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(54) ELEMENTS PHOTOTHERMOGRAPHIQUES ET THERMOGRAPHIQUES NOIRS ET BLANCS CONTENANT DES COMPOSES DE PROPENENITRILE SUBSTITUES AGISSANT COMME ANTIVOILES

(54) BLACK-AND-WHITE PHOTOTHERMOGRAPHIC AND THERMOGRAPHIC ELEMENTS CONTAINING SUBSTITUTED PROPENENITRILE COMPOUNDS AS ANTIFOGGANTS

(57) Certains composés de propènenitrile se sont avérés agir comme des antivoiles et permettent d'améliorer la densité minimale initiale des éléments photothermographiques et thermographiques noirs et blancs.

(57) Certain propenenitrile compounds have been found to function as antifoggants and serve to improve the initial minimum density of black-and-white photothermographic and thermographic elements.

PCT

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(57) Abstract

Certain propenenitrile compounds have been found to function as antifoggants and serve to improve the initial minimum density of black-and-white photo-thermographic and thermographic elements.

BLACK-AND-WHITE PHOTOTHERMOGRAPHIC AND THERMOGRAPHIC ELEMENTS CONTAINING SUBSTITUTED PROPENENITRILE COMPOUNDS AS ANTIFOGGANTS

BACKGROUND OF THE INVENTION

Field of Invention:

Certain substituted propenenitrile compounds are useful as antifoggants to reduce initial Dmin of black-and-white photothermographic and thermographic elements.

Background of the Art:

Silver halide-containing, photothermographic imaging materials (i.e., heat-developable photographic elements) which are developed with heat, without liquid development have been known in the art for many years. These materials are also known as "dry silver" compositions or emulsions and generally comprise a support having coated thereon: (a) a photosensitive compound that generates silver atoms when irradiated; (b) a relatively non-photosensitive, reducible silver source; (c) a reducing agent (i.e., a developer) for silver ion, for example for the silver ion in the non-photosensitive, reducible silver source; and (d) a binder.

The photosensitive compound is generally photographic silver halide which must be in catalytic proximity to the non-photosensitive, reducible silver source. Catalytic proximity requires an intimate physical association of these two materials so that when silver atoms (also known as silver specks, clusters, or nuclei) are generated by irradiation or light exposure of the photographic silver halide, those silver atoms are able to catalyze the reduction of the reducible silver source. It has long been understood that silver atoms (Ag^{o}) are a catalyst for the reduction of silver ions, and that the photosensitive silver halide can be placed into catalytic proximity with the non-photosensitive, reducible silver source in a number of different fashions. The silver halide may be made *"in situ,"* for example by adding a halogen-containing source to the reducible silver source to achieve partial metathesis (see, for example, U.S. Patent No. 3,457,075); or by coprecipitation of silver halide and the reducible silver source material (see, for example, U.S. Patent No. 3,839,049). The silver halide may also be made *"ex situ"* (i.e., be pre-formed) and added to the organic silver salt. The addition of silver halide grains to photothermographic materials is described in *Research Disclosure*, June 1978, Item No. 17029. It is also reported in the art that when silver halide is made *ex situ,* one has the possibility of controlling the composition and size of the grains much more precisely, so that one can impart more specific properties to the photothermographic element and can do so much more consistently than with the *in situ* technique.

The non-photosensitive, reducible silver source is a material that contains silver ions. Typically, the preferred non-photosensitive reducible silver source is a silver salt of a long chain aliphatic carboxylic acid having from 10 to 30 carbon atoms. The silver salt of behenic acid or mixtures of acids of similar molecular weight are generally used. Salts of other organic acids or other organic materials, such as silver imidazolates, have been proposed. U.S. Patent No. 4,260,677 discloses the use of complexes of inorganic or organic silver salts as non-photosensitive, reducible silver sources.

In both photographic and photothermographic emulsions, exposure of the photographic silver halide to light produces small clusters of silver atoms (Ag^o). The imagewise distribution of these clusters is known in the art as a latent image. This latent image is generally not visible by ordinary means. Thus, the photosensitive emulsion must be further developed to produce a visible image. This is accomplished by the reduction of silver ions which are in catalytic proximity to silver halide grains bearing the clusters of silver atoms (i.e., the latent image). This produces a black-and-white image. In photographic elements, the silver halide is reduced to form the black-and-white image. In photothermographic elements, the light-insensitive silver source is reduced to form the visible black-and-white image while much of the silver halide remains as silver halide and is not reduced.

In photothermographic elements the reducing agent for the organic silver salt, often referred to as a "developer," may be any material, preferably any organic material, that can reduce silver ion to metallic silver. At elevated temperatures, in the presence of the latent image, the silver ion of the non-photosensitive reducible silver source (e.g., silver behenate) is reduced by the reducing agent for silver ion. This produces a negative black-and-white image of elemental silver.

While conventional photographic developers such as methyl gallate, hydroquinone, substituted-hydroquinones, catechol, pyrogallol, ascorbic acid, and ascorbic acid derivatives are useful, they tend to result in very reactive photothermographic formulations and cause fog during preparation and coating of photothermographic elements. As a result, hindered phenol reducing agents have traditionally been preferred.

Thermographic imaging constructions (i.e., heat-developable materials) processed with heat, and without liquid development, are widely known in the imaging arts and rely on the use of heat to help produce an image. These elements generally comprise a support or substrate (such as paper, plastics, metals, and glass) having coated thereon: (a) a thermally-sensitive, reducible silver source; (b) a reducing agent for the thermally-sensitive, reducible silver source (i.e., a developer); and (c) a binder.

In a typical thermographic construction, the image-forming layers are based on silver salts of long chain fatty acids. Typically, the preferred non-photosensitive reducible silver source is a silver salt of a long chain aliphatic carboxylic acid having from 10 to 30 carbon atoms. The silver salt of behenic acid or mixtures of acids of similar molecular weight are generally used. At elevated temperatures, silver behenate is reduced by a reducing agent for silver ion such as methyl gallate, hydroquinone, substituted-hydroquinones, hindered phenols, catechol, pyrogallol, ascorbic acid, and ascorbic acid derivatives, whereby an image of elemental silver is formed.

Some thermographic constructions are imaged by contacting them with the thermal head of a thermographic recording apparatus, such as a thermal printer, and thermal facsimile. In such instances, an anti-stick layer is coated on top of the imaging layer to prevent sticking of the thermographic construction to the thermal head of the apparatus utilized. The resulting thermographic construction is then heated to an elevated temperature, typically in the range of 60°-225°C, resulting in the formation of an image.

The imaging arts have long recognized that the fields of photothermography and thermography are clearly distinct from that of photography. Photothermographic and thermographic elements differ significantly from conventional silver halide photographic elements which require wet-processing. See for example the discussion in U.S. Patent No. 5,637,449 and in U.S. Patent No. 5,545,507.

Distinctions between photothermographic and photographic elements are also described in *Imaging Processes and Materials (Neblette's Eighth Edition);* J. Sturge et al. Ed; Van Nostrand Reinhold: New York, 1989; Chapter 9 and in *Unconventional Imaging Processes;* E. Brinckman et al, Ed; The Focal Press: London and New York: 1978; pp. 74-75.

Various techniques are typically employed to try and gain higher sensitivity in a photothermographic element. In efforts to make more sensitive photothermographic elements, one of the most difficult parameters to maintain at a very low level is the various types of fog or Dmin. Fog is spurious image density which appears in non-imaged areas of the element after development and is often reported in sensitometric results as Dmin. Photothermographic emulsions, in a manner similar to photographic emulsions and other light-sensitive systems, tend to suffer from fog.

Traditionally, photothermographic elements have suffered from fog upon coating and drying. The fog level in the non-exposed areas of freshly prepared and imaged photothermographic and thermographic elements will be referred to herein as “initial fog” or “initial Dmin.”

In addition, the fog level of photothermographic elements often rises as the element is stored, or “ages.” This type of fog will be referred to herein as “shelf-aging fog.” Adding to the difficulty of fog control on shelf-aging is the fact that the developer is incorporated in the photothermographic element. This is not the case in most silver halide photographic systems. A great amount of work has been done to improve the shelf-life characteristics of photothermographic elements.

A third type of fog in photothermographic systems results from the instability of the image and/or background after processing. The photoactive silver halide still present in the developed image may continue to catalyze formation of metallic silver during room light handling or post-processing exposure such as in graphic arts contact frames. This is known as "post-processing fog" or "silver print-out."

Some of the problems with the addition of antifoggant stabilizers include thermal fogging during processing or loss of photographic sensitivity, maximum density, or contrast at effective stabilizer concentrations. Thus, there is a continued need for improved antifoggant stabilizer compounds that inhibit all types of fog and do not have any detrimental effects on the photothermographic element.

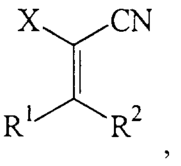
U.S. Patent No. 5,545,515 describes combinations of hindered phenol developers with acrylonitrile compounds as co-developers for black-and-white photothermographic and thermographic elements. A trityl hydrazide or a formyl phenylhydrazine co-developer may also be included.

SUMMARY OF THE INVENTION

Propenenitrile compounds have been found to be effective antifoggants to reduce initial fog and shelf aging fog in photothermographic and thermographic elements. These compounds provide both photothermographic and thermographic elements with improved Dmin without affecting other sensitometric properties. The present invention provides heat-developable, black-and-white photothermographic and thermographic elements which are capable of providing high photospeeds, stable images with high resolution, good sharpness, low Dmin, and good shelf stability.

The black-and-white photothermographic elements of the present invention comprise a support bearing at least one photosensitive, image-forming, photothermographic emulsion layer comprising:

(a) a photosensitive silver halide;
(b) a non-photosensitive, reducible silver source;
(c) a reducing agent for silver ion, e.g., the non-photosensitive, reducible silver source;
(d) a binder; and
(e) at least one substituted propenenitrile compound of the formula



wherein:

R^1 represents a hydroxy group or a metal salt of a hydroxy group (e.g., O^-M^+, wherein M^+ is a metal cation);

R^2 represents an alkyl group or an aryl group;

X represents an electron withdrawing group; or

R^2 and X taken together can form a ring containing the electron withdrawing group as an internal ring component.

The electron-withdrawing group X means a group which is at least as electron withdrawing as -COOR, where R is H, $-CH_3$ or $-CH_2CH_3$.

When the photothermographic element used in this invention is heat developed, preferably at a temperature of from 80°C to 250°C (176°F to 482°F) for a duration of from 1 second to 2 minutes, in a substantially water-free condition after, or simultaneously with, imagewise exposure, a black-and-white silver image is obtained.

In photothermographic elements of the present invention, the layer(s) that contain the photosensitive silver halide and non-photosensitive, reducible silver source are referred to herein as emulsion layer(s). According to the present invention, one or more propenenitrile compounds is added either to the emulsion layer(s) or to a layer(s) adjacent to the emulsion layer(s). Layers that are adjacent to the emulsion layer(s) may be, for example, protective topcoat layers, primer layers, interlayers, opacifying layers, antistatic layers, antihalation layers, barrier layers, auxiliary layers. It is preferred that the propenenitrile compounds be present in the photothermographic emulsion layer or topcoat layer.

The present invention also provides a process comprising the steps of:

(a) exposing the inventive photothermographic element on a support transparent to ultraviolet radiation or short wavelength visible radiation, to electromagnetic radiation to which the photosensitive silver halide of the element is sensitive, to generate a latent image;

(b) heating the exposed element to develop the latent image into a visible image;

(c) positioning the element with a visible image thereon between a source of ultraviolet or short wavelength visible radiation energy and an ultraviolet or short wavelength radiation photosensitive imageable medium; and

(d) thereafter exposing the imageable medium to ultraviolet or short wavelength visible radiation through the visible image on the element, thereby absorbing ultraviolet or short wavelength visible radiation in the areas of the element where there is a visible image and transmitting ultraviolet or short wavelength visible radiation through areas of the element where there is no visible image.

The photothermographic element may be exposed in step (a) with visible, infrared, or laser radiation.

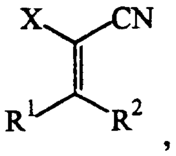
The heat-developable, black-and-white thermographic elements of the present invention comprise a support having coated thereon:

(a) a non-photosensitive, reducible silver source;

(b) a reducing agent for the silver ion, e.g., the non-photosensitive, reducible silver source;

(c) a binder; and

(d) at least one substituted propenenitrile compound of the formula



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wherein R^1, R^2, and X are as defined above.

In thermographic elements of the present invention, the layer(s) that contain the non-photosensitive reducible silver source are referred to herein as thermographic layer(s) or thermographic emulsion layer(s). When used in thermographic elements according to the present invention, one or more propenenitrile compounds is added either to the thermographic emulsion layer(s) or to a layer(s) adjacent to the emulsion layer(s). Layers that are adjacent to the emulsion layer(s) may be, for example, protective topcoat layers, primer layers, antistatic layers, interlayers, opacifying layers, barrier layers, auxiliary layers. It is preferred that the propenenitrile compounds be present in the thermographic layer or topcoat layer.

When the thermographic element used in this invention is heat developed, preferably at a temperature of from 80°C to 250°C (176°F to 482°F) for a duration of from 1 second to 2 minutes in a substantially water-free condition, a black-and-white silver image is obtained.

The present invention further provides a process comprising the steps of:

(a) heating the inventive thermographic element on a support transparent to ultraviolet radiation or short wavelength visible radiation at a temperature sufficient to generate a visible image thereon;

(b) positioning the thermographic element with a visible image thereon between a source of ultraviolet or short wavelength visible radiation and an ultraviolet or short wavelength visible radiation photosensitive imageable medium; and

(c) thereafter exposing the imageable medium to ultraviolet or short wavelength visible radiation through the visible image on the element, thereby absorbing ultraviolet or short wavelength visible radiation in the areas of the element where there is a visible image and transmitting ultraviolet or short wavelength visible radiation through areas of the element where there is no visible image.

The propenenitrile compounds used in this invention provide a significant improvement in Dmin when compared to photothermographic and thermographic elements not incorporating these compounds.

The photothermographic and thermographic elements of this invention may be used to prepare black-and-white images. The photothermographic material of this invention can be used, for example, in conventional black-and-white photothermography, in electronically generated black-and-white hardcopy recording, in the graphic arts area (e.g., phototypesetting), in digital proofing, and in digital radiographic imaging. The material of this invention provides low Dmin, high photospeeds, strongly absorbing black-and-white images, and a dry and rapid process.

Heating in a substantially water-free condition as used herein, means heating at a temperature of 80° to 250°C. The term "substantially water-free condition" means that the reaction system is approximately in equilibrium with water in the air, and water for inducing or promoting the reaction is not particularly or positively supplied from the exterior to the element. Such a condition is described in T. H. James, *The Theory of the Photographic Process,* Fourth Edition, Macmillan 1977, page 374.

As used herein:

"aryl" means any aromatic ring structure (including fused rings and substituted rings) and preferably represents phenyl or naphthyl.

"emulsion layer" means a layer of a photothermographic element that contains the photosensitive silver halide and non-photosensitive reducible silver source material; or a layer of the thermographic element that contains the non-photosensitive reducible silver source material.

"infrared region of the spectrum" means from 750 nm to 1400 nm; "visible region of the spectrum" means from 400 nm to 750 nm; and "red region of the spectrum" means from 640 nm to 750 nm. Preferably the red region of the spectrum is from 650 nm to 700 nm.

"photothermographic element" means a construction comprising at least one photothermographic emulsion layer and any supports, topcoat layers, image receiving layers, blocking layers, antihalation layers, subbing or priming layers.

"short wavelength visible region of the spectrum" means that region of the spectrum from 400 nm to 450 nm; and "thermographic element" means a construction comprising at least one thermographic emulsion layer and any supports, topcoat layers, image receiving layers, blocking layers, antihalation layers, subbing or priming layers.

"ultraviolet region of the spectrum" means that region of the spectrum less than or equal to 400 nm, preferably from 100 nm to 400 nm. More preferably, the ultraviolet region of the spectrum is the region between 190 nm and 400 nm;

In the foregoing-disclosed formulae R^2 and X may contain additional substituent groups. As is well understood in this area, substitution is not only tolerated, but is often advisable and substitution is anticipated on the compounds used in the present invention. As a means of simplifying the discussion and recitation of certain substituent groups, the terms "group" and "moiety" are used to differentiate between those chemical species that may be substituted and those which may not be so substituted. Thus, when the term "group," such as "aryl group," is used to describe a substituent, that substituent includes the use of additional substituents beyond the literal definition of the basic group. Where the term "moiety" is used to describe a substituent, only the unsubstituted group is intended to be included. For example, the phrase, "alkyl group" is intended to include not only pure hydrocarbon alkyl chains, such as methyl, ethyl, propyl, *t*-butyl, cyclohexyl, *iso*-octyl, and octadecyl, but also alkyl chains bearing substituents known in the art, such as hydroxyl, alkoxy, phenyl, halogen atoms (F, Cl, Br, and I), cyano, nitro, amino, carboxy. For example, alkyl group includes ether groups (e.g., CH_3-CH_2-CH_2-O-CH_2-), haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls. On the other hand, the phrase "alkyl moiety" is limited to the inclusion of only pure hydrocarbon alkyl chains, such as methyl, ethyl, propyl, *t*-butyl, cyclohexyl, *iso*-octyl, and octadecyl. Substituents that adversely react with other active ingredients, such as very strongly electrophilic or oxidizing substituents, would of course be excluded by the ordinarily skilled artisan as not being inert or harmless.

Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, examples, and claims.

DETAILED DESCRIPTION OF THE INVENTION

Photothermographic and thermographic systems have not found widespread use as replacement for wet silver halide in imaging systems because of slow speed, low Dmax, poor contrast, and insufficient sharpness at high Dmax. European Laid Open Patent Application No. 0 627 660 and U.S. Patent No. 5,434,043 describe most of the characteristics and attributes of a photothermographic element having, for example, an antihalation system, silver halide grains having an average particle size of less than 0.10 μm, and infrared supersensitization leading to an infrared photothermographic article meeting the requirements for medical or graphic arts laser recording applications.

To function effectively in the photothermographic and thermographic elements of this invention, the propenenitrile compounds are required to have an electron withdrawing group, X, attached to the same carbon atom as the nitrile group. The propenenitrile compounds are also required to have groups R^1 and R^2 attached at the position noted in the formulae.

As noted above, X is an electron withdrawing group. As used herein, the electron withdrawing nature of X is determined by its "Hammet σ_p value." The Hammett σ_p constant is defined by the Hammett Equation $\log K/K^\circ = \sigma_p\rho$ where K° is the acid dissociation constant of the reference in aqueous solution at 25°C, K is the corresponding constant for the *para*-substituted acid, and ρ is defined as 1.0 for the dissociation of *para*-substituted benzoic acids. A positive Hammett sigma (σ) indicates the group is electron withdrawing.

The electron withdrawing group X should be at least as electron withdrawing as -COOR, where R is, for example, H, $-CH_3$ or $-CH_2CH_3$. The reported Hammett σ_p value for $-COOH$ is 0.43, that for $-COOCH_3$ is 0.39, and that for $-COOC_2H_5$ is 0.45. Thus, the electron withdrawing group should have a Hammett σ_p value greater than 0.39. Non-limiting examples of such electron withdrawing groups X, include cyano, alkoxycarbonyl, metaloxycarbonyl, hydroxycarbonyl, nitro, acetyl, perfluoroalkyl, alkylsulfonyl, arylsulfonyl as well as other groups listed in Lange"s *Handbook of Chemistry*, 14th Edition, McGraw-Hill, 1992; Chapter 9, pp 2-7.

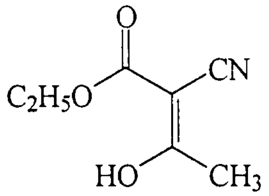
R^1 is hydroxy or metal salts of hydroxy (e.g., OM^+), wherein M^+ is a metal cation. Preferably M^+ is a monovalent cation such as Li^+, Na^+, K^+, Fe^{+2}, although divalent and trivalent cations may be used;

R^2 is an alkyl group or an aryl group. When R^2 is an alkyl group it is preferably an alkyl group containing from 1 to 20 carbon atoms, more preferably containing from 1 to 10 carbon atoms and even more preferably containing from 1 to 4 carbon atoms. Most preferably, R^2 is a methyl group. When R^2 is an aryl group it is preferably an aryl group containing 5 to 10 carbon atoms; more preferably 6 or 10 carbon atoms. Most preferably R^2 is a phenyl group.

Alternatively, R^2 and X taken together can form a ring incorporating the electron withdrawing group. Preferably the ring is a 5-, 6-, or 7-membered ring. An example of such a ring is a lactone ring or the cyclohexenone ring shown in Compound PR-08 below.

Propenitrile compounds may be prepared as described later herein.

Representative propenenitrile compounds useful in the present invention are shown below. Although many of these compounds can exist in either an "enol" or "keto" tautomeric form, they are drawn only in their "enol" form. These representations are exemplary and are not intended to be limiting.



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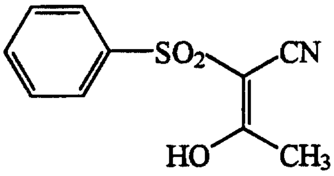

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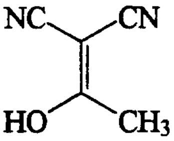

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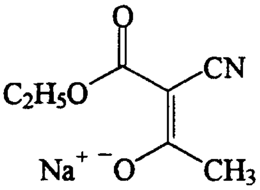

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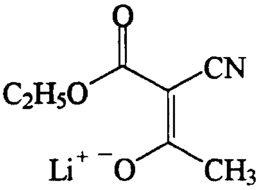

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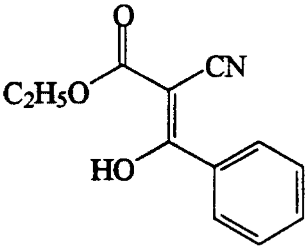

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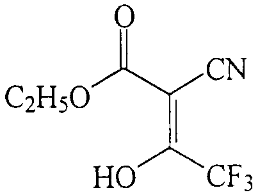
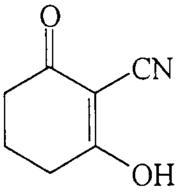


PR-07



PR-08

The compounds useful in this invention differ from those described in U.S. Patent No. 5,545,515. The compounds of U.S. Patent No. 5,545,515 require hydrogen substitution at the terminal position of the acrylonitrile group (i.e., the position corresponding to R^2 of the compounds of this invention) in order to provide the high contrast co-developer effect. In difference to the compounds of U.S. Patent No. 5,545,515; the compounds useful in Applicants' invention have a non-hydrogen substituent at R^2. This reduces initial fog without producing high contrast photothermographic and thermographic elements.

The Photosensitive Silver Halide

As noted above, when used in a photothermographic element, the present invention includes a photosensitive silver halide. The photosensitive silver halide can be any photosensitive silver halide, such as silver bromide, silver iodide, silver chloride, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide. The photosensitive silver halide can be added to the emulsion layer in any fashion so long as it is placed in catalytic proximity to the light-insensitive reducible silver compound which serves as a source of reducible silver.

The silver halide may be in any form which is photosensitive including, but not limited to cubic, octahedral, rhombic dodecahedral, orthorhombic, tetrahedral, other polyhedral habits, and may have epitaxial growth of crystals thereon.

The silver halide grains may have a uniform ratio of halide throughout; they may have a graded halide content, with a continuously varying ratio of, for example, silver bromide and silver iodide; or they may be of the core-shell-type, having a discrete core of one halide ratio, and a discrete shell of another halide ratio. Core-shell silver halide grains useful in photothermographic elements and methods of preparing these materials are described in U.S. Patent No. 5,382,504. A core-shell silver halide grain having an iridium doped core is particularly preferred. Iridium doped core-shell grains of this type are described in U.S. Patent No. 5,434,043.

The silver halide may be prepared *ex situ,* (i.e., be pre-formed) and mixed with the organic silver salt in a binder prior to use to prepare a coating solution. The silver halide may be pre-formed by any means, e.g., in accordance with U.S. Patent No. 3,839,049. For example, it is effective to blend the silver halide and organic silver salt using a homogenizer for a long period of time. Materials of this type are often referred to as "pre-formed emulsions." Methods of preparing these silver halide and organic silver salts and manners of blending them are described in *Research Disclosure,* June 1978, item 17029; U.S. Patent Nos. 3,700,458 and 4,076,539; and Japanese Patent Application Nos. 13224/74, 42529/76, and 17216/75.

It is desirable in the practice of this invention to use pre-formed silver halide grains of less than 0.10 μm in an infrared sensitized, photothermographic material. It is also preferred to use iridium doped silver halide grains and iridium doped core-shell silver halide grains as disclosed in European Laid Open Patent Application No 0 627 660 and U.S. Patent No. 5,434,043 described above.

Pre-formed silver halide emulsions when used in the material of this invention can be unwashed or washed to remove soluble salts. In the latter case, the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed, e.g., by the procedures described in U.S. Patent Nos. 2,618,556; 2,614,928; 2,565,418; 3,241,969; and 2,489,341.

It is also effective to use an *in situ* process, i.e., a process in which a halogen-containing compound is added to an organic silver salt to partially convert the silver of the organic silver salt to silver halide.

The light-sensitive silver halide used in the present invention can be employed in a range of 0.005 mole to 0.5 mole; preferably, from 0.01 mole to 0.15 mole per mole; and more preferably, from 0.03 mole to 0.12 mole of silver halide per mole of non-photosensitive reducible silver salt.

Sensitizers

The silver halide used in the present invention may be chemically and spectrally sensitized in a manner similar to that used to sensitize conventional wet-processed silver halide or state-of-the-art heat-developable photographic materials.

For example, it may be chemically sensitized with a chemical sensitizing agent, such as a compound containing sulfur, selenium, tellurium, or a compound containing gold, platinum, palladium, ruthenium, rhodium, iridium, or combinations thereof, a reducing agent such as a tin halide, or a combination thereof. The details of these procedures are described in T. H. James, *The Theory of the Photographic Process,* Fourth Edition, Chapter 5, pp. 149 to 169. Suitable chemical sensitization procedures are also disclosed in Shepard, U.S. Patent No. 1,623,499; Waller, U.S. Patent No. 2,399,083; McVeigh, U.S. Patent No. 3,297,447; and Dunn, U.S. Patent No. 3,297,446.

Addition of sensitizing dyes to the photosensitive silver halides serves to provide them with high sensitivity to visible and infrared light by spectral sensitization. Thus, the photosensitive silver halides may be spectrally sensitized with various known dyes that spectrally sensitize silver halide. Non-limiting examples of sensitizing dyes that can be employed include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxanol dyes. Of these dyes, cyanine dyes, merocyanine dyes, and complex merocyanine dyes are particularly useful. Cyanine dyes described in U.S. Patent No. 5,441,866 and in U.S. Patent No. 5,541,054 are particularly effective.

An appropriate amount of sensitizing dye added is generally 10^{-10} to 10^{-1} mole; and preferably, 10^{-8} to 10^{-3} moles of dye per mole of silver halide.

Supersensitizers

To get the speed of the photothermographic elements up to maximum levels and further enhance sensitivity, it is often desirable to use supersensitizers. Any supersensitizer can be used which increases the sensitivity. For example, preferred infrared supersensitizers are described in European Laid Open Patent Application No. 0 559 228 and include heteroaromatic mercapto compounds or heteroaromatic disulfide compounds of the formulae:

Ar-S-M
Ar-S-S-Ar

wherein: M represents a hydrogen atom or an alkali metal atom.

In the above noted supersensitizers, Ar represents groups comprising an aromatic ring, a heterocyclic ring, or an aromatic ring fused to a heterocyclic ring containing one or more of nitrogen, sulfur, oxygen, selenium or tellurium atoms.

Preferred supersensitizers are 2-mercaptobenzimidazole, 2-mercapto-5-methylbenzimidazole, 2-mercaptobenzothiazole, and 2-mercaptobenzoxazole.

The supersensitizers are used in a general amount of at least 0.001 moles of sensitizer per mole of silver in the emulsion layer. Usually the range is between 0.001 and 1.0 moles of the compound per mole of silver and preferably between 0.01 and 0.3 moles of compound per mole of silver.

The Non-Photosensitive Reducible Silver Source Material

When used in photothermographic and thermographic elements, the present invention includes a non-photosensitive reducible silver source. The non-photosensitive reducible silver source that can be used in the present invention can be any material that contains a source of reducible silver ions. Preferably, it is a silver salt which is comparatively stable to light and forms a silver image when heated to 80°C or higher in the presence of an exposed photocatalyst (such as silver halide) and a reducing agent.

Silver salts of organic acids, particularly silver salts of long chain fatty carboxylic acids, are preferred. The chains typically contain 10 to 30, preferably 15 to 28, carbon atoms. Suitable organic silver salts include silver salts of organic compounds having a carboxyl group. Examples thereof include a silver salt of an aliphatic carboxylic acid and a silver salt of an aromatic carboxylic acid. Preferred examples of the silver salts of aliphatic carboxylic acids include silver behenate, silver stearate, silver oleate, silver laurate, silver caprate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartarate, silver furoate, silver linoleate, silver butyrate, silver camphorate, and mixtures thereof. Silver salts that can be substituted with a halogen atom or a hydroxyl group also can be effectively used. Preferred examples of the silver salts of aromatic carboxylic acid and other carboxyl group-containing compounds include: silver benzoate, a silver-substituted benzoate, such as silver 3,5-dihydroxybenzoate, silver *o*-methylbenzoate, silver *m*-methylbenzoate, silver *p*-methylbenzoate, silver 2,4-dichlorobenzoate, silver acetamidobenzoate, silver *p*-phenylbenzoate; silver gallate; silver tannate; silver phthalate; silver terephthalate; silver salicylate; silver phenylacetate; silver pyromellilate; a silver salt of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione or the like as described in U.S. Patent No. 3,785,830; and a silver salt of an aliphatic carboxylic acid containing a thioether group as described in U.S. Patent No. 3,330,663.

Silver salts of compounds containing mercapto or thione groups and derivatives thereof can also be used. Preferred examples of these compounds include: a silver salt of 3-mercapto-4-phenyl-1,2,4-triazole; a silver salt of 2-mercaptobenzimidazole; a silver salt of 2-mercapto-5-aminothiadiazole; a silver salt of 2-(2-ethylglycolamido)benzothiazole; a silver salt of thioglycolic acid, such as a silver salt of a S-alkylthioglycolic acid (wherein the alkyl group has from 12 to 22 carbon atoms); a silver salt of a dithiocarboxylic acid such as a silver salt of dithioacetic acid; a silver salt of thioamide; a silver salt of 5-carboxylic-l-methyl-2-phenyl-4-thiopyridine; a silver salt of mercaptotriazine; a silver salt of 2-mercaptobenzoxazole; a silver salt as described in U.S. Patent No. 4,123,274, for example, a silver salt of a 1,2,4-mercaptothiazole derivative, such as a silver salt of 3-amino-5-benzylthio-1,2,4-thiazole; and a silver salt of a thione compound, such as a silver salt of 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione as disclosed in U.S. Patent No. 3,201,678.

Furthermore, a silver salt of a compound containing an imino group can be used. Preferred examples of these compounds include: silver salts of benzotriazole and substituted derivatives thereof, for example, silver methylbenzotriazole and silver 5-chlorobenzotriazole; silver salts of 1,2,4-triazoles or 1-*H*-tetrazoles as described in U.S. Patent No. 4,220,709; and silver salts of imidazoles and imidazole derivatives.

Silver salts of acetylenes can also be used. Silver acetylides are described in U.S. Patent Nos. 4,761,361 and 4,775,613.

It is also found convenient to use silver half soaps. A preferred example of a silver half soap is an equimolar blend of silver behenate and behenic acid, which analyzes for 14.5% by weight silver and which is prepared by precipitation from an aqueous solution of the sodium salt of commercial behenic acid.

Transparent sheet materials made on transparent film backing require a transparent coating. For this purpose a silver behenate full soap, containing not more than 15% of free behenic acid and analyzing 22% silver, can be used.

The method used for making silver soap emulsions is well known in the art and is disclosed in *Research Disclosure,* April 1983, item 22812, *Research Disclosure,* October 1983, item 23419, and U.S. Patent No. 3,985,565.

The silver halide and the non-photosensitive reducible silver source material that form a starting point of development should be in catalytic proximity, i.e., reactive association. "Catalytic proximity" or "reactive association" means that they should be in the same layer, in adjacent layers, or in layers separated from each other by an intermediate layer having a thickness of less than 1 micrometer (1 μm). It is preferred that the silver halide and the non-photosensitive reducible silver source material be present in the same layer.

Photothermographic emulsions containing pre-formed silver halide in accordance with this invention can be sensitized with chemical sensitizers, or with spectral sensitizers as described above.

The source of reducible silver material generally constitutes 5 to 70% by weight of the emulsion layer. It is preferably present at a level of 10 to 50% by weight of the emulsion layer.

The Reducing Agent for Silver Ion

When used in black-and-white photothermographic elements, the reducing agent for the silver ion (e.g., the non-photosensitive reducible silver source such as an organic silver salt) may be any compound, preferably organic compound, that can reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful, but hindered bisphenol reducing agents are preferred.

Hindered bisphenol developers are compounds that contain only one hydroxy group on a given phenyl ring and have at least one additional substituent located *ortho* to the hydroxy group. They differ from traditional photographic developers which contain two hydroxy groups on the same phenyl ring (such as is found in hydroquinones). Hindered phenol developers may contain more than one hydroxy group as long as each hydroxy group is located on different phenyl rings. Hindered phenol developers include, for example, binaphthols (i.e., dihydroxybinaphthyls), biphenols (i.e., dihydroxybiphenyls), bis(hydroxynaphthyl)methanes, bis(hydroxyphenyl)methanes, hindered phenols, and hindered naphthols, each of which may be variously substituted.

Non-limiting representative binaphthols include 1,1'-bi-2-naphthol; 1,1'-bi-4-methyl-2-naphthol; and 6,6'-dibromo-bi-2-naphthol. For additional compounds see U.S. Patent No. 5,262,295 at column 6, lines 12-13, incorporated herein by reference.

Non-limiting representative biphenols include 2,2'-dihydroxy-3,3'-di-*t*-butyl-5,5-dimethylbiphenyl; 2,2'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl; 2,2'-dihydroxy-3,3'-di-*t*-butyl-5,5'-dichlorobiphenyl; 2-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-4-methyl-6-*n*-hexylphenol; 4,4'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl; and 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl. For additional compounds see U.S. Patent No. 5,262,295 at column 4, lines 17-47, incorporated herein by reference.

Non-limiting representative bis(hydroxynaphthyl)methanes include 4,4'-methylenebis(2-methyl-1-naphthol). For additional compounds see U.S. Patent No. 5,262,295 at column 6, lines 14-16, incorporated herein by reference.

Non-limiting representative bis(hydroxyphenyl)methanes include bis(2-hydroxy-3-*t*-butyl-5-methylphenyl)methane (CAO-5); 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane (Permanax™); 1,1-bis(3,5-di-*t*-butyl-4-hydroxyphenyl)methane; 2,2-bis(4-hydroxy-3-methylphenyl)propane;

4,4-ethylidene-bis(2-*t*-butyl-6-methylphenol); and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane. For additional compounds see U.S. Patent No. 5,262,295 at column 5, line 63, to column 6, line 8, incorporated herein by reference.

Non-limiting representative hindered phenols include 2,6-di-*t*-butylphenol; 2,6-di-*t*-butyl-4-methylphenol; 2,4-di-*t*-butylphenol; 2,6-dichlorophenol; 2,6-dimethylphenol; and 2-*t*-butyl-6-methylphenol.

Non-limiting representative hindered naphthols include 1-naphthol; 4-methyl-1-naphthol; 4-methoxy-1-naphthol; 4-chloro-1-naphthol; and 2-methyl-1-naphthol. For additional compounds see U.S. Patent No. 5,262,295 at column 6, lines 17-20, incorporated herein by reference.

The hindered phenol developer should be present at from 1 to 15% by weight of the imaging layer.

The amounts of the above described reducing agents that are added to the photothermographic or thermographic element of the present invention may be varied depending upon the particular compound used, upon the type of emulsion layer, and whether components of the reducing agentare located in the emulsion layer or a topcoat layer. However, when present in the emulsion layer, the hindered phenol should be present in an amount of from 0.01 to 50 mole, preferably from 0.05 to 25 mole of silver.

In multilayer constructions, if one of the developers of the reducing agent system is added to a layer other than the emulsion layer, slightly higher proportions may be necessary and the hindered phenol should be present at from 2 to 20% by weight.

Photothermographic elements of the invention may contain other co-developers or mixtures of co-developers in combination with the hindered phenol developer. For example, the trityl hydrazide or formyl phenylhydrazine compounds described in U. S. Patent No. 5,496,695 may be used; the acrylonitrile compounds described in U.S. Patent No. 5,545,515 may be used; the amine compounds described in U.S. Patent No. 5,545,505 may be used; the hydrogen atom donor compounds described in U.S. Patent Number 5,637,449 may be used; the hydroxamic acid compounds described in U.S. Patent No. 5,545,507 may be used; the 2-substituted malondialdehyde compounds described in U.S. Patent

Number 5,654,130 may be used; the 4-substituted isoxazole compounds described in U.S. Patent Number 5,705,324; and the 3-heteroaromatic-substituted acrylonitrile compounds described in U.S. Patent Number 5,635,339 may be used.

The Binder

The photosensitive silver halide, the non-photosensitive reducible source of silver, the reducing agent, and any other addenda used in the present invention are generally added to at least one binder. The binder(s) that can be used in the present invention can be employed individually or in combination with one another. It is preferred that the binder be selected from polymeric materials, such as, for example, natural and synthetic resins that are sufficiently polar to hold the other ingredients in solution or suspension.

A typical hydrophilic binder is a transparent or translucent hydrophilic colloid. Examples of hydrophilic binders include: a natural substance, for example, a protein such as gelatin, a gelatin derivative, a cellulose derivative; a polysaccharide such as starch, gum arabic, pullulan, dextrin; and a synthetic polymer, for example, a water-soluble polyvinyl compound such as polyvinyl alcohol, polyvinyl pyrrolidone, acrylamide polymer. Another example of a hydrophilic binder is a dispersed vinyl compound in latex form which is used for the purpose of increasing dimensional stability of a photothermographic element.

Examples of typical hydrophobic binders are polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, methacrylate copolymers, maleic anhydride ester copolymers, and butadiene-styrene copolymers. Copolymers, e.g., terpolymers, are also included in the definition of polymers. The polyvinyl acetals, such as polyvinyl butyral and polyvinyl formal, and vinyl copolymers such as polyvinyl acetate and polyvinyl chloride are particularly preferred.

Although the binder can be hydrophilic or hydrophobic, preferably it is hydrophobic in the silver containing layer(s). Optionally, these polymers may be used in combination of two or more thereof.

The binders are preferably used at a level of 30-90% by weight of the emulsion layer, and more preferably at a level of 45-85% by weight. Where the proportions and activities of the reducing agent for the non-photosensitive reducible source of silver require a particular developing time and temperature, the binder should be able to withstand those conditions. Generally, it is preferred that the binder not decompose or lose its structural integrity at 250°F (121°C) for 60 seconds, and more preferred that it not decompose or lose its structural integrity at 350°F (177°C) for 60 seconds.

The polymer binder is used in an amount sufficient to carry the components dispersed therein, that is, within the effective range of the action as the binder. The effective range can be appropriately determined by one skilled in the art.

Photothermographic and Thermographic Formulations

The formulation for the photothermographic and thermographic emulsion layer can be prepared in a variety of manners. For example single layer formulations can be prepared by dissolving and dispersing the binder, the photosensitive silver halide, (when used) the non-photosensitive reducible source of silver, the reducing agent for the non-photosensitive reducible silver source, the propenenitrile compound, and optional additives, in an inert organic solvent, such as, for example, toluene, 2-butanone, or tetrahydrofuran.

Photothermographic elements of the invention may also contain other additives such as shelf-life stabilizers, toners, development accelerators, acutance dyes, post-processing stabilizers or stabilizer precursors, and other image-modifying agents.

The use of "toners" or derivatives thereof which improve the image, is highly desirable, but is not essential to the element. Toners can be present in an amount of 0.01-10% by weight of the emulsion layer, preferably 0.1-10% by weight. Toners are well known materials in the photothermographic and thermographic art, as shown in U.S. Patent Nos. 3,080,254; 3,847,612; and 4,123,282.

Examples of toners include: phthalimide and *N*-hydroxyphthalimide; cyclic imides, such as succinimide, pyrazoline-5-ones, quinazolinone, 1-phenylurazole, 3-phenyl-2-pyrazoline-5-one, and 2,4-thiazolidinedione; naphthalimides, such as *N*-hydroxy-1,8-naphthalimide; cobalt complexes, such as cobaltic hexamine trifluoroacetate; mercaptans such as 3-mercapto-1,2,4-triazole, 2,4-dimercaptopyrimidine, 3-mercapto-4,5-diphenyl-1,2,4-triazole and 2,5-dimercapto-1,3,4-thiadiazole; *N*-(aminomethyl)aryldicarboximides, such as (*N*,*N*-dimethylaminomethyl)phthalimide, and *N*-(dimethylaminomethyl)naphthalene-2,3-dicarboximide; a combination of blocked pyrazoles, isothiuronium derivatives, and certain photobleach agents, such as a combination of *N,N'*-hexamethylene-bis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoctane)bis(isothiuronium)-trifluoroacetate, and 2-(tribromomethylsulfonyl benzothiazole); merocyanine dyes such as 3-ethyl-5-[(3-ethyl-2-benzothiazolinylidene)-1-methyl-ethylidene]-2-thio-2,4-*o*-azolidinedione; phthalazinone, phthalazinone derivatives, or metal salts or these derivatives, such as 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone, and 2,3-dihydro-1,4-phthalazinedione; a combination of phthalazine plus one or more phthalic acid derivatives, such as phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, and tetrachlorophthalic anhydride, quinazolinediones, benzoxazine or naphthoxazine derivatives; rhodium complexes functioning not only as tone modifiers but also as sources of halide ion for silver halide formation *in situ,* such as ammonium hexachlororhodate (III), rhodium bromide, rhodium nitrate, and potassium hexachlororhodate (III); inorganic peroxides and persulfates, such as ammonium peroxydisulfate and hydrogen peroxide; benzoxazine-2,4-diones, such as 1,3-benzoxazine-2,4-dione, 8-methyl-1,3-benzoxazine-2,4-dione, and 6-nitro-1,3-benzoxazine-2,4-dione; pyrimidines and asym-triazines, such as 2,4-dihydroxypyrimidine, 2-hydroxy-4-amino-pyrimidine, and azauracil; and tetraazapentalene derivatives, such as 3,6-dimercapto-1,4-diphenyl-*1H,4H*-2,3a,5,6a-tetraazapentalene and 1,4-di-(*o*-chlorophenyl)-3,6-dimercapto-*1H,4H*-2,3a,5,6a-tetraazapentalene.

The photothermographic elements used in this invention can be further protected against the production of fog and can be stabilized against loss of sensitivity during storage. While not necessary for the practice of the invention, it may be advantageous to add mercury (II) salts to the emulsion layer(s) as an additional antifoggant. Preferred mercury (II) salts for this purpose are mercuric acetate and mercuric bromide.

Other suitable antifoggants and stabilizers, which can be used alone or in combination with the propenenitrile compounds useful in this invention, include the thiazolium salts described in U.S. Patent Nos. 2,131,038 and U.S. Patent No. 2,694,716; the azaindenes described in U.S. Patent Nos. 2,886,437; the triazaindolizines described in U.S. Patent No. 2,444,605; the mercury salts described in U.S. Patent No. 2,728,663; the urazoles described in U.S. Patent No. 3,287,135; the sulfocatechols described in U.S. Patent No. 3,235,652; the oximes described in British Patent No. 623,448; the polyvalent metal salts described in U.S. Patent No. 2,839,405; the thiuronium salts described in U.S. Patent No. 3,220,839; the palladium, platinum and gold salts described in U.S. Patent Nos. 2,566,263 and 2,597,915; and the 2-(tribromomethylsulfonyl)quinolines described in U.S. Patent No. 5,460,938. Stabilizer precursor compounds capable of releasing stabilizers upon application of heat during development can also be use in combination with the stabilizers used in this invention. Such precursor compounds are described in, for example, U.S. Patent Nos. 5,158,866, 5,175,081, 5,298,390, and 5,300,420

Photothermographic and thermographic elements of the invention can contain plasticizers and lubricants such as polyalcohols and diols of the type described in U.S. Patent No. 2,960,404; fatty acids or esters, such as those described in U.S. Patent Nos. 2,588,765 and 3,121,060; and silicone resins, such as those described in British Patent No. 955,061.

Photothermographic and thermographic elements containing emulsion layers described herein may contain matting agents such as starch, titanium dioxide, zinc oxide, silica, and polymeric beads including beads of the type described in U.S. Patent Nos. 2,992,101 and 2,701,245.

Emulsions in accordance with this invention may be used in photothermographic and thermographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, evaporated metal layers, ionic polymers such as those described in U.S. Patent Nos. 2,861,056, and 3,206,312 or insoluble inorganic salts such as those described in U.S. Patent No. 3,428,451.

The photothermographic and thermographic elements of this invention may also contain electroconductive under-layers to reduce static electricity effects and improve transport through processing equipment. Such layers are described in U.S. Patent No. 5,310,640.

Photothermographic Constructions

The photothermographic and thermographic elements of this invention may be constructed of one or more layers on a support. Single layer elements should contain the silver halide (when used), the non-photosensitive, reducible silver source material, the reducing for the non-photosensitive reducible silver source, the binder as well as optional materials such as toners, acutance dyes, coating aids, and other adjuvants.

Two-layer constructions should contain silver halide (when used) and non-photosensitive, reducible silver source in one emulsion layer (usually the layer adjacent to the support) and the propenenitrile compound and other ingredients in the second layer or distributed between both layers. Two layer constructions comprising a single emulsion layer coating containing all the ingredients and a protective topcoat are also envisioned.

Photothermographic and thermographic emulsions used in this invention can be coated by various coating procedures including wire wound rod coating, dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in U.S. Patent No. 2,681,294. If desired, two or more layers can be coated simultaneously by the procedures described in U.S. Patent Nos. 2,761,791; 5,340,613; and British Patent No. 837,095. Typical wet thickness of the emulsion layer can be 10-150 micrometers (μm), and the layer can be dried in forced air at a temperature of 20-100°C. It is preferred that the thickness of the layer be selected to provide maximum image densities greater than 0.2, and, more preferably, in the range 0.5 to 4.0, as measured by a MacBeth Color Densitometer Model TD 504.

Photothermographic and thermographic elements according to the present invention can contain acutance dyes and antihalation dyes. The dyes may be incorporated into the photothermographic emulsion layer as acutance dyes according to known techniques. The dyes may also be incorporated into antihalation layers according to known techniques as an antihalation backing layer, an antihalation underlayer or as an overcoat. It is preferred that the photothermographic elements of this invention contain an antihalation coating on the support opposite to the side on which the emulsion and topcoat layers are coated.

Antihalation and acutance dyes useful in the present invention are described in U.S. Patent Nos. 5,135,842; 5,266,452; 5,314,795; and 5,380,635.

Development conditions will vary, depending on the construction used, but will typically involve heating the imagewise exposed material at a suitably elevated temperature. When used in a photothermographic element, the latent image obtained after exposure can be developed by heating the material at a moderately elevated temperature of, for example, 80-250°C, preferably 100-200°C, for a sufficient period of time, generally 1 second to 2 minutes. Heating may be carried out by the typical heating means such as a hot plate, an iron, a hot roller, a heat generator using carbon or titanium white, a resistive layer in the element, or the like.

If desired, the imaged element may be subjected to a first heating step at a temperature and for a time sufficient to intensify and improve the stability of the latent image but insufficient to produce a visible image and later subjected to a second heating step at a temperature and for a time sufficient to produce the visible image. Such a method and its advantages are described in U.S. Patent No. 5,279,928.

When used in a thermographic element, the image may be developed merely by heating at the above noted temperatures using a thermal stylus or print head, or by heating while in contact with a heat absorbing material.

Thermographic elements of the invention may also include a dye to facilitate direct development by exposure to laser radiation. Preferably the dye is an infrared absorbing dye and the laser is a diode laser emitting in the infrared. Upon exposure to radiation the radiation absorbed by the dye is converted to heat which develops the thermographic element.

The Support

Photothermographic and thermographic emulsions used in the invention can be coated on a wide variety of supports. The support, or substrate, can be selected from a wide range of materials depending on the imaging requirement. Supports may be transparent or at least translucent. Typical supports include polyester film, subbed polyester film (e.g., polyethylene terephthalate or polyethylene naphthalate), cellulose acetate film, cellulose ester film, polyvinyl acetal film, polyolefinic film (e.g., polyethylene or polypropylene or blends thereof), polycarbonate film and related or resinous materials, as well as glass, and paper. Typically, a flexible support is employed, especially a polymeric film support, which can be partially acetylated or coated, particularly with a polymeric subbing or priming agent. Preferred polymeric materials for the support include polymers having good heat stability, such as polyesters. Particularly preferred polyesters are polyethylene terephthalate and polyethylene naphthalate.

Where the photothermographic or thermographic element is to be used as a photomask, the support should be transparent or highly transmissive of the radiation (i.e., ultraviolet or short wavelength visible radiation) which is used in the final imaging process.

A support with a backside resistive heating layer can also be used in photothermographic imaging systems such as shown in U.S. Patent No. 4,374,921.

Use as a Photomask

As noted above, the possibility of low absorbance of the photothermographic and thermographic element in the range of 350-450 nm in non-imaged areas facilitates the use of the photothermographic and thermographic elements of the present invention in a process where there is a subsequent exposure of an ultraviolet or short wavelength visible radiation sensitive imageable medium. For example, imaging the photothermographic or thermographic element and subsequent development affords a visible image. The developed photothermographic or thermographic element absorbs ultraviolet or short wavelength visible radiation in the areas where there is a visible image and transmits ultraviolet or short wavelength visible radiation where there is no visible image. The developed element may then be used as a mask and placed between an ultraviolet or short wavelength visible radiation energy source and an ultraviolet or short wavelength visible radiation photosensitive imageable medium such as, for example, a photopolymer, diazo material, or photoresist. This process is particularly useful where the imageable medium comprises a printing plate and the photothermographic or thermographic element serves as an imagesetting film.

Objects and advantages of this invention will now be illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

EXAMPLES

All materials used in the following examples are readily available from standard commercial sources, such as Aldrich Chemical Co. Milwaukee, WI, unless otherwise specified. All percentages are by weight unless otherwise indicated. The following additional terms and materials were used.

Acryloid™ A-21 is an acrylic copolymer available from Rohm and Haas, Philadelphia, PA.

Butvar™ B-79 is a polyvinyl butyral resin available from Monsanto Company, St. Louis, MO.

CAB 171-15S is a cellulose acetate butyrate resin available from Eastman Kodak Co.

CBBA is 2-(4-chlorobenzoyl)benzoic acid.

Desmodur™ N3300 is an aliphatic hexamethylene diisocyanate available from Bayer Chemicals, Pittsburgh, PA.

MEK is methyl ethyl ketone (2-butanone).

MeOH is methanol.

MMBI is 2-mercapto-5-methylbenzimidazole.

4-MPA is 4-methylphthalic acid.

Permanax™ WSO is 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane [CAS RN=7292-14-0] and is available from St-Jean PhotoChemicals, Inc. Quebec. It is a reducing agent (i.e., a hindered phenol developer) for the non-photosensitive reducible source of silver. It is also known as Nonox™.

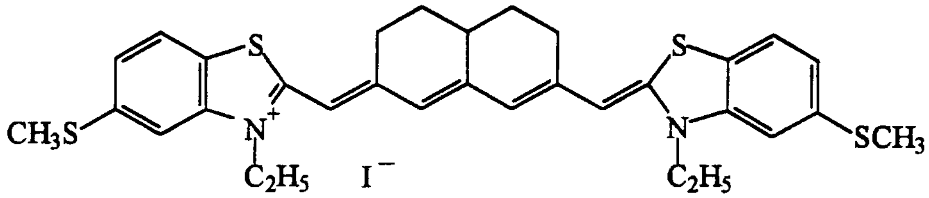
PET is polyethylene terephthalate.

PHP is pyridinium hydrobromide perbromide.

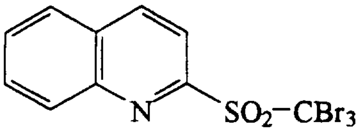
PHZ is phthalazine.

TCPA is tetrachlorophthalic acid.

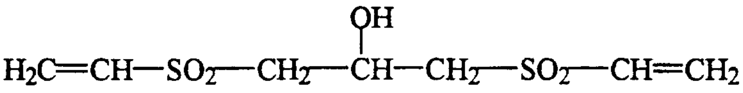
Sensitizing Dye-1 is described in U.S. Patent No. 5,541,054 and has the structure shown below.



Antifoggant A is 2-(tribromomethylsulfonyl)quinoline and is described in U.S. Patent No 5,460,938. It has the structure shown below.

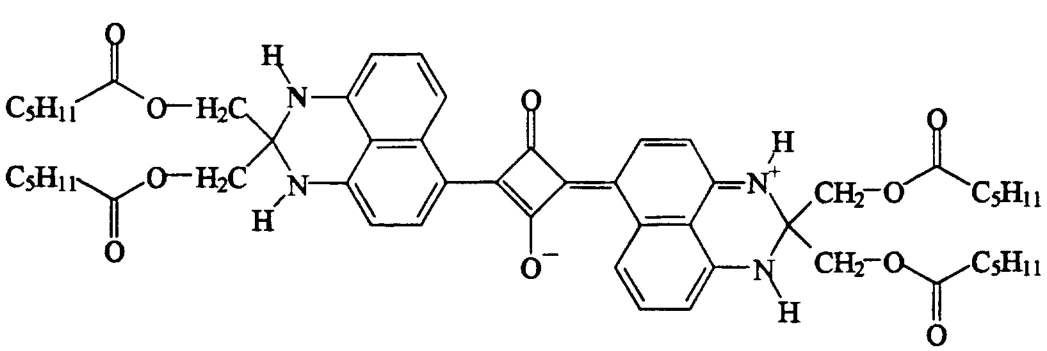


Vinyl Sulfone-1 (**VS-1**) is described in European Laid Open Patent Application No. 0 600 589 A2 and has the following structure.



$$H_2C{=}CH{-}SO_2{-}CH_2{-}\overset{\displaystyle OH}{\overset{|}{C}H}{-}CH_2{-}SO_2{-}CH{=}CH_2$$

Antihalation Dye-1 (**AH-1**) has the following structure. The preparation of this compound is described in PCT Patent Application No. WO 95/23,357 (filed January 11, 1995)



The following examples provide exemplary synthetic procedures and preparatory procedures using the compounds useful in the invention.

Preparation of 2-cyano-3-hydroxybutenoic acid ethyl ester (PR-01): This compound was prepared according to the procedure of Hori, I.; Midorikawa,H. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn)*, **1962,** *56,* 216 (*Chem Abstr.*, **1963,** *58,* 3311).

Preparation of 3-hydroxy-2-phenylsulfonylbutenenitrile (PR-02): Phenylsulfonylacetonitrile (1.0 g, 5.5 mmol) was dissolved in 10 mL of acetic anhydride. Anhydrous potassium carbonate (0.91 g, 6.6 mmol) was added and the resulting solution was stirred for 3 days under nitrogen. The solution was then diluted with water (10 mL) and acidified with 2N HCl. The aqueous layer was extracted with ether (3 x 50 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated to dryness. The resulting solid was triturated with hexanes to yield 0.85 g of a colorless solid.

Preparation of 3-hydroxy-2-cyanobutenenitrile (PR-03): Ethoxymethylenemalononitrile (5.0 g, 36.8 mmol) was dissolved in 100 mL of 2N sodium hydroxide and 20 mL of methanol. After 15 minutes the solution was acidified to pH 3 with 2N HCl. The aqueous layer was then extracted with methylene chloride (3 x 100 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated to dryness. The resulting solid was recrystallized in toluene to yield 1.3 g of a yellow solid.

Preparation of ethyl 2-cyano-3-hydoxybutenoic acid ethyl ester sodium salt (PR-04): This compound was prepared as described by Oeckl, S. *et al.* in GB 1,450,300.

Preparation of ethyl 2-cyano-3-hydroxybutenoic acid ethyl ester lithium salt (PR-05): This compound was prepared as described Oeckl, S. *et al.* in GB 1,450,300.

Preparation of 2-cyano-3-hydroxy-3-phenylpropenoic acid ethyl ester (PR-06): This compound was prepared according to the procedure of Hori, I.; Midorikawa,H. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn)*, **1962,** *56,* 216 (*Chem Abstr.*, **1963,** *58,* 3311).

Preparation of 2-cyano-3-hydroxy-4,4,4-trifluorobutenoic acid ethyl ester (PR-07): To a solution of ethyl cyanoacetate (1.0 g, 8.8 mmol) in 20 mL of tetrahydrofuran was added 1,8-diazabicyclo[5.4.0]undec-7-ene (2.7 g, 8.8 mmol) over 15 minutes. Trifluoroacetic anhydride (3.7 g, 17.7 mmol) was then added at 0°C *via* the addition funnel over 30 minutes. The solution was then stirred for 2 hours at room temperature. The organic layer was washed with 2N HCl (3 x 15 mL), dried over magnesium sulfate, and evaporated to dryness. The resulting liquid was purified by Kugelrohr distillation (80°C @ 3 mm Hg) to yield 0.95 g of colorless liquid.

Preparation of 2-cyano-3-hydroxy-cyclohexene-2-one (PR-08): This compound is also known as 2-cyano-1,3-cyclohexandione. It was prepared as described in Menozzi,G.; Schenone, P.; Mosti, L. *J. Heterocyclic Chem.* **1983,** *20,* 645-648.

Emulsion Preparation

The following examples demonstrate the use of substituted propenenitrile compounds in photothermographic elements to reduce initial Dmin.

The preparation of a pre-formed silver iodobromide emulsion, silver soap dispersion, homogenate, and halidized homogenate solutions used in the Examples is described below.

Formulation A - The following formulation was prepared. Substituted propenenitrile compounds were incorporated in the topcoat layer.

A pre-formed iridium-doped core-shell silver behenate soap was prepared as described in U.S. Patent No. 5,434,043 incorporated herein by reference.

The pre-formed soap contained 2.0% by weight of a 0.05 μm diameter iridium-doped core-shell silver iodobromide emulsion (25% core containing 8% iodide, 92% bromide; and 75% all-bromide shell containing 1 x 10^{-5} mole of iridium). A dispersion of this silver behenate soap was homogenized to 26.1% solids in 2-butanone containing 1.00% Butvar™ B-79 polyvinyl butyral resin.

To 172.0 g of this silver soap dispersion, was added 27 g of 2-butanone, and 2.10 mL of a solution of 0.23 g of pyridinium hydrobromide perbromide in 1.88 g of methanol. After 1 hour of mixing 1.50 mL of a solution of 0.170 g of calcium bromide in 1.35 g methanol was added. After 30 minutes the following infrared sensitizing dye premix was added.

Material	Amount
CBBA	1.520 g
Sensitizing Dye-1	0.006 g
MMBI	0.140 g
Methanol	4.800 g

After 1.5 hours of mixing, 45.8 g of Butvar™ B-79 polyvinyl butyral was added. Stirring for 30 minutes was followed by addition of 1.23 g of 2-(tribromomethylsulfonyl)quinoline and 10.6 g of 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane (Permanax™). After 15 minutes 4.97 g of a solution of 0.580 g of Desmodur™ N3300 in 4.7 g of 2-butanone was added. After 15 minutes, 1.05 g of phthalazine was added. After an additional 15 minutes 0.35 g of tetrachlorophthalic acid was added. Finally, after another 15 minutes, 0.470 g of 4-methylphthalic acid was added.

A topcoat solution was prepared in the following manner; 4.52 g of Acryloid™ A-21 polymethyl methacrylate and 115 g of CAB 171-15S cellulose acetate butyrate were mixed in 1.236 Kg of 2-butanone until dissolved. To 100 g of this premix were then added 0.0780 g of benzotriazole, 0.090 g of **AH-1**, and 0.125 g of Vinyl Sulfone-1 (**VS-1**), and the amount of propenenitrile described in the Examples below.

Samples were coated out under infrared safelights using a dual-knife coater. The photothermographic emulsion and topcoat formulations were coated onto a 7 mil (178 μm) blue tinted polyethylene terephthalate support provided with an antihalation back coating containing **AH-1** in CAB 171-15S resin. After raising the hinged knives, the support was placed in position on the coater bed. The knives were then lowered and locked into place. The height of the knives was adjusted with wedges controlled by screw knobs and measured with electronic gauges. Knife #1 was raised to a clearance corresponding to the desired thickness of the support plus the wet thickness of layer #1. Knife #2 was raised to a height equal to the desired thickness of the support plus the wet thickness of layer #1 plus the wet thickness of layer #2.

Aliquots of solutions #1 and #2 were simultaneously poured onto the support in front of the corresponding knives. The support was immediately drawn past the knives and into an oven to produce a double layered coating. The coated photothermographic or thermographic element was then dried by taping the support to a belt which was rotated inside a BlueM™ oven.

Sensitometry: The coated and dried photothermographic elements prepared from Formulation A were cut into 1.5 inch x 11 inch strips (3.8 cm x 27.9 cm) and exposed with a laser sensitometer incorporating a 811 nm laser diode sensitometer for 6 seconds. The coatings were processed on a roll processor for the amount of time indicated in the Examples below.

Sensitometry measurements were made on a custom built computer scanned densitometer using a filter appropriate to the sensitivity of the photothermographic element and are believed to be comparable to measurements from commercially available densitometers.

Dmin is the density of the non-exposed areas after development. It is the average of eight lowest density values on the exposed side of the fiducial mark.

Dmax is the highest density value on the exposed side of the fiducial mark.

Speed-2 is Log 1/E + 4 corresponding to the density value of 1.00 above Dmin where E is the exposure in ergs/cm^2.

Speed-3 is Log 1/E + 4 corresponding to the density value of 2.90 above Dmin where E is the exposure in ergs/cm^2.

Contrast-1 is the absolute value of the slope of the line joining the density points of 0.60 and 2.00 above Dmin.

Contrast-2 is the absolute value of the slope of the line joining the density points of 1.00 and 2.40 above Dmin.

Propenenitrile compounds having an electron withdrawing group substituted at the 2-position were studied using Permanax™ as the hindered phenol developer. Propenenitrile compound studied were PR-01, PR-02, PR-03, PR-04, PR-05, PR-06, and PR-07. The structures of these compounds are shown above.

Example 1

To 20 g of the topcoat solution prepared as described above, were added one of the following:

1.9×10^{-4} moles PR-01 (–)
7.74×10^{-4} moles PR-01 (+)
0.45×10^{-4} moles PR-02 (–)
0.90×10^{-4} moles PR-02 (+)
1.85×10^{-4} moles PR-03 (–)
4.63×10^{-4} moles PR-03 (+)
A sample containing only Permanax™ developer served as a control.

The photothermographic emulsion layer and topcoat layer were dual knife coated onto a 7 mil (178 μm) blue tinted polyethylene terephthalate support containing **AH-1** in an antihalation backcoat. The first knife gap for the photothermographic emulsion layer was set to 3.9 mil (99 μm) above the support and the second knife gap for the topcoat layer was set at 5.2 mil (132 μm) above the support. Samples were dried for 6 minutes at 180°F (82.2°C) in a BlueM™ oven. This typically gave coating weights of 2.3 to 2.5 g/m^2. Samples were stored overnight before testing.

The effects on the sensitometric response by the addition of the substituted propenenitriles to the Permanax™ developer are summarized for various processing conditions. The sensitometric results, shown below, demonstrate that addition of the propenenitriles substituted with an electron withdrawing group in the 2-position and with a hydroxy group in the 3-position reduces Dmin of the photothermographic element.

Ex.	Developer	Processing Conditions	Dmin	Dmax
1-1	Permanax™	15 seconds/255°F(124°C)	0.195	4.021
1-2	Permanax™ + PR-01 (–)	15 seconds/255°F(124°C)	0.189	3.992
1-3	Permanax™ + PR-01 (+)	15 seconds/255°F(124°C)	0.181	3.834
1-4	Permanax™ + PR-02 (–)	15 seconds/255°F(124°C)	0.179	4.023
1-5	Permanax™ + PR-02 (+)	15 seconds/255°F(124°C)	0.172	3.857
1-6	Permanax™ + PR-03 (–)	15 seconds/255°F(124°C)	0.172	2.966
1-7	Permanax™ + PR-03 (+)	15 seconds/255°F(124°C)	0.182	1.778
1-8	Permanax™	25 seconds/255°F(124°C)	0.277	4.035
1-9	Permanax™ + PR-01 (–)	25 seconds/255°F(124°C)	0.244	3.913
1-10	Permanax™ + PR-01 (+)	25 seconds/255°F(124°C)	0.206	3.796

1-11	Permanax™ + PR-02 (–)	25 seconds/255°F(124°C)	0.232	3.901
1-12	Permanax™ + PR-02 (+)	25 seconds/255°F(124°C)	0.206	3.935
1-13	Permanax™ + PR-03 (–)	25 seconds/255°F(124°C)	0.18	3.396
1-14	Permanax™ + PR-03 (+)	25 seconds/255°F(124°C)	0.186	3.014

Ex.	Speed-2	Speed-3	Contrast-1	Contrast-2
1-1	1.63	1.23	4.508	5.371
1-2	1.61	1.21	4.668	5.632
1-3	1.54	1.18	4.83	5.46
1-4	1.7	1.35	5.15	5.858
1-5	1.65	1.31	5.291	5.888
1-6	1.35	*	3.009	2.686
1-7	0.96	*	*	*
1-8	1.81	1.17	3.345	3.392
1-9	1.79	1.14	3.52	3.628
1-10	1.74	1.15	4.039	3.803
1-11	1.86	1.3	4.065	3.745
1-12	1.82	1.3	4.572	4.121
1-13	1.6	1.05	5.005	5.209
1-14	1.34	*	3.691	3.299

*Speed-3, Contrast-1 or Contrast-2 could not be measured for these samples.

Example 2

To 20 g of the topcoat solution prepared as described above, were added one of the following:

6.45×10^{-4} moles PR-01 (–)
3.11×10^{-4} moles PR-05 (–)
6.83×10^{-4} moles PR-05 (+)
2.82×10^{-4} moles PR-04 (–)
5.65×10^{-4} moles PR-04 (+)
A sample containing only Permanax™ developer served as a control.

The photothermographic emulsion layer and topcoat layer were dual knife coated and dried as described in Example 1 above.

The effects on the sensitometric response by the addition of the substituted propenenitriles to the Permanax™ developer are summarized for various processing conditions. The sensitometric results, shown below, demonstrate that addition of the propenenitriles substituted with an electron withdrawing group in the 2-position and with a metaloxy group in the 3-position reduces Dmin of the photothermographic element.

Ex.	Developer	Processing Conditions	Dmin	Dmax
2-1	Permanax™	15 seconds/255°F(124°C)	0.189	3.97
2-2	Permanax™ + PR-01	15 seconds/255°F(124°C)	0.171	3.885
2-3	Permanax™ + PR-05 (–)	15 seconds/255°F(124°C)	0.174	4.042
2-4	Permanax™ + PR-05 (+)	15 seconds/255°F(124°C)	0.168	3.886
2-5	Permanax™ + PR-04 (–)	15 seconds/255°F(124°C)	0.171	3.868
2-6	Permanax™ + PR-04 (+)	15 seconds/255°F(124°C)	0.167	3.591
2-7	Permanax™	25 seconds/255°F(124°C)	0.276	3.879
2-8	Permanax™ + PR-01	25 seconds/255°F(124°C)	0.189	3.838
2-9	Permanax™ + PR-05 (–)	25 seconds/255°F(124°C)	0.207	3.927
2-10	Permanax™ + PR-05 (+)	25 seconds/255°F(124°C)	0.179	3.82
2-11	Permanax™ + PR-04 (–)	25 seconds/255°F(124°C)	0.194	3.76
2-12	Permanax™ + PR-04 (+)	25 seconds/255°F(124°C)	0.173	3.404

Ex.	Speed-2	Speed-3	Contrast-1	Contrast-2
2-1	1.77	1.35	4.941	5.101
2-2	1.63	1.28	5.407	5.955
2-3	1.72	1.41	5.6	6.208
2-4	1.55	1.24	5.678	6.538
2-5	1.66	1.31	5.319	5.819
2-6	1.45	1.01	4.523	4.684
2-7	1.91	1.26	3.424	3.255
2-8	1.77	1.28	5.055	4.472
2-9	1.88	1.38	4.654	4.141
2-10	1.73	1.37	6.523	6.514
2-11	1.83	1.3	5.011	4.301
2-12	1.71	1.17	6.929	6.527

Example 3

To 20 g of the topcoat solution prepared as described above, were added one of the following:

3.87×10^{-4} moles PR-01 (–)
0.92×10^{-4} moles PR-06 (–)
3.46×10^{-4} moles PR-06 (+)
1.20×10^{-4} moles PR-07 (–)
2.87×10^{-4} moles PR-07 (+)
A sample containing only Permanax™ developer served as a control.

The photothermographic emulsion layer and topcoat layer were dual knife coated and dried as described in Example 1 above.

The effects on the sensitometric response by the addition of the substituted propenenitriles to the Permanax™ developer are summarized for various processing conditions. The sensitometric results, shown below, demonstrate that addition of the propenenitriles substituted with an electron withdrawing group in the 2-position and with a hydroxy group in the 3-position reduces Dmin of the photothermographic element.

Ex.	Developer	Processing Conditions	Dmin	Dmax
3-1	Permanax™	15 seconds/255°F(124°C)	0.196	4.139
3-2	Permanax™ + PR-01	15 seconds/255°F(124°C)	0.165	3.718
3-3	Permanax™ + PR-06(–)	15 seconds/255°F(124°C)	0.185	4.074
3-4	Permanax™ + PR-06 (+)	15 seconds/255°F(124°C)	0.178	4.034
3-5	Permanax™ + PR-07 (–)	15 seconds/255°F(124°C)	0.192	4.257
3-6	Permanax™ + PR-07 (+)	15 seconds/255°F(124°C)	0.159	3.509
3-7	Permanax™	25 seconds/255°F(124°C)	0.287	3.986
3-8	Permanax™ + PR-01	25 seconds/255°F(124°C)	0.21	3.778
3-9	Permanax™ + PR-06 (–)	25 seconds/255°F(124°C)	0.242	4.354
3-10	Permanax™ + PR-06 (+)	25 seconds/255°F(124°C)	0.212	3.916
3-11	Permanax™ + PR-07 (–)	25 seconds/255°F(124°C)	0.246	4.304
3-12	Permanax™ + PR-07 (+)	25 seconds/255°F(124°C)	0.193	3.61

Ex.	Speed-2	Speed-3	Contrast-1	Contrast-2
3-1	1.767	1.403	5.299	5.770
3-2	1.64	1.21	5.628	5.66
3-3	1.719	1.385	5.491	6.067
3-4	1.644	1.334	5.594	6.578
3-5	1.77	1.45	5.362	6.249
3-6	1.50	1.07	4.725	5.005
3-7	1.924	1.343	3.731	3.394
3-8	1.79	1.23	4.168	4.325
3-9	1.875	1.266	4.006	3.600
3-10	1.814	1.317	4.881	4.289
3-11	1.93	1.43	4.560	4.342
3-12	1.78	1.15	4.831	4.296

Example 4

To 20 g of the topcoat solution prepared as described above, were added one of the following:

6.45×10^{-4} moles PR-01 (–)
3.11×10^{-4} moles PR-05 (–)
6.83×10^{-4} moles PR-05 (+)
2.82×10^{-4} moles PR-04 (–)
5.65×10^{-4} moles PR-04 (+)

A sample containing only Permanax™ developer served as a control.

The photothermographic emulsion layer and topcoat layer were dual knife coated and dried as described in Example 1 above. Duplicate samples were prepared.

One set of samples were imaged one day after coating. The second set of samples were stored at ambient conditions for three months and then imaged. The sensitometric results, shown below, demonstrate that the propenenitrile compounds retain their ability to decrease Dmin over time.

Ex.	Developer	When Processed	Dmin	Dmax
4-1	Permanax™	Initial	0.189	3.978
4-2	Permanax™ + PR-01	Initial	0.171	3.885
4-3	Permanax™ + PR-05 (–)	Initial	0.174	4.042
4-4	Permanax™ + PR-05 (+)	Initial	0.168	3.886
4-5	Permanax™ + PR-04 (–)	Initial	0.171	3.868
4-6	Permanax™ + PR-04 (+)	Initial	0.167	3.591
4-7	Permanax™	3 Months	0.193	3.806
4-8	Permanax™ + PR-01	3 Months	0.173	3.668
4-9	Permanax™ + PR-05 (–)	3 Months	0.18	3.837
4-10	Permanax™ + PR-05 (+)	3 Months	0.176	3.849
4-11	Permanax™ + PR-04 (–)	3 Months	0.177	3.868
4-12	Permanax™ + PR-04 (+)	3 Months	0.177	3.549

Ex.	Speed-2	Speed-3	Contrast-1	Contrast-2
4-1	1.77	1.35	4.941	5.101
4-2	1.63	1.28	5.407	5.955
4-3	1.72	1.41	5.6	6.208
4-4	1.55	1.24	5.678	6.538
4-5	1.66	1.31	5.319	5.819
4-6	1.45	1.01	4.523	4.684
4-7	1.722	1.23	4.136	4.53
4-8	1.582	1.093	4.382	4.501
4-9	1.648	1.2	4.243	4.579
4-10	1.529	1.039	4.139	4.425
4-11	1.694	1.294	4.757	5.295
4-12	1.564	1.101	4.523	4.85

Example 5 (Comparative)

To 20 g of the topcoat solution prepared as described above, were added one of the following:

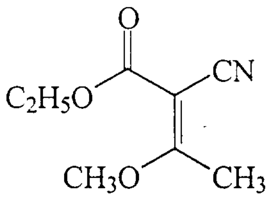
5.92×10^{-4} moles PR C-01
2.56×10^{-4} moles PR C-02
3.14×10^{-4} moles PR C-03
0.58×10^{-4} moles PR C-04
1.59×10^{-4} moles PR C-05
A sample containing only Permanax™ developer served as a control.

Compounds PR C-1, PR C-4 and PR C-5 do not contain a hydroxy group or a metal salt of a hydroxy group substituted at the 3-position.

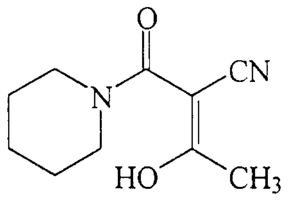
Compounds PR C-2 and PR C-3 do not contain an electron withdrawing group having a Hammet σ_p constant greater than 0.39 substituted at the 2-position.

The photothermographic emulsion layer and topcoat layer were dual knife coated and dried as described in Example 1 above.

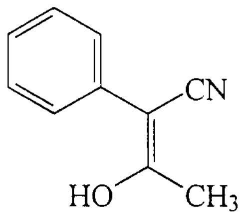
The effects on the sensitometric response by the addition of these comparative substituted propenenitriles to the Permanax™ developer are summarized for various processing conditions. The sensitometric results, shown below, demonstrate that addition of these propenenitriles did not reduce Dmin of the photothermographic element.



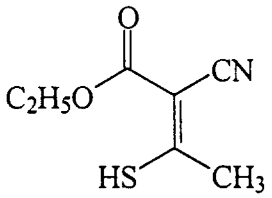
PR C-1



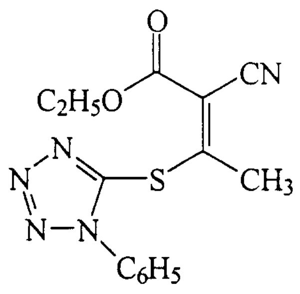
PR C-2



PR C-3



PR C-4



PR C-5

Ex.	Developer	Processing Conditions	Dmin	Dmax
5-1	Permanax™	15 seconds/255°F(124°C)	0.195	4.021
5-2	Permanax™ + PR C-1	15 seconds/255°F(124°C)	0.209	4.062
5-4	Permanax™ + PR C-2	15 seconds/255°F(124°C)	0.194	3.305
5-3	Permanax™ + PR C-3	15 seconds/255°F(124°C)	0.317	3.527
5-6	Permanax™ + PR C-4	15 seconds/255°F(124°C)	0.215	3.913
5-5	Permanax™ + PR C-5	15 seconds/255°F(124°C)	0.194	3.868
5-7	Permanax™	25 seconds/255°F(124°C)	0.277	4.035
5-8	Permanax™ + PR C-1	25 seconds/255°F(124°C)	0.294	3.926
5-9	Permanax™ + PR C-2	25 seconds/255°F(124°C)	0.274	3.715
5-10	Permanax™ + PR C-3	25 seconds/255°F(124°C)	0.522	3.482
5-11	Permanax™ + PR C-4	25 seconds/255°F(124°C)	sample fogged	
5-12	Permanax™ + PR C-5	25 seconds/255°F(124°C)	0.238	3.701

Ex	Speed-2	Speed-3	Contrast-1	Contrast-2
5-1	1.63	1.23	4.508	5.371
5-2	1.64	1.22	4.486	5.246
5-3	1.65	0.957	4.192	4.519
5-4	1.77	0.989	3.783	3.695
5-5	1.7	1.3	5.084	5.722
5-6	1.62	1.2	4.944	6.812
5-7	1.81	1.17	3.345	3.392
5-8	1.8	1.15	3.313	3.094
5-9	1.75	1.15	3.687	3.688
5-10	1.92	0.736	1.917	2.212
5-11		sample fogged		
5-12	1.77	1.14	3.855	3.577

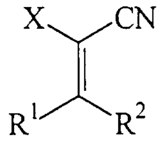
Reasonable modifications and variations are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined by the claims.

WHAT IS CLAIMED IS:

1. A black-and-white photothermographic element comprising a support bearing at least one photosensitive, image-forming, photothermographic emulsion layer comprising:

(a) a photosensitive silver halide;
(b) a non-photosensitive, reducible silver source;
(c) a reducing agent for silver ion; and
(d) a binder;

wherein said photothermographic emulsion layer or a layer adjacent thereto further comprises at least one substituted propenenitrile compound of the formula:



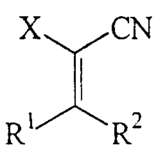
wherein:

R^1 represents a hydroxy group or a metal salt of a hydroxy group;
R^2 represents an alkyl group or an aryl group; and
X represents an electron withdrawing group at least as withdrawing as methoxycarbonyl; or
R^2 and X taken together can form a ring containing the electron withdrawing group.

2. A black-and-white thermographic element comprising a support bearing at least one image-forming, thermographic emulsion layer comprising:

(a) a non-photosensitive, reducible silver source;
(b) a reducing agent for silver ion; and
(c) a binder;

wherein said thermographic emulsion layer or a layer adjacent thereto further comprises at least one substituted propenenitrile compound of the formula:



wherein:

R^1 represents a hydroxy group or a metal salt of a hydroxy group;

R^2 represents an alkyl group or an aryl group; and

X represents an electron withdrawing group at least as withdrawing as methoxycarbonyl; or

R^2 and X taken together can form a ring containing the electron withdrawing group.

3. The element according to Claim 1 or 2 wherein X is an electron withdrawing group having a Hammett σ_p value greater than 0.39.

4. The element according to Claim 1 or 2 wherein X is selected from the group consisting of cyano, alkoxycarbonyl, hydroxycarbonyl, metaloxycarbonyl, nitro, acetyl, perfluoroalkyl, alkylsulfonyl, and arylsulfonyl.

5. The element according to Claim 1 or 2 wherein said non-photosensitive, reducible source of silver is a silver salt of a carboxylic acid having from 10 to 30 carbon atoms.

6. The element according to Claim 1 or 2 wherein R^2 represents an alkyl group having from 1 to 20 carbon atoms.

7. The element according to Claim 1 or 2 wherein R^2 represents an aryl group having 6 or 10 carbon atoms.

8. The element according to Claim 1 or 2 wherein said binder is hydrophobic.

9. The element according to Claim 1 or 2 wherein said reducing agent is a hindered phenol selected from the group consisting of binaphthols, biphenols, bis(hydroxynaphthyl)methanes, bis(hydroxyphenyl)methanes, and naphthols.

10. A process comprising the steps of:

(a) exposing the photothermographic element of Claim 1 on a support transparent to ultraviolet radiation or short wavelength visible radiation, to electromagnetic radiation to which the photosensitive silver halide of the element is sensitive to generate a latent image; and thereafter heating said element to form a visible image thereon;

(b) positioning said element with a visible image thereon between a source of ultraviolet or short wavelength visible radiation and an ultraviolet or short wavelength visible radiation photosensitive imageable medium; and

(c) then exposing said ultraviolet or short wavelength visible radiation sensitive imageable medium to ultraviolet or short wavelength visible radiation through said visible image on said element, thereby absorbing ultraviolet or short wavelength visible radiation in the areas of said element where there is a visible image and transmitting ultraviolet or short wavelength visible radiation where there is no visible image on said element.

11. A process comprising the steps of:

(a) heating the thermographic element of Claim 2 on a support transparent to ultraviolet radiation or short wavelength visible radiation, to a temperature sufficient to form a visible image thereon;

(b) positioning said element with a visible image thereon between a source of ultraviolet or short wavelength visible radiation and an ultraviolet or short wavelength visible radiation photosensitive imageable medium; and

(c) then exposing said ultraviolet or short wavelength visible radiation sensitive imageable medium to ultraviolet or short wavelength visible radiation through said visible image on said element, thereby absorbing ultraviolet or short wavelength visible radiation in the areas of said element where there is a visible image and transmitting ultraviolet or short wavelength visible radiation where there is no visible image on said element.

12. The process of Claim 10 or 11 wherein said imageable medium is a resist developable, ultraviolet or short wavelength visible radiation sensitive imageable medium.

13. The process of Claim 10 or 11 wherein said ultraviolet or short wavelength visible radiation sensitive imageable medium is a printing plate, a contact proof, or a duplicating film.