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Sutton et al.

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[54] **PHOTOTHERMOGRAPHIC ELEMENT AND PROCESS**

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[52] **U.S. Cl.** ..... **96/66 T;** 96/48 HD; 96/76 R; 96/114.1

[51] **Int. Cl.** **G03c 5/30;** G03c 1/04; G03c 1/72

[58] **Field of Search** ..... 96/48 HD, 66 T, 76 R, 95, 96/114.1

[56] **References Cited**

UNITED STATES PATENTS

2,732,304	1/1956	Vanselow et al.	96/114.1
3,094,417	6/1963	Workman	96/114.1
3,468,664	9/1969	Stewart	96/114.1
3,672,904	6/1972	deMauriac	96/114.1
3,785,830	1/1974	Sullivan et al.	96/114.1
3,856,526	12/1974	Hamb et al.	96/114.1

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[57] **ABSTRACT**

Certain acrylamide polymers in a layer contiguous to a photothermographic layer comprising (a) photographic silver halide in association with (b) a silver salt of certain heterocyclic thione compounds, (c) an organic reducing agent, and (d) a polymeric, synthetic binder for the photothermographic layer of a photothermographic element provide, for example, increased stability prior to imagewise exposure without significantly adversely affecting sensitometric properties of the photothermographic element. The acrylamide polymers can comprise an overcoat layer or a layer between the photothermographic layer and a support for the photothermographic element or can be in both such layers.

17 Claims, No Drawings

PHOTOTHERMOGRAPHIC ELEMENT AND PROCESS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to certain acrylamide polymers in certain photothermographic materials comprising photographic silver halide in association with a silver salt of certain heterocyclic thione compounds. In one of its aspects, it relates to a photothermographic element comprising a support having thereon (I) a layer comprising the described silver salts of a heterocyclic thione and a contiguous layer (II) comprising certain acrylamide copolymers. In another of its aspects, it relates to a method of developing a latent image in a photothermographic element comprising the described acrylamide polymers.

Description of the State of the Art

Photothermographic materials comprising photographic silver halide in association with a silver salt of certain heterocyclic thione compounds and an organic reducing agent are known in the art. These photothermographic materials are described, for example, in U.S. Pat. No. 3,785,830 issued Jan. 15, 1974. One problem which has been encountered with these photothermographic materials is the need for increased preprocessing stability of the photothermographic element. This problem is illustrated in the following comparative Example 2. This problem is illustrated by failure of the photothermographic material to provide a desired developed image after storage at elevated temperatures such as storage at 38° C. at 50% relative humidity.

It has been proposed in some cases to provide the photothermographic material with a protective layer, such as a protective overcoat layer. A commonly employed overcoat layer for photothermographic elements comprises cellulose acetate. Such an overcoat layer is described, for example, in Belgian Pat. No. 729,043 and U.S. Pat. No. 2,732,304 issued Jan. 24, 1956. Such an overcoat comprising cellulose acetate does not provide a useful solution to problems encountered with photothermographic materials comprising photographic silver halide in association with silver salts of certain heterocyclic thiones as described in U.S. Pat. No. 3,785,830 issued Jan. 15, 1974.

Polymer overcoat layers have been proposed for photothermographic elements to reduce susceptibility to abrasion marks, especially in machine processing wherein the photothermographic layer side of the element is contacted with a metal roller or the like. In addition, the processing of photothermographic elements by contacting the photothermographic element with a heating means can cause undesired physical properties such as surface cracking, reticulation and bubbling which can detract from the overall image quality desired in the photothermographic element. An ethyl cellulose overcoat layer and other overcoat layers have not satisfactorily overcome these problems in a photothermographic element as described.

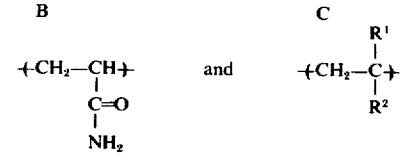
In the application of polymeric layers, i.e., either overcoat layers or layers between the support and the photothermographic layer, it is necessary to employ polymers which are resistant to decomposition or other undesired effects at the processing temperatures employed, such as temperatures above about 100° C.

Polymers, in order to be satisfactory with the photothermographic materials as described, must satisfy each of the following characteristics in addition to those described: (1) they provide sufficient resistance to abrasion and fingerprint marking to enable machine processing, (2) they provide sufficient resistance to reticulation and surface cracking upon processing with heat in a photothermographic element, (3) they provide sufficient resistance to surface bubbling in a photothermographic material upon processing with heat, (4) they do not significantly adversely affect sensitometric properties of the photothermographic materials, and (5) they are sufficiently transparent for desired viewing of an image. Although there are many polymers that are resistant to high-temperature decomposition, these polymers, as a class, are not satisfactory for use with the described photothermographic materials because properties are required other than the property of resistance to decomposition at high temperatures. This is illustrated by appended comparative examples.

There has, accordingly, been a continuing need to provide improved photothermographic materials comprising photographic silver halide in association with silver salts of certain heterocyclic thione compounds, as described, to provide the desired described properties such as improved stability prior to imagewise exposure, resistance to abrasion marks, fingerprint marks and undesired surface properties, without significantly adversely affecting sensitometric properties of the photothermographic material.

Summary of the Invention

It has been found, according to this invention, that the described properties are provided in a photothermographic element comprising a support having thereon a layer comprising (a) photographic silver halide in association with (b) a silver salt of a heterocyclic thione as described herein, (c) an organic reducing agent for the silver salt of the heterocyclic thione, and (d) a polymeric, synthetic binder for layer (I) and a polymer layer (II), contiguous to layer (I), wherein the polymer layer (II) comprises at least 50% by weight of a polymer (A) comprising the repeating units represented by the formulas:



wherein:

R^1 is hydrogen or alkyl containing 1 to 4 carbon atoms;

R^2 is an imidazolyl; N-substituted carbamoyl such as N-hydroxymethylcarbamoyl; 2-pyrrolidonyl; an active methylene-containing group such as acetoacetoxyethoxycarbonyl, acetoacetonylmethylphenyl and ethoxycarbonylaceto; pyridyl; hydroxy or an hydroxyl-containing group such as hydroxyalkyl containing 1 to 4 carbon atoms, including hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl; carboxy or a carboxyl-containing group such as carboxyethoxycarbonyl; or a heterocyclic ammonium salt group having a 5-

or 6-membered azonia nitrogen-containing ring such as an imidazolium salt group, such as a 1-aza-3-methyl-3-azoniacyclopenta-2,4-diene-1-yl methosulfate salt group, or a pyridinium salt group, such as 1,2-dimethyl-1-azonia-5-phenyl methosulfate salt group; and

the weight ratio of starting monomers for the units B and C is, respectively, about 60:40 to 100:0.

The described polymers are acrylamide polymers. The acrylamide polymers are preferably copolymers which exhibit reduced or no adverse physical or chemical properties resulting from the thermal processing described herein. This is intended to mean that the described polymers are preferably copolymers which do not adversely discolor, decompose, crystallize, flow or the like as a result of the heating described herein.

Also, according to the invention, a process is provided for developing an image in the described photothermographic element by uniformly heating the element, such as from about 80° to about 200° C., for a sufficient time to provide the desired developed image. This process can be carried out by contacting the photothermographic element with a suitable heating means to provide the described temperature.

Detailed Description of the Invention

Various acrylamide polymers within the designated formula are useful in photothermographic materials according to the invention.

Useful acrylamide polymers do not adversely flow, smear or distort at the processing temperatures for a described photothermographic material. The acrylamide polymers also do not cause adverse opacification of the photothermographic material. Useful acrylamide polymers have an average molecular weight of at least about 50,000, and preferably from about 100,000 to about 2,000,000. The molecular weight can be determined by methods known in the polymer art. Useful acrylamide polymers have inherent viscosities, measured at a concentration of 0.25 g. per deciliter in 1 normal sodium chloride solution at 25° C., ranging from 0.2 to 2.0, and preferably from 0.6 to 1.7.

Useful acrylamide polymers are typically transparent and colorless. It is necessary, if the polymer is not completely transparent, that it be at least transparent to the wavelength of radiation employed to provide a latent image in the photothermographic element of the invention when exposure is through a layer comprising the acrylamide polymer.

Some acrylamide polymers, especially acrylamide copolymers, useful in photothermographic elements according to the invention are described in, for example, U.S. Pat. No. 3,658,878 of Smith issued Apr. 25, 1972, U.S. Pat. No. 3,591,386 of Abbott et al. issued July 6, 1971, U.S. Pat. No. 3,488,708 of Smith issued Jan. 6, 1970, U.S. Pat. No. 3,459,790 of Smith issued Aug. 5, 1969, and U.S. Pat. No. 3,554,987 of of Smith issued Jan. 12, 1971.

Useful acrylamide polymers, especially acrylamide copolymers, can be prepared empolying procedures known in the polymer art, such as described in the above U.S. patents. Generally, any of the known polymerization procedures, particularly copolymerization procedures used in the polymer art, are useful for making the described acrylamide polymers.

Typical reactants employed when preparing the polymers within the described structure (A) are acrylamide and acrylamide copolymerized with one of the following monomers:

1-vinylimidazole
2-methyl-1-vinylimidazole
3-methyl-1-vinylimidazolium methosulfate
N-methylolacrylamide
2-acetoacetoxyethyl methacrylate
acrylic acid
1-vinyl-2-pyrrolidone
2-methyl-5-vinylpyridine
1,2-dimethyl-5-vinylpyridinium methosulfate

The described acrylamide polymers do not, in the absence of interfering components, significantly adversely affect the sensitometric properties of the described photothermographic materials, such as minimum density, maximum density, photographic speed and the like, whereas cellulose acetate, a commonly employed overcoat, causes significant undesired changes in sensitometric behavior. The described acrylamide polymers also provide desired increased stability prior to imagewise exposure of a described photothermographic element. This is illustrated in the following examples.

Examples of useful acrylamide polymers according to the invention include:

Polymer No.	Polymer
I	poly(acrylamide-co-1-vinylimidazole)(weight ratio 90:10)
II	poly(acrylamide-co-2-methyl-1-vinylimidazole)(weight ratio 90:10)
III	poly(acrylamide-co-3-methyl-1-vinylimidazolium methosulfate)(weight ratio 90:10)
IV	poly(acrylamide-co-N-methylolacrylamide)(weight ratio 80:20)
V	polyacrylamide
VI	poly(acrylamide-co-2-acetoacetoxyethyl methacrylate)(weight ratio 90:10)
VII	poly(acrylamide-co-2-acetoacetoxyethyl methacrylate)(weight ratio 98:2)
VIII	poly(acrylamide-co-acrylic acid)(weight ratio 90:10)
IX	poly(acrylamide-co-1-vinyl-2-pyrrolidone)(weight ratio 90:10)
X	poly(acrylamide-co-2-methyl-5-vinylpyridine)(weight ratio 90:10)
XI	poly(acrylamide-co-1,2-dimethyl-5-vinyl-pyridinium methosulfate)(weight ratio 88:12)
XII	poly(acrylamide-co-2-vinylpyridine)(weight ratio 89:11)

The concentration of acrylamide polymer which is useful in a layer of a photothermographic element according to this invention can vary, depending upon such factors as the particular photothermographic element, processing conditions, components in the photothermographic element, particular acrylamide polymer and the like. A useful concentration range or coating coverage, is about 0.1 g. to about 1.08 g. of acrylamide polymer/m.^{2} of support of the photothermographic element. A useful concentration of acrylamide polymer, when the acrylamide polymer is used as an overcoat layer, is about 0.3 g. to about 7.5 g., such as about 0.40 g. to about 2.15 g., of acrylamide polymer/m.^{2} of support of the photothermographic element. When the acrylamide polymer is used as a so-called undercoat, that is, a coating on the support between the support and the photothermographic layer, a useful concentration of acrylamide polymer is about 0.3 g. to about 5.0 g., such as about 2.15 g. of acrylamide polymer/m.^{2} of support of the photothermographic element.

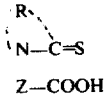
The described acrylamide polymer comprises at least 50% by weight of the layer contiguous the photother-

mographic layer (I) as described. Other polymers can be useful with the acrylamide copolymers. However, typically, the acrylamide polymer comprises about 100% of the contiguous layer. Other polymers which can be useful with the acrylamide polymers include, for example, poly(vinyl alcohol) and polymers having properties similar to poly(vinyl alcohol) such as other acrylamide and N-substituted acrylamide copolymers including, for instance, poly-(acrylamide-co-acrylic acid), and cellulosic materials such as sulfoethyl cellulose and sodium cellulose sulfate. Photothermographic elements according to this invention can comprise, if desired, multiple polymer-containing layers. For example, the photothermographic element can comprise an overcoat layer containing an acrylamide polymer as described and an additional overcoat layer comprising another polymer such as poly(vinyl alcohol).

One embodiment of the invention is in a photothermographic element comprising a support having thereon (I):

a. photographic silver halide in association with

b. a silver salt of a heterocyclic thione, said heterocyclic thione being represented by the formula:



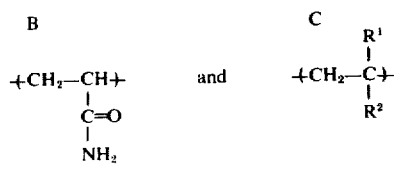
(XX)

wherein R represents the atoms completing a 5-member heterocyclic nucleus and Z is alkylene containing 1 to 30 carbon atoms, typically 1 to 10 carbon atoms,

c. an organic reducing agent for said silver salt of a heterocyclic thione, and

d. a polymeric, synthetic binder and,

contiguous to (I), at least one polymer layer (II), the improvement being one wherein said polymer layer (II) comprises at least 50% by weight of a polymer (A) comprising the repeating units represented by the formulas:



wherein R^1 is hydrogen or alkyl containing 1 to 4 carbon atoms, R^2 is as described, and the weight ratio of starting monomers for the units B and C are respectively about 60:40 to 100:0.

Various photographic silver halides can be employed in the described photothermographic element. The concentration of photographic silver halide which is useful in a photothermographic element of the invention can be very low compared with photographic materials which contain photographic silver halide in the absence of the other components of the photothermographic element of the invention. For example, the concentration of photographic silver halide which is suitable in a photothermographic element of the invention, can be about 0.0025 to about 0.3 mole of photographic silver halide per mole of silver as the silver salt of the described heterocyclic thione. In a photothermographic element of the invention, the concentration of photographic silver halide is typically about 0.10 times 10^{-3} to about 1.29 times 10^{-3} moles of photographic silver halide/m^2 of support. Useful photographic silver halides include, for example, silver chloride, silver bromide, silver iodide, silver bromoiodide, silver chlorobromoiodide, silver iodide, or mixtures thereof. The photographic silver halide can be coarse- or fine-grain, very fine-grain silver halide being especially useful. The photographic silver halide can be prepared by any of the known procedures employed in the photographic art. The silver halide can be prepared, for example, employing single-jet preparation techniques or double-jet preparation techniques such as techniques employed in preparing Lippmann emulsions and the like. Surface-image silver halide can be useful. If desired, mixtures of surface- and internal-image silver halide can be used. Negative-type silver halide is typically employed. The silver halide can be regular-grain silver halide such as described in Klein and Moisar, *Journal of Photographic Science*, Vol. 12, No. 5, Sept.–Oct., 1964, pp. 242–251. Photographic silver iodide is especially useful as the photographic silver halide.

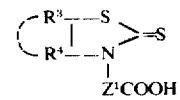
The photographic silver halide according to this invention can be unwashed or washed, and can be chemically sensitized employing techniques empolyed in the photographic art.

It is believed that the latent image formed in the photographic silver halide upon imagewise exposure of the photothermographic material increases the reaction rate between the components of the photothermographic material upon heating of the photothermographic material. It is believed this enables a lower processing temperature to be employed for developing an image which otherwise would not be possible.

The term "photographic silver halide in association with" is intended to mean the photographic silver halide is in a location with respect to the other described components of the photothermographic material which enables this desired lower processing temperature and provides a more useful developed image.

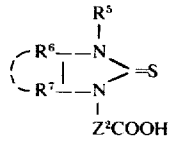
Various silver salts of a heterocyclic thione are useful in the described photothermographic materials of the invention. A useful silver salt of a heterocyclic thione is a silver salt of a heterocyclic thione represented by the formula (XX) as described. Selection of an optimum heterocyclic thione silver salt will depend upon such factors as the particular photothermographic material, particular toning agent, processing temperature, desired image and the like. Examples of useful 5-member heterocyclic nuclei containing the described carboxyalkyl group are thiazoline-2-thione, benzothiazoline-2-thione, imidazoline-2-thione, oxazoline-2-thione, or similar heterocyclic thione nuclei. The heterocyclic thione nucleus can be substituted with groups which do not adversely affect the photothermographic properties of the photothermographic element of the invention, such as alkyl containing 1 to 3 carbon atoms, or phenyl.

especially useful thione compounds within formula (XX) are thiazoline-2-thiones represented by the formula:



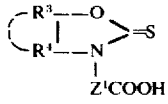
(XXI)

wherein Z^1 is alkylene containing 1 to 4 carbon atoms; and R^3 and R^4 are each, independently, hydrogen, alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl, propyl or butyl, or aryl containing 6 to 10 carbon atoms, such as phenyl or tolyl, or taken together are the atoms necessary to complete a benzo group represented by the broken line between R^3 and R^4. Other useful heterocyclic thiones within formula (XX) are imidazoline-2-thiones represented by the formula:



(XXII)

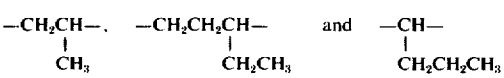
wherein Z^2 is alkylene containing 1 to 4 carbon atoms; R^6 and R^7 are each, independently, hydrogen, alkyl containing 1 to 4 carbon atoms, such as methyl, ethyl, propyl or butyl, or aryl containing 6 to 10 carbon atoms, such as phenyl or tolyl, or taken together are the atoms necessary to complete a benzo group represented by the broken line between R^6 and R^7; and R^5 is alkyl, typically alkyl containing 1 to 3 carbon atoms, such as methyl, ethyl or propyl, aryl containing 6 to 10 carbon atoms, such as phenyl, or carboxyalkyl such as carboxyalkyl containing 1 to 3 carbon atoms, for example, carboxymethyl and carboxyethyl. Other useful heterocyclic thiones within structure (XX) are oxazoline-2-thiones represented by the formula:



(XXIII)

wherein Z^1, R^3 and R^4 are as defined.

In the definition of Z, as well as Z^1, Z^2 and Z^3, as employed herein, alkylene includes straight-chain alkylene and branched-chain alkylene, such as:



Examples of useful thione compounds within the described formulae include:

3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione
3-(2-carboxyethyl)benzothiazoline-2-thione
3-(2-carboxyethyl)-5-phenyl-1,3,4-oxadiazoline-2-thione
3-(2-carboxyethyl)-5-phenyl-1,3,4-thiadiazoline-2-thione
3-carboxymethyl-4-methyl-4-thiazoline-2-thione
3-(2-carboxyethyl)-1-phenyl-1,3,4-triazoline-2-thione
1,3-bis(2-carboxyethyl)imidazoline-2-thione
1,3-bis(2-carboxyethyl)benzimidazoline-2-thione
3-(2-carboxyethyl)-1-methylimidazoline-2-thione
3-(2-carboxyethyl)benzoxazoline-2-thione
3-(1-carboxyethyl)-4-methyl-4-thiazoline-2-thione

The silver salt of the described thione can be prepared directly in the photothermographic composition by combining a source of silver, such as silver trifluoroacetate, with the thione compound in the composition, or the silver salts can be preformed and isolated before addition to the photothermographic composition. The described thione compounds can be prepared employing processes known in the art. It is desirable to avoid preparation of the silver salt in the presence of compounds which could cause reduction.

Preparation of the thione compounds can be carried out employing procedures described, for example, in an article of R. W. Lamon and W. J. Humphlett, *Journal of Heterocyclic Chemistry*, Vol. 4, pp. 605–609, 1967, or as described in Belgian Pat. No. 739,705. Preparation of 4-thiazoline-2-thiones bearing a carboxyalkyl group in the 3 position can, for instance, be effected by treating a dithiocarbamic acid derived from an amino acid and carbon disulfide with an α-halogenated ketone. In this process the use of methyl alcohol as a solvent can improve the solubility of the reactants.

The preparation of the silver salt of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione is typical. This silver complex is prepared by mixing the described thiazoline-2-thione with silver trifluoroacetate in water and thoroughly dispersing the reactants. Concentrations of the reactants can be varied to provide the desired ratio of silver to heterocyclic compound. Typically, the ratio of the thione compound to silver ion is less than about 2:1. The resulting silver salt can be purified and stored for later mixture with other components of the described photothermographic materials. Dispersing of the silver trifluoroacetate with the heterocyclic compound is typically carried out at about 38° to about 71° C.

Various reducing agents can be employed in the photothermographic materials of the invention. These are typically silver halide developing agents and include, for example, polyhydroxybenzenes such as hydroquinones including, for instance, hydroquinone; alkyl-substituted hydroquinones such as tertiarybutylhydroquinone, 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; and the like. Other silver halide developing agents which can be employed as reducing agents include reductones such as anhydro dihydro piperidino hexose reductone; hydroxytetronic acids and hydroxytetronimides; 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone, and those described in British Pat. No. 930,572 published July 3, 1963; hydroxylamines; ascorbic acids such as ascorbic acid, ascorbic acid ketals, and other ascorbic acid derivatives; phenylenediamines; aminophenols; and the like. Combinations of reducing agents can also be employed. A suitable reducing agent typically is one which in the photothermographic compositions of the invention provides a developed image within about 90 sec. at a temperature of about 100° to 250° C.

A range of concentrations of each component is useful in the described photothermographic material. Typically, a photothermographic element according to the invention can comprise a support having thereon in the photothermographic layer (A) about 0.10 times 10^{-3} to about 1.29 times 10^{-3} moles of photographic silver halide in association with (B) about 2.69 times 10^{-3} to about 21.5 times 10^{-3} moles of reducing agent and (C) about 2.69 times 10^{-3} to about 21.5 times 10^{-3} moles

of silver as the described complex per m^2 of support. An optimum concentration of each component will depend upon such factors as the particular components, the desired image, processing temperature and the like.

If desired, one or more components of the photothermographic element can be present in one or more layers of the element. For example, in some cases it can be desirable to include certain percentages of the reducing agent, silver salt of the described heterocyclic thione and/or photographic silver halide in the described layer (II) comprising an acrylamide polymer. This can reduce, for example, migration of certain addenda throughout the layers of the photothermographic element.

Suitable binders for photothermographic layer (I) can be hydrophilic or hydrophobic, transparent or translucent, and include synthetic polymeric materials useful in the described photothermographic materials. It is desirable in many cases to use an acrylamide polymer both as a component of polymer layer (II) and as a binder for layer (I). Useful acrylamide polymers for this purpose are within the described formulae.

Various supports are useful for the described photothermographic element. Typical supports include those film supports which can withstand processing temperatures employed for developing an image in a photothermographic element of the invention. Such film supports include, for example, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film, film supports as described in U.S. Pat. No. 3,634,089 of Hamb issued Jan. 11, 1972, and U.S. Pat. No. 3,725,070 of Hamb et al. issued Apr. 3, 1973, and related films or resinous materials. Other useful supports include glass, paper, metal and the like. Typically, a flexible support is employed.

The photothermographic elements according to the invention can contain addenda commonly employed in photothermographic elements, such as antistatic and/or conducting layers, plasticizers, lubricants, surfactants, matting agents, sensitizing dyes, brightening agents, light-absorbing materials, filter dyes, antihalation dyes, absorbing dyes and the like.

If desired, a toning agent can be employed in the photothermographic element of the invention to provide a desired image. Useful toning agents include, for example, certain heterocyclic compounds which can provide a more neutral tone image. Examples of useful toning agents include 3-mercapto-1,2,4-triazole and 2,4-dimercaptopyrimidine, described in copending U.S. application Ser. No. 466,331, of White, filed May 2, 1974.

The various components of the photothermographic materials of the invention can be added from water solutions, or suitable organic solvents can be useful to aid in addition. The components can be mixed using various procedures known in the photographic art.

It is desirable in some cases to incorporate a hardener, especially an aldehyde hardener like formaldehyde, into the described acrylamide polymer materials. This can provide improved incubation stability. A range of concentration of the aldehyde hardener can be employed depending upon such factors as the particular acrylamide polymer, particular components of the photothermographic element, desired image, desired stability and the like. Typically, a concentration of about 0.1 to about 10%, such as about 0.1 to about 5%, by weight of aldehyde hardener, particularly formaldehyde, is incorporated in the acrylamide polymer before coating on the photothermographic element. In some cases, it is desirable to incorporate the aldehyde hardener in the acrylamide polymer when the acrylamide polymer is coated directly on the support before coating of the photothermographic layer. The aldehyde hardener, however, can be employed in any one or more of the layers of the photothermographic element.

In some cases, improved incubation stability is observed when the photothermographic element containing the aldehyde hardener is stored for a period of time, such as about at least 2 days, before imagewise exposure and processing as described. It is believed that this storage time permits a crosslinking of the polymer in the photothermographic element. However, the exact mechanism which results in the improved incubation stability is not fully understood.

An especially useful embodiment of the invention comprises a photothermographic element comprising a support having thereon, respectively, (A) a layer comprising about 1.08 g./$m.^2$ of support of poly(acrylamide-co-1-vinylimidazole) (weight ratio 90:10) containing 1% by weight of formaldehyde, (B) a photothermographic layer containing photographic silver iodide in association with a silver salt of a heterocyclic thione as described, a hydroquinone reducing agent for the silver salt of the heterocyclic thione, and a synthetic polymeric binder comprising poly(acrylamide-co-2-acetoacetoxyethyl mmethacrylate) (weight ratio 98:2) or poly(acrylamide-co-1-vinylimidazole) (weight ratio 90:10), and (C) an overcoat layer comprising about 1.08 g./$m.^2$ of support of poly(acrylamide-co-1-vinylimidazole (weight ratio 90:10).

A range of concentration of the described acrylamide polymer can be useful in an overcoat on the described photothermographic element according to the invention. While such factors as the particular photothermographic materials, the particular acrylamide copolymer, processing temperature and the like will influence the optimum concentration range of acrylamide copolymer in the overcoat layer, typically a concentration of about 0.3 to about 7.5 g., such as about 0.4 to about 2.15 g., of acrylamide copolymer in the overcoat layer per $m.^2$ of support is useful.

In some cases, it is desirable to incorporate a portion of the described reducing agent in the acrylamide copolymer layers as described. While the concentration which is most useful of the described reducing agent will depend upon the described factors, such as particular reducing agent, desired image, processing temperature, particular acrylamide polymer and the like, a useful reducing agent concentration range in the acrylamide copolymer when the acrylamide copolymer is used as an overcoat is typically about 0.25 to about 0.55 g. of reducing agent per $m.^2$ of support. When the reducing agent is employed in an acrylamide polymer layer between the support and the photothermographic layer, typically a concentration of about 2.15 to about 4.30 g. of reducing agent is used per $m.^2$ of support.

Various imagewise-exposure means are useful with the photothermographic materials according to the invention. Photothermographic materials according to the invention are typically sensitive to the ultraviolet and blue regions of the spectrum and exposure means which provide this radiation are preferred. Typically, a photothermographic element according to the inven-

tion is exposed imagewise with a visible light source such as a tungsten lamp.

A visible image can be developed in a photothermographic element as described, after imagewise exposure, within a short time by overall heating of the photothermographic element. For example, the photothermographic element can be overall heated for about 1 to about 90 sec. at a temperature of about 100° to about 200° C., preferably about 140° to about 170° C. Usually, the time of heating is less than about 20 sec., such as about 1 to about 4 sec., at a temperature of about 150° to about 170° C. Increasing or decreasing the length of time of heating can enable use of a lower or higher temperature within the described range.

Any suitable means can be useful for providing the desired processing temperature range. The heating means can be, for example, a simple hot plate, iron or roller; or hot-air convection heating means; or dielectric heating means.

The described acrylamide polymers can be useful in various layers of photothermographic materials known in the art, such as materials described in U.S. Pat. No. 3,589,903 of Birkeland issued June 29, 1971, U.S. Pat. No. Reissue 26,719 of Sorenson et al. issued Nov. 18, 1969, U.S. Pat. No. 3,429,706 of Shepard et al. issued Feb. 25, 1969, U.S. Pat. No. 3,645,739 of Ohkubo et al. issued Feb. 29, 1972, U.S. Pat. No. 3,515,559 of Druker et al. issued June 2, 1970, and U.S. Pat. No. 3,672,904 of DeMauriac issued June 27, 1972. The described acrylamide polymers can be useful in thermographic materials also. Thermographic materials in which the acrylamide polymers can be useful are described, for example, in U.S. Pat. Nos. 2,910,377 and 3,094,417 of Workman issued June 18, 1963. Selection of an optimum acrylamide polymer as described for use in one or more layers of the photothermographic materials or thermographic materials described in the above art will depend upon such factors as the compatability of the acrylamide polymer with the other components of the photothermographic or thermographic material, the desired image, processing temperature and the like. Preferably, the acrylamide polymers described are used with hydrophilic materials such as photothermographic materials coated from aqueous formulations.

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

EXAMPLE 1

A photothermographic element (A) was prepared as follows. The following components were mixed and then coated on a resin-coated paper support at the designated concentrations:

poly(vinyl alcohol) as a binder	2.15 g./m.²
hydroquinone	1.62 mg./m.²

The resulting layer was designated layer (1).

The following components were mixed and then coated on layer (1):

poly(vinyl alcohol) as a binder	0.38	g./m.²
surfactant (Surfactant 10G which is a nonylphenoxypolyglycidol sold by Rohm and Haas Co., U.S.A.	0.008	g./m.²
total silver as silver iodide and silver complex of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione	0.75–.81	g./m.²
i) 10% by weight of silver as silver iodide in a gelatino emulsion		
ii) 90% by weight of silver as a 1.6:1 (molar ratio) of silver to 3-carboxymethyl-4-methyl-4-thiazoline-2-thione		

The resulting layer was designated as layer (2).

Poly(acrylamide-co-2-acetoacetoxyethyl methacrylate) (weight ratio 98:2) (inherent viscosity 1.40) measured in 1.0 N NaCl solution at a concentration of 0.25 g./dl. at a temperature of 25° C. was then coated on layer (2) at the concentration of 7.26 g. of the acrylamide copolymer per m.² of support. The acrylamide copolymer layer was designated layer (3).

The resulting photothermographic element was packaged in a so-called double paper envelope, that is, a black paper envelope inside a yellow paper envelope. The double paper envelope was stored in a controlled temperature-relative humidity chamber at 38° C. and 50% relative humidity. After 7 days and after 14 days, samples of the photothermographic element were removed from the double paper envelope and imagewise-exposed for 10^{-3} sec. to xenon light in a sensitometer. The samples of exposed photothermographic element were uniformly heated after exposure by passing them over a metal roller for 4 sec. at 160° C. A developed image was observed in each of the samples. The Dmax, Dmin and photographic speed for each of the images in the samples were the same as those of an image developed in an equivalent photothermographic element with the exception that the imagewise exposure and image development were carried out without storing the photothermographic element for a period of time.

EXAMPLE 2

This is a comparative example.

A control photothermographic element (B) was prepared as in Example 1 without the described acrylamide copolymer overcoat (layer 3), and then imagewise-exposed and developed in the same manner as in Example 1. This control photothermographic element provided no acceptable developed image after storage for 14 days under the described incubation conditions in a double paper envelope.

EXAMPLE 3

This is a comparative example.

Another control photothermographic element (C) was prepared as in Example 1 without the described acrylamide copolymer overcoat (layer 3) and with hydroquinone in layer 2 at a concentration of 1.62 g./m.². This control photothermographic element provided no acceptable developed image after storage for 14 days under the described incubation conditions in a double paper envelope.

EXAMPLES 4–10

A photothermographic element was prepared as follows.

The following components were mixed and then coated on a resin-coated paper support:

poly(vinyl alcohol) as a binder	0.38	g./m.²
surfactant (Surfactant 10G)	0.008	g./m.²

-Continued

total silver as silver iodide and silver complex of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione i) 10% by weight of silver as silver iodide gelatino emulsion ii) 90% by weight of silver as 1.6:1 (molar ratio) of silver to 3-carboxymethyl-4-methyl-4-thiazoline-2-thione	0.81	g./m.²
t-butylhydroquinone	1.40–1.50	g./m.²
3-mercapto-1,2,4-triazole	0.011	g./m.²

The resulting photothermmographic layer was overcoated with the polymers designated in the polymer column of following Table 1.

The overcoated photothermographic element was imagewise-exposed to tungsten light in a sensitometer for 5 sec. The exposed photothermographic element was overall heated by contacting it with a metal block at 160° C. for 4 sec. Similar samples of the photothermographic element were incubated in a double paper envelope at 38° C. and 50% relative humidity for up to 15 days. The resulting samples were then imagewise-exposed and overall heated as above. The Dmin, Dmax and relative photographic speed values for each photothermographic element are given in following Table 1.

Table 1

Example No.	Incubation	Dmin	Dmax	Log E Relative Speed at 0.6 Density Above Dmin	Polymer Overcoat
4	fresh	0.08	1.36	reference point	no overcoat
	7 days	0.07	1.20	−0.90	
	14 days	0.06	1.02	−1.07	
5	fresh	0.05	1.08	+0.08	1.08 g./m.² of poly(acrylamide-co-2-acetoacetoxyethyl methylacrylate)(weight ratio 98:2) (polymer VII)
	7 days	0.05	1.11	−0.30	
	15 days	0.07	1.28	−0.31	
6	fresh	0.06	1.13	+0.04	2.15 g./m.² of equal parts by weight of polymer VII and poly(vinyl alcohol)
	7 days	0.10	1.12	+0.04	
	15 days	0.07	1.28	+0.04	
7	fresh	0.06	1.32	−0.08	double overcoat; first overcoat consisting of 1.08 g./m.² of polymer VII and a top overcoat consisting of 1.08 g./m.² of poly(vinyl alcohol)
	7 days	0.08	1.24	−0.04	
	14 days	0.08	1.30	−0.12	
8*	fresh	0.09	0.94	same as ref.	0.54 g./m.² of sulfoethylcellulose
	4 days	0.13	1.21	+0.06	
	13 days	0.05	1.18	−0.48	
9*	fresh	0.16	0.96	+0.02	1.08 g./m.² of sodium cellulose sulfate
	4 days	0.08	1.17	+0.11	
	13 days	0.14	1.28	−0.04	
10	fresh	0.09	1.16	+0.06	2.15 g./m.² of equal parts by weight of poly(acrylamide-co-acrylic acid) and poly(vinyl alcohol)
	4 days	0.09	1.16	+0.06	
	13 days	0.09	1.29	−0.18	

*comparative example

EXAMPLE 11

This is a comparative example.

A resin-coated paper support was coated with 1.08 g./m.² of polymer VII containing 1% by weight of formaldehyde based on the weight of the polymer. This was designated as layer (1).

On layer (1) was coated a photothermographic composition containing:

3-mercapto-1,2,4-triazole	0.022	g./m.²
isopropylhydroquinone	1.62	g./m.²
Surfactant 10G	0.008	g./m.²
total silver as silver iodide and silver complex of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione i) 10% by weight of silver as silver iodide in a gelatino emulsion ii) 90% by weight of silver as a 1.6:1 (molar ratio) of silver to 3-carboxymethyl-4-methyl-4-thiazoline-2-thione	0.81	g./m.²

The resulting layer was designated as layer (2).

The resulting photothermographic element was imagewise-exposed to tungsten light as described in Examples 4–10 and then overall heated by contacting the element with a metal block at 160° C. for 4 sec. A developed image is observed. The image had the sensitometric properties given in following Table 2.

EXAMPLE 12

The procedure in Example 11 was repeated with the exception that an overcoat containing 1.08 g./m.² of poly(acrylamide-co-2-acetoacetoxyethyl methacrylate) (weight ratio 98:2) was applied to layer (2) prior to imagewise exposure. The resulting sensitometric properties are reported in following Table 2.

Table 2

Example No.	Incubation (38° C. at 50% Relative Humidity	Dmax	Log E Relative Speed at 0.6 Density Above Dmin
11	fresh	1.3	reference point
	1 week	1.3	−.1
	2 weeks	0.64	>−3
12	fresh	1.08	reference point
	1 week	1.08	−.06
	2 weeks	0.98	−.14
	3 weeks	1.16	−.14

EXAMPLE 13

A photothermographic element was prepared as follows:

A resin-coated paper support was coated with a layer comprising a mixture of the following:

poly(acrylamide-co-2-acetoacetoxyethyl)methacrylate (weight ratio 98:2)	2.42	g./m.²
tertiary-butylhydroquinone	1.61	g./m.²
Surfactant 10G	0.008	g./m.²

The resulting layer was designated as layer (1).

A photothermographic coating was then applied to layer (1). This photothermographic coating was designated as layer (2). Layer (2) was the same as layer (1) described in Example 11 with the exception that the layer contained 0.40 g./m.² of tertiary-butylhydroquinone.

The resulting photothermographic element was im-

agewise-exposed and then overall heated to develop an image as described in Example 1.

The sensitometric results of the photothermographic element are given in following Table 3, including the results from incubation.

Table 3

Incubation (38° C. at 50% Relative Humidity	Dmax	Log E Relative Speed at 0.6 Density Above Dmin
fresh	1.2	reference point
1 week	1.2	+.06
2 weeks	1.15	−.2
3 weeks	1.1	−.2

EXAMPLES 14–25

In each of the following examples, a photothermographic element was prepared by coating the following composition on a resin-coated paper support at the designated concentrations:

silver iodide gelatino emulsion	0.075	g. Ag/m.²
silver complex of 3-carboxy-methyl-4-methyl-4-thiazoline-2-thione	0.68	g. Ag/m.²
tertiary-butylhydroquinone	1.88	g./m.²
3-mercapto-1,2,4-triazole	0.0094	g./m.²
2,4-dimercaptopyrimidine	0.0024	g./m.²
Surfactant 10G	0.008	g./m.²

Imagewise exposure was to tungsten light for 4 seconds and processing of the photothermographic element was carried out by overall heating the exposed element for 4 seconds at 155°C. The sensitometric results, polymer location and particular polymers employed for Examples 14–25 are described in following Table 4.

EXAMPLES 26–37

The procedure described in Examples 14–25 was repeated with the exception that 2% by weight formaldehyde was added to each of the described polymer layers. The resulting photothermographic element was imagewise-exposed and processed as described in Example 1. The sensitometric results, particular polymer location are given in following Table 5.

Table 4

Example	Polymer Location*** U-ct	T-ct	Polymer**	Fresh Relative Speed*	Contrast	Dmin	Dmax	1 Wk./37.8° C./50% RH Relative Speed*	Contrast	Dmin	Dmax
14		X	V	100	1.41	0.03	1.05	25	1.04	0.03	1.03
15	X	X	V	82	1.21	0.05	0.97	16.5	0.77	0.05	0.80
16		X	VI	62	1.07	0.02	1.16	9.1	0.42	0.02	0.45
17	X	X	VI	31	0.67	0.05	0.90	3.2	0.34	0.05	0.40
18		X	VII	89	1.26	0.02	1.06	18.5	0.48	0.02	0.78
19	X	X	VII	50	1.00	0.05	0.95	11.8	0.62	0.07	0.74
20		X	VIII	94	1.29	0.03	1.12	28	0.65	0.03	0.93
21	X	X	VIII	73	1.09	0.05	1.00	15.5	0.50	0.05	0.66
22		X	IX	69	1.09	0.02	1.16	25	0.59	0.02	0.90
23	X	X	IX	19.5	0.60	0.05	0.82	6.5	0.42	0.05	0.54
24		X	I	83	1.08	0.02	1.18	32.5	0.65	0.02	0.98
25	X	X	I	63	0.97	0.03	1.06	22.5	0.57	0.03	0.64

*relative speed measured at 0.30 above Dmin; 4 sec. imagewise exposure to tungsten light; processed 4 sec./155° C.
**all polymers coated at 1.08 g./m.²
***U-ct means a coating directly on the support and under the photothermographic layer; T-ct means a coating directly on the photothermographic layer

Table 5

Example	Polymer Location U-ct	T-ct	Fresh Relative Speed**	Contrast	Dmin	Dmax	1 Wk./37.8° C./50% RH Relative Speed**	Contrast	Dmin	Dmax	Polymer*
26		X	100	1.25	0.01	1.10	28	0.65	0.01	0.94	V
27	X	X	107	1.26	0.07	0.78	57	1.14	0.08	1.02	V
28		X	53	0.91	0.01	1.06	25	0.70	0.01	0.82	VI
29	X	X	29	0.85	0.06	0.93	8.5	0.51	0.07	0.48	VI
30		X	95	1.22	0.01	1.05	43	0.86	0.01	1.05	VII
31	X	X	89	1.07	0.08	0.76	57	1.21	0.10	0.90	VII
32		X	95	1.25	0.01	1.06	41	0.75	0.01	1.06	VIII
33	X	X	107	1.15	0.06	0.72	105	1.28	0.09	0.86	VIII
34		X	69	1.06	0.01	1.19	27	0.63	0.01	0.90	IX
35	X	X	32.5	1.12	0.06	1.03	20	0.97	0.08	1.08	IX
36		X	100	1.40	0.01	1.10	54	1.06	0.01	1.20	I
37	X	X	107	1.22	0.01	0.84	87	1.40	0.03	1.10	I

*all polymers at 1.08 g./m.²
**relative speed measured at 0.30 above Dmin

EXAMPLE 38

Results similar to Examples 14–25 were observed when 0.43 g./m.^{2} of polymer VII was employed as a binder in the photothermographic layer and the described overcoat layer comprised polymer I having the weight ratios of 60:40, 80:20, 90:10 or 95:5. The sensitometric results provided with these materials are given in following Table 6.

orthosilicate was employed in both the undercoat layer and the overcoat layer for the photothermographic element according to Example 43. Each of the photothermographic elements contained 0.43 g. polymer VII per m.^{2} as a binder in the photothermographic layer. Imagewise exposure and processing were carried out as described in Example 11. The sensitometric results are given in following Table 8.

Table 8

	Fresh				1 Wk./37.8° C./50% RH				
Example	Relative Speed*	Contrast	Dmin	Dmax	Relative Speed*	Contrast	Dmin	Dmax	Polymer
43	68	0.76	0.02	1.04	17.5	0.55	0.02	0.69	IV
44	89	0.94	0.02	1.00	74	0.87	0.02	1.00	III
45	83	0.82	0.02	0.90	29	0.80	0.02	0.90	II
46	17.2	0.63	0.02	0.65	—	—	0.02	0.10	**
47	100	0.91	0.02	1.10	85	1.04	0.02	1.03	I

*relative speed measured at 0.30 above Dmin
**poly(1-vinyl-2-pyrrolidone) (comparative example)

Table 6

	Fresh				1 Wk./37.8° C./50% RH				
Example	Relative Speed**	Contrast	Dmin	Dmax	Relative Speed**	Contrast	Dmin	Dmax	Weight Ratio of Monomers Used to Prepare Polymer*
38A	100	1.07	0.01	1.26	45	0.94	0.01	0.80	(60:40)
38B	97	1.23	0.01	1.17	62	0.88	0.01	1.02	(80:20)
38C	132	1.16	0.01	1.22	59	1.00	0.01	1.11	(90:10) (polymer I)
38D	87	1.11	0.01	1.12	45	1.22	0.01	0.92	(95:5)

*all polymers at 1.08 g./m.^{2} in overcoat layer; polymer is poly(acrylamide-co-1-vinylimidazole)
**relative speed measured at 0.30 above Dmin

EXAMPLES 39–42

The photothermographic element as described in Example 38 was used, with the exception that an overcoat layer was used comprising 1.08 g./m.^{2} of polymer I and a layer was used between the resin-coated paper support and the photothermographic layer also comprising polymer I. The resulting photothermographic element was imagewise-exposed and processed as described in Example 14. The developed image resulting and the sensitometric properties of the developed image are given in following Table 7.

The described polymer (A) useful in photothermographic materials are most conveniently prepared as solution polymers and then used as such without isolation. Some of the resulting polymer solutions have rather high pH and should be adjusted to the desired coating pH, usually about pH 4, prior to coating.

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.

Table 7

	Fresh				1 Wk./37.8° C./50% RH				
Example	Relative Speed**	Contrast	Dmin	Dmax	Relative Speed**	Contrast	Dmin	Dmax	Weight Ratio of Monomers Used to Prepare Polymer*
39	100	0.60	0.08	0.88	63	0.40	0.08	0.55	(60:40)
40	302	1.24	0.02	1.18	246	1.11	0.02	1.18	(80:20)
41	339	1.07	0.02	1.10	289	1.48	0.02	1.26	(90:10) (polymer I)
42	316	0.95	0.02	1.00	276	1.60	0.02	1.20	(95.5)

*all polymers at 1.08 g./m.^{2} in undercoat layer and overcoat layer; formaldehyde is present only in the undercoat layer; the polymer is used in each of the overcoat and undercoat layers; the polymer is poly(acrylamide-co-1-vinylimidazole)
**relative speed measured at 0.30 above Dmin

EXAMPLES 43–47

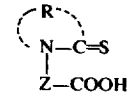
A photothermographic element was prepared as described in Examples 14–25, with the exception that the polymers indicated in following Table 8 were used as an undercoat layer and an overcoat layer at 1.08 g./m.^{2} of support each. Except for Example 43, the undercoat layers in each photothermographic element contained 2% by weight formaldehyde. The formaldehyde was not present in the overcoat layer. Hydrolyzed tetraethyl

What is claimed is:

1. In a photothermographic element comprising a support having thereon (I):

a. photographic silver halide in association with

b. a silver salt of a heterocyclic thione, said heterocyclic thione being represented by the formula:



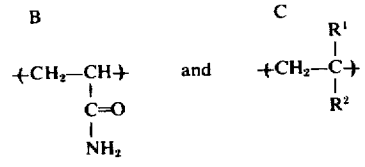
(XX)

wherein R represents atoms completing a 5-member heterocyclic nucleus and Z is alkylene containing 1 to 30 carbon atoms,

c. an organic reducing agent for said silver salt of a heterocyclic thione, and

d. a polymeric, synthetic binder and

contiguous to (I), at least one polymer layer (II), the improvement wherein said polymer layer (II) comprises at least 50% by weight of a polymer (A) comprising the repeating units represented by the formulas:



wherein:

R^1 is hydrogen or alkyl containing 1 to 4 carbon atoms;

R^2 is an imidazolyl, N-substituted carbamoyl, 2-pyrrolidonyl, acetoacetoxyethoxycarbonyl, acetoacetonylmethylphenyl, ethoxycarbonylaceto, pyridyl, hydroxy, hydroxyalkyl containing 1 to 4 carbon atoms, carboxy, carboxyethoxycarbonyl, a heterocyclic ammonium salt group having a 5- or 6-membered azonia nitrogen-containing ring, or a pyridinium salt group, and

the weight ratio of starting monomers for said units B and C is, respectively, about 60:40 to 100:0.

2. A photothermographic element as in claim **1** also comprising in said layer (II) at least one polymer other than said copolymer (A).

3. A photothermographic element as in claim **1** wherein said copolymer (A) comprises at least 50% by weight of poly-(acrylamide-co-3-methyl-1-vinylimidazolium methosulfate).

4. A photothermographic element as in claim **1** wherein said copolymer (A) comprises at least 50% by weight of poly-(acrylamide).

5. A photothermographic element as in claim **1** wherein said copolymer (A) comprises at least 50% by weight of poly-(acrylamide-co-1-vinylimidazole).

6. A photothermographic element as in claim **1** wherein said copolymer (A) comprises at least 50% by weight of poly-(acrylamide-co-2-methyl-1-vinylimidazole).

7. A photothermographic element as in claim **1** wherein said copolymer (A) comprises at least 50% by weight of poly-(acrylamide-co-1-vinyl-2-pyrrolidone).

8. A photothermographic element as in claim **1** comprising a support having thereon, in sequence:

I. a layer of poly(acrylamide-co-1-vinylimidazole), wherein the weight ratio of starting monomers for said copolymer is, respectively, about 60:40 to about 98:2.

II. a photothermographic layer comprising:

a. photographic silver iodide in association with

b. a silver salt of a heterocyclic thione selected from the group consisting of silver salts of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione, 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione, 3-(2-carboxyethyl)benzothiazoline-2-thione, 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione, and combinations thereof,

c. t-butylhydroquinone, and

d. a poly(acrylamide-co-2-acetoacetoxyethyl methacrylate or poly(acrylamide-co-1-vinylimidazole) binder, and

III. an overcoat layer of poly(acrylamide-co-1-vinylimidazole) wherein the weight ratio of starting monomers for said copolymer is, respectively, about 60:40 to about 98:2.

9. A photothermographic element as in claim **1** wherein said layer (II) also comprises a silver halide developing agent.

10. A photothermographic element as in claim **1** wherein said layer (II) comprises about 0.40 to about 2.15 g. of said copolymer (A) per $m.^2$ of said support.

11. A photothermographic element as in claim **1** wherein said polymeric synthetic binder comprises a polymer selected from the group consisting of poly(acrylamide), poly(acrylamide-co-2-acetoacetoxyethyl methacrylate), poly(acrylamide-co-α-chloroacrylic acid), poly(acrylamide-co-1-vinylimidazole), poly-(vinyl alcohol), and combinations thereof.

12. A photothermographic element as in claim **1** also comprising a hardener in said layer (II).

13. A photothermographic element as in claim **1** also comprising a aldehyde hardener in said layer (II).

14. A photothermographic element as in claim **1** also comprising a 3-mercapto-1,2,4-triazole toner.

15. A photothermographic element as in claim **1** also comprising a 2,4-dimercaptopyrimidine toner.

16. A process of developing a latent image in a photothermographic element as defined in claim **1** comprising heating said element to a temperature of about 80° to about 200° C.

17. A process as in claim **16** wherein said photothermographic element is heated for about 0.5 to about 60 sec.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

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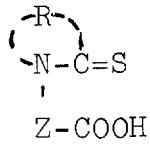
DATED : July 8, 1975

INVENTOR(S) : Richard C. Sutton and Heinz E. Stapelfeldt

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

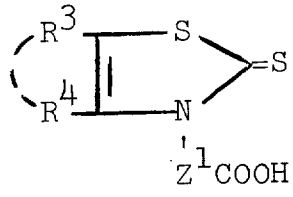
Column 3, line 20, "80°" should read ---80°C.---.

Column 5, line 25, the formula should read as follows:



(XX)

Column 6, line 60, "especially" should read ---Especially. Line 65, the formula should read as follows:



(XXI)

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

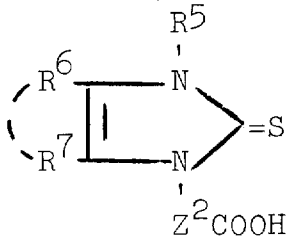
PATENT NO. : 3,893,860

DATED : July 8, 1975

INVENTOR(S) : Richard C. Sutton and Heinz E. Stapelfeldt

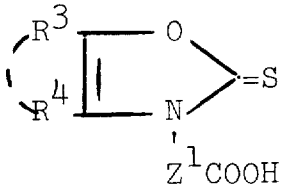
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 15, the formula should read as follows:



(XXII)

Column 7, line 35, the formula should read as follows:



(XXIII)

Column 8, line 30, "38°" should read ---38°C---.

Column 10, line 30, "mmethacrylate" should read ---methacrylate---.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,893,860

DATED : July 8, 1975

INVENTOR(S) : Richard C. Sutton and Heinz E. Stapelfeldt

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

Column 11, line 8, "100°" should read ---100°C.---. Line 9, "140°" should read ---140°C.---. Line 12, "150°" should read ---150°C.---.

Column 13, line 13, "photothermmographic" should read ---photothermographic---.

Column 16, lines 22-23, "particular polymer location" should read ---particular polymer and polymer location---.

Column 20, line 40, "a aldehyde" should read ---an aldehyde---.

Signed and Sealed this

twentieth Day of *April 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks