sensitometric properties of the described photographic materials at the processing temperatures employed. Typical supports include cellulose ester

film, poly(vinyl acetal) film, poly(ethylene terephthalate) film, polycarbonate film and related films and resinous materials, as well as glass, paper or metal.

The stabilizer according to the invention is in a location in the photographic material which enables the stabilizer to react with the silver halide in the unexposed areas upon processing to form a stable silver (I) complex. The stabilizer is useful in one or more layers of a photographic material according to the invention. The stabilizer is preferably in an overcoat layer or in a layer between the support and the layer containing silver halide. It is important that the stabilizer be in a location which enables the desired interaction between the stabilizer and the silver halide at the proper time during processing. The term "in reactive association" is often used to mean that the stabilizer and silver halide are in such locations as to enable such desired interaction

Many silver halide developing agents are useful according to the invention. Combinations of silver halide developing agents are useful. Useful silver halide developing agents include those described in, for instance, Research Disclosure, June 1978, Item No. 17029. A preferred silver halide developing agent is ascorbic acid.

Many thermal base releasing compounds are useful in a heat developable and heat stabilizable photographic material according to the invention. The term "thermal base releasing compound" as used herein means a compound which releases an organic base when heated to processing temperature in a photographic material according to the invention. The released base activates development of the exposed photographic silver halide at processing

temperature. The "activating concentration" of the base release agent means that the concentration of base release agent is sufficient in the photographic material to release a sufficient amount of base upon processing to activate development. The base released also helps stabilization by the stabilizer according to the invention. Examples of useful thermal base releasing compounds are described in Research Disclosure, June 1978, Item No. 17029, and include guanidinium trichloroacetate, 1,1-dimethyl-1-(2-hydroxypropyl)amine adipimide, 1-(ß-amino-ethyl)-2-imidazolidone, trichloroacetate, zinc oxide and urea.

The optimum concentration of each of (a) the photographic silver halide, (b) photographic silver halide developing agent, (c) thermal base release agent, and (d) stabilizer according to the invention will depend upon such factors as the desired image, processing conditions and particular components and their respective concentration in the heat developable and heat stabilizable photographic material. In a photographic material according to the invention, useful concentrations, per square meter of support, are within the following ranges:

(a) photographic silver halide: 2.5×10^{-3} to 1.0×10^{-1} moles, preferably 1.0×10^{-2} to 3.0×10^{-2} moles;

(b) photographic silver halide developing agent: 2.5×10^{-3} to 1.0×10^{-1} moles, preferably 1.0×10^{-2} to 3.0×10^{-2} moles;

(c) thermal base releasing agent: 1.15×10^{-3} to 5.0×10^{-2} moles, preferably 5.0×10^{-3} to 1.5×10^{-2} moles;

(d) stabilizer: 2.5×10^{-3} to 1.0×10^{-1} moles, preferably 1.0×10^{-2} to 3×10^{-2} moles.

An especially useful heat developable and heat stabilizable photographic material according to the invention comprises a support having thereon a layer which contains, or adjacent layers which together contain:

(a) photographic silver halide gelatino emulsion, such as a photographic silver bromide gelatino emulsion;

(b) a photographic silver halide developing agent, such as a photographic silver bromide developing agent, preferably ascorbic acid;

(c) an activating concentration of a thermal base releasing compound consisting essentially of an ethylenebis(sulfonyl acetic acid) compound,

(d) a stabilizing concentration of a 1,2,4-triazolium-3-thiolate stabilizer consisting essentially of mesoionic 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate, and

(e) a gelatino binder.

The stabilizer compounds are useful in photographic silver halide processing compositions. Such processing compositions include silver halide monobaths, stabilizing compositions, fixing compositions, hardeners and other processing compositions that enable the stabilizer according to the invention to form a silver (1) complex without adversely affecting desired properties of the processing composition and the photographic silver halide material. An example of a silver halide

processing composition comprises a silver halide developing agent, a thermal base release agent and a stabilizer according to the invention, such as mesoionic 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate. The processing composition generally comprises a solvent or binder.

A processing composition according to the invention is useful as a layer of a photographic silver halide material, such as a layer contiguous to the layer of the material comprising photographic silver halide. Alternatively, the processing composition is useful in the form of a bath into which an exposed and developed photographic silver halide material is immersed. Other processing methods and processing compositions in which the mesoionic silver halide stabilizers according to the invention are useful are described in, for instance, Research Disclosure, December 1978, Item No. 17643.

A useful processing composition according to the invention is a photographic silver halide fixing composition comprising a silver halide fixing concentration of a mesionic 1,2,4-triazolium-3-thiolate. A preferred photographic silver halide fixing composition comprises a fixing solution comprising, in an aqueous solvent, a fixing concentration of a mesoionic 1,2,4-triazolium-3-thiolate and an organic acid, such as acetic acid.

Because the described stabilizer compounds provide stable silver (I) complexes, no additional silver halide stabilizer is necessary in a photographic material according to the invention.

After exposure of a photographic silver halide material according to the invention, an image is developed and stabilized by heating the material to a processing temperature within the range of about 100°C to about 180°C, such as about 130°C to about

140°C, until the image is developed and stabilized. An image is generally developed and stabilized by heating for about one to about 60 seconds, such as about 10 to about 30 seconds. Normal atmospheric conditions of pressure and humidity are preferred for processing.

Various means are useful for heating the exposed photographic silver halide material, including a simple hot plate, iron, rollers, dielectric heating means or microwave heating means.

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

Example 1 -- Silver Halide Stabilization

Compound A was added to the following composition:

Component	Concentration per dm^2
Silver chloride (0.24 micron grain size)	0.1 mmol
ethylenebis(sulfonyl acetic acid) (thermal base releasing compound)	0.05 mmol
photographic gelatin	27.0 mg
surfactant (Surfactant 10G, trade mark for a para-isononyl-phenoxypolyglycidol available from the Olin Corporation, U.S.A.)	1 mg
Compound A (stabilizer)	0.1 mmol

The resulting composition was coated on a gelatin subbed poly(ethylene terephthalate) film support at a 0.1mm wet coating thickness. The coating was

permitted to dry and then the resulting material was heated on a heating block at 180°C for 30 seconds. Inspection of the coating indicated that the silver halide had been completely dissolved prior to heating. Light exposure of the coating resulted in no print-up, indicating complete silver halide stabilization.

Example 2 -- Silver Halide Stabilization

The procedure described in Example 1 was repeated, with the exception that Compound A was replaced by Compound B and the silver chloride was replaced by silver bromoiodide (0.24 micron grain size) (2.5 mole percent iodide). Results similar to Example 1 were observed.

Example 3 -- Silver Halide Stabilization

Compound C was added to the following composition:

Component	Concentration per dm^2	
photographic gelatin	200	mg
surfactant (Surfactant 10G)	10	mg
silver bromoiodide (2.5 mole percent iodide)	0.46	mmol
Compound C (stabilizer)	0.69	mmol
water	10	ml

The composition was coated at a 0.1 mm wet coating thickness on a gelatin subbed poly(ethylene terephthalate) film support. The coating was permitted to dry at about 49°C. The coating was light stable.

Example 4 -- Silver Halide Stabilization

The procedure described in Example 3 was repeated, with the exception that Compound A replaced Compound C. Similar results to those of Example 3 were observed.

Example 5 -- Fixing Bath

A silver halide fixing solution (Fixing Solution A) was prepared by mixing the following:

Compound A (fixing agent)	10.0 g/liter
Acetic acid (28 percent)	48 ml/liter
Water to one liter	

A photographic silver bromide gelatino emulsion layer (0.20 m grains) was coated on a gelatin subbed poly-(ethylene terephthalate) film support at 1 mg of silver per 6.2 cm^2. The resulting photographic material was sensitometrically exposed to provide a developable latent image. The exposed photographic material was then developed for 3.0 minutes at 25°C in the following silver halide developer composition:

Water, about 50°C	500 ml
'Elon' (trade mark, developing agent)	2.0 g
Sodium sulfite (anhydrous)	90.0 g
Hydroquinone (developing agent)	8.0 g
Sodium carbonate (monohydrated)	52.5 g
Potassium bromide (anhydrous)	5.0 g
Water to one liter	

The developed material was then immersed in a stop bath for 30 seconds at 25°C having the following composition:

Water	1.0 liter
28 percent acetic acid	48.0 ml

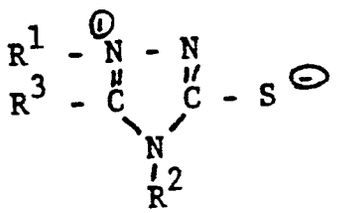
The material was then immersed for 90 seconds at 25°C in Fixing Solution A according to the invention. Then the developed and fixed material was washed in water and permitted to dry in air at 20°C.

The results indicated that the undeveloped silver bromide was dissolved upon treatment in the fixing solution, leaving the D_{min} areas free of silver. Silver analysis of the material after washing and drying showed 1620 mg of silver per square meter in the D_{max} areas of the material and no silver remaining in the D_{min} areas.

Example 6 -- Fixing Baths

Compounds identified below in Table I can be used in the preparation of fixing solutions of the type described as Solution A in Example 5 above in order to obtain exposed, developed and fixed photographic materials similar to the results reported in Example 5. In some instances it is desirable to add a small amount of an organic solvent, for example methyl alcohol, to the fixing solutions in order to enhance solubility of the fixing agent employed.

TABLE I



Example	Stabilizer Compound R^1	R^2	R^3
6	CH_3	$CH_2CH_2OCH_3$	phenyl
6(b)	CH_3	i-propyl	CH_3
6(c)	CH_3	phenyl	CH_3
6(d)	CH_3	C_2H_5	CH_3
6(e)	CH_3	$CH_2CH(OCH_3)_2$	CH_3

Example 7 -- Photothermographic Material

A photographic silver chloride material was prepared by coating the following on a first gelatin subbed poly(ethylene terephthalate) film support:

	Concentration (per 0.093m^2)
Ascorbic acid (developing agent)	200 mg
Methyl urea (base)	100 mg
Malic acid (buffer)	100 mg
Photographic gelatin (binder)	250 mg
Surfactant (Surfactant 10G, trade mark for a para-isononylphenoxy-polyglycidol available from the Olin Corporation, U.S.A.)	10 mg

	Concentration (per 0.093m^2)
Silver chloride (0.20 μm grain size)	150 mg

pH adjusted to 4.5 by KOH

A silver halide stabilizing material was prepared by coating the following at a 0.1mm wet coating thickness on a second gelatin subbed poly(ethylene terephthalate) film support:

	Concentration (per 0.093m^2)
Compound D (stabilizer)	1.0 g
Methyl urea (base)	200.0 mg
Gelatin (binder)	250.0 mg
Surfactant (Surfacfant 10G)	10.0 mg

The photographic silver halide material was sensitometrically exposed to light to provide a developable latent image in the material. The exposed photographic silver chloride material and the silver halide stabilizing material were then laminated together in face-to-face contact and heated on a metal block at 140°C for 10 seconds. A photographic

silver image was developed and the D_{min} areas were cleared. The resulting developed and stabilized image had a D_{max} of 0.63 and a D_{min} of 0.06. The processed, laminated materials were taped for one week to a window exposed to ambient conditions of temperature (about 19°C), humidity, sunlight and white fluoroescent light. The developed and stabilized image was then observed. The D_{min} had increased slightly to 0.10.

Example 8 --Photothermographic Materials

Photographic silver chloride materials were prepared as described in Example 7. Silver halide stabilizing materials were prepared by coating compositions as described below at a 0.1 mm wet coating thickness on a gelatin subbed second poly(ethylene terephthalate) film support:

	Concentration (per 0.093m^2)
Stabilizer compound (see Table II)	1.0 g
Methyl urea (base)	200 mg
Gelatin (binder	250 mg
Surfactant(Surfactant 10G)	10.0 mg

The photographic silver halide materials were exposed, laminated to a silver halide stabilizing material and processed as described in Example 7. The stabilizing compounds employed are indicated below in Table II.

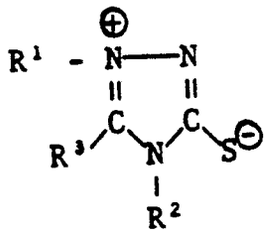


TABLE II

Example	Stabilizer Compound R^1	R^2	R^3
8(a)	CH_3	$CH_2CH_2OCH_3$	phenyl
8(b)	i-propyl	CH_3	CH_3
8(c)	CH_3	i-propyl	CH_3
8(d)	dodecyl	CH_3	CH_3
8(e)	CH_3	phenyl	phenyl
8(f)	4-CH_3-phenyl	CH_3	C_2H_5
8(g)	CH_3	phenyl	CH_3
8(h)	phenyl	pentyl	CH_3
8(i)	CH_3	C_2H_5	CH_3
8(j)	CH_3	4-OCH_3-phenyl	CH_3
8(k)	CH_3	$CH_2CH(OCH_3)_2$	CH_3
8(l)	CH_3	CH_3	i-propyl
8(m)	CH_3	$C_{18}H_{37}$	CH_3
8(n)	CH_3	CH_3	C_5H_{11}
8(o)	CH_3	NH_2	CH_3
8(p)	CH_3	CH_2CHCH_2	CH_3
8(q)	cyclohexane	CH_3	CH_3
8(r)	CH_3	NHC_6H_5	C_9H_{19}
8(s)	CH_3	NHC_6H_5	CH_3
8(t)	CH_3	$N(iC_3H_7)_2$	CH_3

Example 9 -- Fixing of Processed Photothermographic Silver Halide Material

A photothermographic silver halide film was prepared by coating on a gelatin subbed poly(ethylene terephthalate) film support a photothermographic silver halide layer comprising, in a poly(vinylbutyral) binder, photographic silver bromoiodide in reactive association with an image-forming combination comprising 2,6-dichloro-4-benzenesulfonamidophenol (reducing agent) and silver behenate (oxidizing agent) as described in, for example, European Patent 11,392 and Research Disclosure, Volume 177, January 1979, Item No. 17710. The photothermographic film was imagewise exposed to light in a commercial sensitometer to provide a developable latent image in the film. The latent image was developed by heating the film. The resulting film was then immersed for 30 seconds in a solution (B) comprising 3 milliliters of water and 47 milliliters of methanol at about 19°C. Then the film was immersed for 60 seconds in a silver halide fixing solution (A) comprising 1 gram of 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate (Compound A) dissolved in a mixture of 3 milliliters of water and 47 milliliters of methanol. Finally, the film was again immersed for 30 seconds in solution (B). The film in each solution was agitated by a rocking motion. The film before processing contained 611 mg Ag/m^2. The film, after treatment in the silver halide fixing solution, contained 13 mg Ag/m^2. The results indicated that 98 percent of the silver had been removed from the film.

CLAIMS

1. A heat developable and heat stabilizable photographic silver halide recording material comprising a support having thereon a layer which contains, or adjacent layers which together contain:

(a) photographic silver halide,

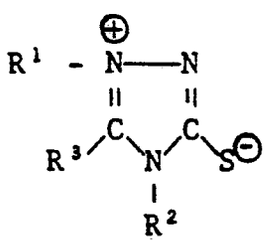
(b) a photographic silver halide developing agent,

(c) an activating concentration of a thermal base releasing compound,

(d) a stabilizer compound, characterized in that said stabilizer compound is a mesoionic 1,2,4-triazolium-3-thiolate compound, and

(e) a binder.

2. A photographic recording material according to Claim 1 characterized in that said thiolate compound is represented by the formula:



wherein:

R^1 is alkyl containing 1 to 18 carbon atoms or substituted or unsubstituted aryl containing 6 to 20 carbon atoms or cycloalkyl containing from 3 to 12 carbon atoms;

R^2 is NR^4R^5 wherein R^4 and R^5 can be hydrogen; substituted or unsubstituted alkyl containing from 1 to 18 carbon atoms; or substituted or unsubstituted aryl containing from 6 to 20 carbon atoms, with the proviso that when R^4 is alkyl, R^5 is also alkyl; alkenyl containing 3 to 18 carbon atoms; substituted or unsubstituted alkyl containing 1 to 18 carbon atoms; substituted or unsubstituted aryl containing 6 to 20 carbon atoms, cycloalkyl containing from 5 to 12 carbon atoms; or alkoxyalkyl containing 2 to 12 carbon atoms; and

R^3 is substituted or unsubstituted alkyl containing 1 to 9 carbon atoms or substituted or unsubstituted aryl containing 6 to 12 carbon atoms.

3. A photographic recording material according to Claims 1 or 2 characterized in that said thiolate compound is 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate.

4. A heat activatable photographic silver halide processing composition comprising a photographic silver halide developing agent, a thermal base releasing compound and a silver halide stabilizer compound characterized in that said stabilizer compound is a mesoionic 1,2,4-triazolium-3-thiolate.

5. A photographic composition according to Claim 4 characterized in that said thiolate compound is 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate.

6. A photographic silver halide fixing composition characterized in that it comprises a silver halide fixing concentration of a mesoionic 1,2,4-triazolium-3-thiolate compound and an organic acid.

7. A photographic silver halide fixing composition according to Claim 6 characterized in that said acid is acetic acid.

8. A photographic silver halide fixing composition according to Claims 6 or 7 characterized in that said composition contains an aqueous solvent.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 81305830.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 105 451 (SMITH) * Claims 1,11,18,20,24,35,36,38, 39; column 5, lines 9-50 *	1
A	GB - A - 1 379 876 (FUJI) * Claims 1,2 *	1
A	GB - A - 1 177 287 (ILFORD) * Claim 1 *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

G 03 C 1/42
G 03 C 5/39
G 03 C 5/38
G 03 C 1/02
G 03 C 1/06
G 03 C 5/30

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

G 03 C
B 41 M
C 07 D 249/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	10-03-1982	SCHÄFER