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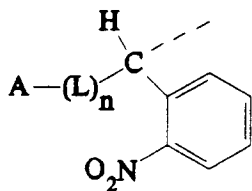
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**Post-processing stabilizers for photothermographic articles.**

Photothermographic compositions comprising a photographic silver halide, an organic silver salt, and a reducing agent for the organic silver salt, display improved stability in the presence of a compound having a nucleus of the formula :



wherein :

**A** represents any monovalent group for which the corresponding compound **AH** functions as a post-processing stabilizer,

**L** is a  $-\text{CO}_2-$  or a  $-\text{CH}_2\text{O}-$  group that is lost during or after the deblocking step, with **A** bonded to a carbon atom of this group, and

**n** is 0 or 1.

## FIELD OF THE INVENTION

This invention relates to photothermographic materials and in particular to post-processing stabilization of photothermographic silver-containing materials.

## BACKGROUND OF THE INVENTION

Silver halide containing photothermographic imaging materials processed with heat, and without liquid development have been known in the art for many years. These materials generally comprise a support having thereon a photographic light-sensitive silver halide, a light-insensitive organic silver salt, and a reducing agent for the organic silver salt.

The light-sensitive silver halide is in catalytic proximity to the light-insensitive organic silver salt so that the latent image, formed by irradiation of the silver halide, serves as a catalyst nucleus for the oxidation-reduction reaction of the organic silver salt with the reducing agent when the emulsion is heated above about 80° C. Such media are described, for example, in U.S. Pat. Nos. 3,457,075, 3,839,049, and 4,260,677. The silver halide may also be generated in the media by a preheating step in which halide ion is released to form silver halide.

A variety of ingredients may be added to these basic components to enhance performance. For example, toning agents may be incorporated to improve the color of the silver image of the photothermographic emulsions, as described in U.S. Pat. Nos. 3,846,136; 3,994,732 and 4,021,249. Various methods to produce dye images and multicolor images with photographic color couplers and leuco dyes are known and described in U.S. Pat. Nos. 4,022,617; 3,531,286; 3,180,731; 3,761,270; 4,460,681; 4,883,747 and *Research Disclosure*, March 1989, item 29963.

A common problem that exists with photothermographic systems is post-processing instability of the image. The photoactive silver halide still present in the developed image may continue to catalyze print-out of metallic silver during room light handling. Thus, there exists a need for stabilization of the unreacted silver halide. The addition of separate post-processing image stabilizers have been used to impart post-processing stability. Most often these are sulfur containing compounds such as mercaptans, thiones, and thioethers as described in *Research Disclosure*, June 1978, item 17029. U.S. Pat. Nos. 4,245,033; 4,837,141 and 4,451,561 describe sulfur compounds that are development restrainers for photothermographic systems. Mesoionic 1,2,4-triazolium-3-thiolates as fixing agents and silver halide stabilizers are described in U.S. Pat. No. 4,378,424. Substituted 5-mercapto-1,2,4-triazoles such as 3-amino-5-benzothio-1,2,4-triazole as post-processing stabilizers are described in U.S. Pat. Nos. 4,128,557; 4,137,079; 4,138,265, and *Research Disclosure*, May 1978, items 16977 and 16979.

Problems arising from the addition of stabilizers may include thermal fogging during processing and losses in photographic speed, maximum density or contrast at effective stabilizer concentrations.

Stabilizer precursors have blocking or modifying groups that are usually cleaved during processing with heat and/or alkali. This provides the primary active stabilizer which can combine with the photoactive silver halide in the unexposed and undeveloped areas of the photographic material. For example, in the presence of a stabilizer precursor in which the sulfur atom is unblocked upon processing, the resulting silver mercaptide will be more stable than the silver halide to light, atmospheric, and ambient conditions.

Various blocking techniques have been utilized in developing the stabilizer precursors. U.S. Pat. No. 3,615,617 describes acyl blocked photographically useful stabilizers. U.S. Pat. Nos. 3,674,478 and 3,993,661 describe hydroxyarylmethyl blocking groups. Benzylthio releasing groups are described in U.S. Pat. No. 3,698,898. Thiocarbonate blocking groups are described in U.S. Pat. No. 3,791,830, and thioether blocking groups in U.S. Pat. Nos. 4,335,200, 4,416,977, and 4,420,554. Photographically useful stabilizers which are blocked as urea or thiourea derivatives are described in U.S. Pat. No. 4,310,612. Blocked imidomethyl derivatives are described in U.S. Pat. No. 4,350,752, and imide or thioimide derivatives are described in U.S. Pat. No. 4,888,268. Removal of all of these aforementioned blocking groups from the photographically useful stabilizers is accomplished by an increase of pH during alkaline processing conditions of the exposed imaging material.

Thermally sensitive blocking groups have also been utilized. These blocking groups are removed by heating the imaging material during processing. Photographically useful stabilizers blocked as thermally sensitive carbamate derivatives are described in U.S. Pat. Nos. 3,844,797 and 4,144,072. These carbamate derivatives presumably regenerate the photographic stabilizer through loss of an isocyanate. Hydroxymethyl blocked photographic reagents which are unblocked through loss of formaldehyde during heating are described in U.S. Pat. No. 4,510,236. Development inhibitor releasing couplers releasing tetrazolythio moieties are described in U.S. Pat. No. 3,700,457. Substituted benzylthio releasing groups are described in U.S. Pat. No. 4,678,735. U.S.

Pat. Nos. 4,351,896 and 4,404,390 utilize carboxybenzylthio blocking groups for mesoionic 1,2,4-triazolium-3-thiolate stabilizers. Photographic stabilizers that are blocked by a Michael-type addition to the carbon-carbon double bond of either acrylonitrile or alkyl acrylates are described in U.S. Pat. Nos. 4,009,029 and 4,511,644, respectively. Heating of these blocked derivatives causes unblocking by a retro-Michael reaction.

Various disadvantages attend these different blocking techniques. Highly basic solutions, that are necessary to cause deblocking of the alkali sensitive blocked derivatives, are corrosive and irritating to the skin. With photographic stabilizers that are blocked with a heat removable group, it is often found that the liberated reagent or by-product can react with other components of the imaging construction and cause adverse effects. Also, inadequate or premature release of the stabilizing moiety during heat processing may occur.

There has been a continued need for improved post-processing stabilizers or stabilizer precursors that do not fog or desensitize photothermographic materials, and for stabilizer precursors that release the stabilizing moiety at the appropriate time and do not have any detrimental effects on the photosensitive material or user of said material.

Blocking groups which are removed by actinic radiation are discussed in the context of organic synthesis utility in Amit et al., *Israel J. Chem.* **1974**, *12*, 103; and V. N. R. Pillai, *Synthesis*, **1980**, 1-26. The *o*-nitrobenzyl group has been known as a photocleavable blocking group for some time (J. Barltrop et al, *J. Chem. Soc. Chem. Comm.* **1966**, 822-823.) Various substituted analogues have been prepared in order to maximize the photochemical efficiency and chemical yield, and to suppress colored products of the photolysis. The *o*-nitrobenzyl group has been used to protect many different functional groups, including carboxylic acids, amines, phenols, phosphates, and thiols.

The *o*-nitrobenzyl moiety has been used in various imaging and photoactive constructions. It has been used to block surfactants for radiation-induced tape removal as described in U.S. Pat. Nos. 4,478,967; 4,599,273; and 4,740,600; and peel-apart imaging as described in U.S. Pat. No. 4,554,238. Nitrobenzylated acids as sources of photogenerated acid for photoresists have been extensively studied, in for example F. M. Houlihan et al, *Proc. SPIE-Int. Soc. Opt. Eng. Vol. 920 (Advances in Resist Technology and Processing V)* **1988**, 67-74 and references therein. Other photoresist applications are as follows. Nitrobenzyl groups incorporated into polymeric structures are described in U.S. Pat. Nos. 4,108,839; 4,576,902; 4,465,760 and 4,456,679. Photoinhibitors for photopolymers are described in British Pat. No. 1,547,548; German Pat. No. 2,710,417, and U.S. Pat. No. 4,477,556. Nitrobenzyl compounds used as photoreductants and photoinhibitors for non-silver based photothermographic systems are described in U. S. Pat. Nos. 4,284,704; 4,273,860 and 3,880,659.

*o*-Nitrobenzylidene dyes have been used as photobleachable sensitizers for nitrate ion based non-silver photothermographic systems as described in co-pending cases U.S. Ser. Nos. 07/539,572 and 07/754,169, and U.S. Pat. No. 5,077,178.

In U. S. Pat. Nos. 4,343,893 and 4,501,896 the *o*-nitrobenzyl protecting group has been used in photographic applications along with other electron-poor benzyl protecting groups to mask development image modifier compounds.

U.S. Pat. No. 4,416,981 describes substituted benzothiazolines as photographic antifoggants but no special advantage is noted for the *o*-nitrobenzyl substitution.

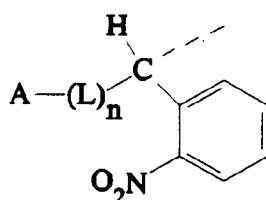
U. S. Pat. No. 4,187,110 also describes a development inhibitor releaser (DIR) coupler for conventional silver halide emulsions containing the *o*-nitrobenzyl functionality. In those applications as well, a photographically useful group is released from the blocking group by the action of processing, specifically electron transfer.

Photolytically active stabilizer precursors for photothermographic silver imaging compositions which apparently release bromine atoms are described in U.S. Pat. No. 4,459,350 and references cited therein.

Stabilizer precursors of the present invention are deblocked to release a stabilizer by the action of actinic radiation. Additionally, stabilizer precursors of this type can be added to photothermographic formulations without the necessity of rebalancing the formulation to compensate for effects on sensitometry, as is often the case with other stabilizers in the art.

## SUMMARY OF THE INVENTION

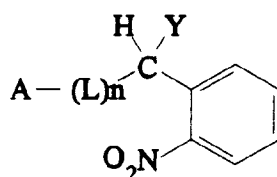
In one aspect this invention relates to photothermographic articles comprising a photothermographic composition coated on a substrate wherein the photothermographic composition comprises a photographic silver salt, an organic silver salt, and a reducing agent for the organic silver salt, and a stabilizer having a central nucleus of the formula:



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10 The dashed line (---) on the bridging methine group is defined as indicating that the valence of the carbon atom of the methine group is satisfied by any conveniently selected chemical group covalently bonded to that carbon.

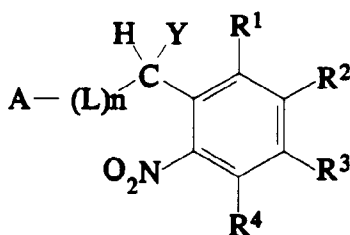
or a central nucleus of the formula:



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or a compound having the formula:



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wherein:

35 **A** represents any monovalent group for which the corresponding compound **AH** functions as a post-processing stabilizer having from 1 to 50 carbon atoms, and

**Y**, **R<sup>1</sup>**, **R<sup>2</sup>**, **R<sup>3</sup>**, and **R<sup>4</sup>** independently represent a group selected from hydrogen, alkyl, alkoxycarbonyl, alkenyl, aryl, hydroxy, mercapto, amino, amido, thioamido, carbamoyl, thiocarbamoyl, cyano, nitro, sulfo, carboxyl, fluoro, formyl, sulfoxyl, sulfonyl, hydrodithio, ammonio, phosphonio, silyl, and silyloxy groups having up to 18 carbon atoms, and wherein any two of **R<sup>1</sup>**, **R<sup>2</sup>**, **R<sup>3</sup>**, and **R<sup>4</sup>** may together form a fused ring structure with the central benzene ring, and

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**L** is a  $\text{-CO}_2\text{-}$  or  $\text{-CH}_2\text{O-}$  group wherein **A** is bonded to the carbon atom of **L**, and wherein **L** is lost during or after the deblocking step, and

**n** is 0 or 1.

The stabilizer precursors of the present invention may also be described as having the general formula

45



wherein:

**A** is as previously defined, and

**T** represents a covalent bond, or a  $\text{-CO}_2\text{-}$  or  $\text{-CH}_2\text{O-}$  group, (wherein **A** is bonded to the carbon atom of this group), and

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**M** represents a carbon atom having at least one hydrogen atom, and bonded thereto

**Z** represents an aromatic group having at least one nitro group substituent in the position *ortho*- to the substituent **A-T-M**.

Preferred stabilizer precursors are *o*-nitrobenzyl blocked derivatives of heterocyclic compounds that stabilize silver images. They typically comprise from about 0.01 wt% to 10 wt% of the dry photothermographic composition. They may be incorporated directly into the silver containing layer or into an adjacent layer. The stabilizer precursors of the invention are especially useful in articles and compositions for the preparation of photothermographic color and black and white images.

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Photothermographic articles of the present invention are useful for color and black and white imaging ap-

plications.

*o*-Nitrobenzyl blocked stabilizers of the present invention stabilize silver halide and/or minimize untimely leuco oxidation for improved post-processing stabilization without desensitization or fogging during heat processing.

As used herein, the term *o*-nitrobenzyl refers to a 2-nitrobenzyl moiety having at least one hydrogen on the benzylic carbon and one other substituent which may be hydrogen, and optionally having substituents on the aromatic ring, including ring fusions, or having the benzene ring replaced by a substituted or unsubstituted polycyclic aromatic moiety.

Where the term group is used in describing substituents, substitution is anticipated on the substituent for example, alkyl group includes ether groups (e.g.,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-}$ ), haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls, etc. while the term alkyl includes only hydrocarbons. Substituents which react with active ingredients, such as very strongly electrophilic or oxidizing substituents, would of course be excluded as not being inert or harmless.

As used herein the symbol " $\phi$ " means phenyl.

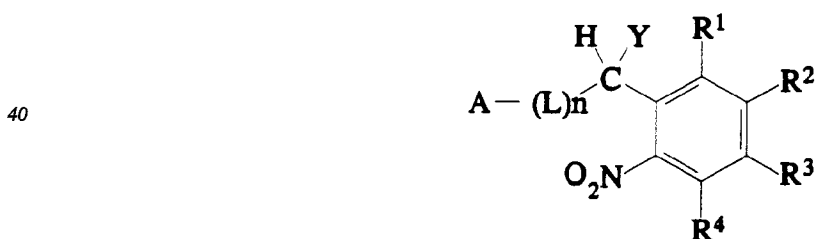
The stabilizer precursors of this invention are deblocked to release the parent stabilizer by the action of actinic radiation and therefore offer the advantage over unprotected stabilizers and heat-releasable stabilizers of being inert and inactive during the processing step, and resistant to thermal release during shelf aging. They are only released when they are needed. They are useful in a wide range of photothermographic media and processing conditions, since they do not appear to have specific requirements for release that attend most other masking groups in the art such as heating, acids or bases, or coupling with a reduction step.

## DETAILED DESCRIPTION OF THE INVENTION

Photothermographic articles of the present invention comprise a photothermographic composition coated on a substrate wherein the photothermographic construction comprises a photographic silver salt, an organic silver salt, a reducing agent for the organic silver salt, and a stabilizer having the formula:



or a compound of the formula:



wherein:

**A** represents any monovalent group for which the corresponding compound **AH** functions as a post-processing stabilizer having from 1 to 50 carbon atoms.

**Y**, **R<sup>1</sup>**, **R<sup>2</sup>**, **R<sup>3</sup>**, and **R<sup>4</sup>** independently represent a group selected from hydrogen, alkyl, alkoxy carbonyl, alkenyl, aryl, hydroxy, mercapto, amino, amido, thioamido, carbamoyl, thiocarbamoyl, cyano, nitro, sulfo, carboxyl, fluoro, chloro, bromo, formyl, sulfoxyl, sulfonyl, hydrodithio, ammonio, phosphonio, silyl, and silyloxy groups having up to 18 carbon atoms, and wherein any two of **R<sup>1</sup>**, **R<sup>2</sup>**, **R<sup>3</sup>**, and **R<sup>4</sup>** may together form a fused ring structure with the central benzene ring. Preferably, **R<sup>1</sup>**, **R<sup>2</sup>**, **R<sup>3</sup>**, and **R<sup>4</sup>** are hydrogen. **Y** is preferably selected from hydrogen, alkyl, and alkoxy carbonyl. More preferably **Y** is hydrogen.

**L** is a  $\text{-CO}_2\text{-}$  or  $\text{-CH}_2\text{O-}$  group wherein **A** is bonded to the carbon atom of **L**, and wherein **L** is lost during or after the deblocking step.

**n** is 0 or 1. Preferably **n** is 0.

The stabilizer precursors of the present invention may also be described as having the general formula

## A - T - M - Z

wherein:

**A** is as previously defined, and

**T** represents a covalent bond, or a -CO<sub>2</sub>- or -CH<sub>2</sub>O- group, (with **A** bonded to a carbon atom of this group)

5 and

**M** represents a carbon atom having at least one hydrogen atom, and bonded thereto

**Z** represents an aromatic group having at least one nitro group substituent in the position *ortho*- to the substituent **A-T-M**.

10 In photothermographic articles of the present invention the layer(s) that contain the photographic silver salt are referred to herein as emulsion layer(s). According to the present invention the *o*-nitrobenzyl blocked stabilizer is added either to one or more emulsion layers or to a layer or layers adjacent to one or more emulsion layers. Layers that are adjacent to emulsion layers may be for example, primer layers, image-receiving layers, interlayers, opacifying layers, antihalation layer, barrier layer, auxiliary layers, etc.

15 The *o*-nitrobenzyl group acts as a blocking group to block the activity of the primary stabilizer **AH**. If **AH** is left unblocked and added to the photothermographic emulsion at the same molar equivalent concentration as the blocked compound, **AH** desensitizes or fogs the emulsion. Unblocking to release the active stabilizer occurs after exposure and development, during exposure to ambient light or to light in an accelerated aging device. Thus, the blocked stabilizers of the present invention overcome the problems of desensitization and fogging that occur when the stabilizers are used in their unblocked form.

20 The substituents **Y**, **R<sup>1</sup>**, **R<sup>2</sup>**, **R<sup>3</sup>**, and **R<sup>4</sup>** are chosen so that the compound or a model compound in which **A** is replaced by H passes the following test for photoreactivity and low background stain.

25 To a solution of 3 g of 7.5 weight percent polyvinyl butyral in ethanol is added a solution of 8.5 millimoles of the compound in question in 0.5 mL of ethanol or tetrahydrofuran. The resulting solution is knife-coated 3 mil thick wet on unprimed opaque polyethylene terephthalate film and dried in a 70° C convection oven for 3 minutes. Samples of the coated film are exposed to 1200 foot-candle intensity fluorescent lights in a constant temperature 26°C and constant humidity (65% relative humidity) chamber for zero, one, and six hours. The polyvinylbutyral films are peeled from the polyester. If the infrared spectra of the films show greater than ten percent loss of intensity of the nitro band at about 1520 to 1540 cm<sup>-1</sup> after light exposure for one to six hours the compound is suitable for use in the present invention.

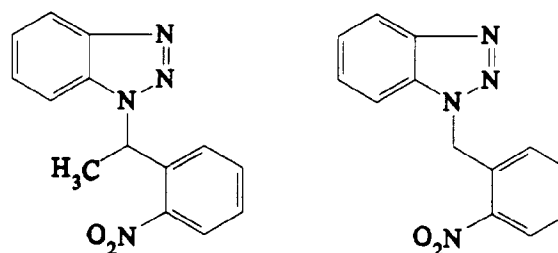
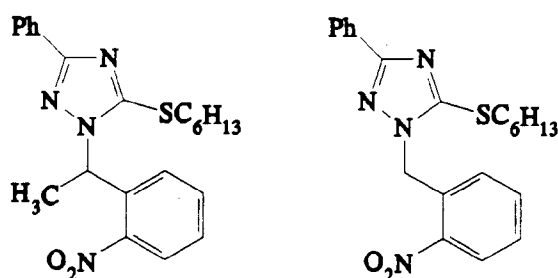
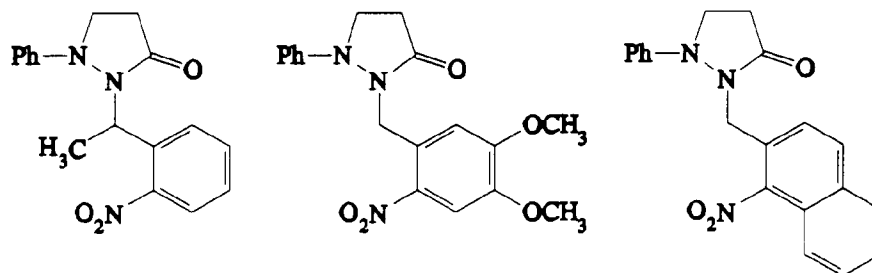
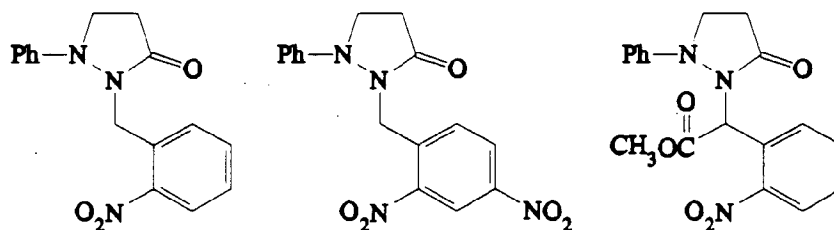
30 Preferably *o*-nitrobenzyl moieties that are used in the present invention show little or no color formation in the abovementioned film after light exposure for several hours.

**A** is preferably attached through a nitrogen atom. Post-processing stabilizing groups for stabilizing silver ion **AH** usually have a heteroatom such as nitrogen available for complexing silver ion. The compounds are usually ring structures with the heteroatom within the ring or external to the ring. These compounds are well known to one ordinarily skilled in the photographic art. Examples of **AH** include nitrogen-containing heterocycles, substituted or unsubstituted, including but not limited to benzimidazole, benzotriazole, triazoles, tetrazoles, phenylmercaptotetrazoles, imidazoles, pyrazolidinones or any such compound that stabilizes the emulsion layer, and particularly those that have deleterious effects on the initial sensitometry or excessive fog if used unblocked. Non-limiting examples of **AH** include imidazoles such as benzimidazole and benzimidazole derivatives; triazoles such as benzotriazole, 1,2,4-triazole, 3-amino-1,2,4-triazole, and 2-thioalkyl-5-phenyl-1,2,4-triazoles; tetrazoles such as 5-amino tetrazole; triazines such as mercaptotetrahydrotriazine; piperidones; tetraazaindanes; 8-azaguanine; thymine; thiazolines such as 2-amino-2-thiazoline, indazoles; hypoxanthines; 2H-pyridooxazin-3(4H)-one and other nitrogen containing heterocycles. Many of such compounds are summarized in *Research Disclosure*, March 1989, item 29963. **AH** may also be a compound which stabilizes a leuco dye, usually a reducing agent which has an active hydrogen which can be masked by replacement with the nitrobenzyl group. An example of a useful reducing agent is 1-phenyl-3-pyrazolidinone (described in U.S. Pat. No. 4,423,139 for stabilizing leuco dyes). Masking of such reducing agents during the processing step is usually necessary since they may act as developers or development accelerators to cause unacceptable fogging.

50 In another preferred embodiment of the invention, **Y** represents a hydrogen, alkyl, or an alkoxycarbonyl group; **R<sup>1</sup>-R<sup>4</sup>** represent hydrogen, **n** is 0, and **AH** is a post-processing stabilizer identified to be most advantageous for a given photothermographic construction; for instance, 1-phenyl-3-pyrazolidinone, benzotriazole, or 3-(*n*-hexylthio)-5-phenyl-1,2,4-triazole.

55 Photothermographic articles of the invention may contain other post-processing stabilizers or stabilizer precursors in combination with the compounds of the invention, as well as other additives in combination with the compound of the invention such as shelf-life stabilizers, toners, development accelerators and other image modifying agents.

Non-limiting examples of *o*-nitrobenzyl protected stabilizer precursors are:



The amounts of the above described ingredients that are added to the emulsion layer according to the present invention may be varied depending upon the particular compound used and upon the type of emulsion layer (i.e., black and white or color). However, the ingredients are preferably added in an amount of 0.01 to 100 mol, and more preferably from 0.1 to 50 mol per mol of silver halide in the emulsion layer.

The photothermographic dry silver emulsions of this invention may be constructed of one or more layers on a substrate. Single layer constructions must contain the silver source material, the silver halide, the developer and binder as well as optional additional materials such as toners, coating aids, and other adjuvants. Two-layer constructions must contain the silver source and silver halide in one emulsion layer (usually the layer adjacent to the substrate) and some of the other ingredients in the second layer or both layers, although two layer constructions comprising a single emulsion layer containing all the ingredients and a protective topcoat are envisioned. Multicolor photothermographic dry silver constructions may contain sets of these bilayers for each color, or they may contain all ingredients within a single layer as described in U.S. Pat. No. 4,708,928. In the case of multilayer multicolor photothermographic articles the various emulsion layers are generally main-

tained distinct from each other by the use of functional or non-functional barrier layers between the various photosensitive layers as described in U.S. Pat. No. 4,460,681.

While not necessary for practice of the present invention, it may be advantageous to add mercury (II) salts to the emulsion layer(s) as an antifoggant. Preferred mercury (II) salts for this purpose are mercuric acetate and mercuric bromide.

The light sensitive silver halide used in the present invention may typically be employed in a range of 0.75 to 25 mol percent and, preferably, from 2 to 20 mol percent of organic silver salt.

The silver halide may be any photosensitive silver halide such as silver bromide, silver iodide, silver chloride, silver bromiodide, silver chlorobromiodide, silver chlorobromide, etc. The silver halide may be in any form which is photosensitive including, but not limited to cubic, orthorhombic, tabular, tetrahedral, etc., and may have epitaxial growth of crystals thereon.

The silver halide used in the present invention may be employed without modification. However, it may be chemically sensitized with a chemical sensitizing agent such as a compound containing sulfur, selenium or tellurium etc., or a compound containing gold, platinum, palladium, rhodium or iridium, etc., a reducing agent such as a tin halide, etc., or a combination thereof. The details of these procedures are described in T.N. James "The Theory of the Photographic Process", Fourth Edition, Chapter 5, pages 149 to 169.

The silver halide may be added to the emulsion layer in any fashion which places it in catalytic proximity to the silver source. Silver halide and the organic silver salt which are separately formed or "preformed" in a binder can be mixed prior to use to prepare a coating solution, but it is also effective to blend both of them in a ball mill for a long period of time. Further, it is effective to use a process which comprises adding a halogen-containing compound in the organic silver salt prepared to partially convert the silver of the organic silver salt to silver halide.

Methods of preparing these silver halide and organic silver salts and manners of blending them are known in the art and described in *Research Disclosure*, June 1978, item 17029, and U.S. Pat. No. 3,700,458.

The use of preformed silver halide emulsions 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. Pat. Nos. 2,618,556; 2,614,928; 2,565,418; 3,241,969; and 2,489,341. The silver halide grains may have any crystalline habit including, but not limited to cubic, tetrahedral, orthorhombic, tabular, laminar, platelet, etc.

The organic silver salt may be any organic material which contains a reducible source of silver ions. Silver salts of organic acids, particularly long chain (10 to 30 preferably 15 to 28 carbon atoms) fatty carboxylic acids are preferred. Complexes of organic or inorganic silver salts wherein the ligand has a gross stability constant between 4.0 and 10.0 are also desirable. The silver source material should preferably constitute from about 5 to 30 percent by weight of the imaging layer.

The organic silver salt which can be used in the present invention is a silver salt which is comparatively stable to light, but forms a silver image when heated to 80° C or higher in the presence of an exposed photocatalyst (such as photographic silver halide) and a reducing agent.

Preferred organic silver salts include silver salts of organic compounds having a carboxy group. Non-limiting examples thereof include silver salts 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 caproate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartrate, silver linoleate, silver butyrate and silver camphorate, mixtures thereof, etc. Silver salts with a halogen atom or a hydroxyl on the aliphatic carboxylic acid can also be effectively used. Preferred examples of the silver salts of aromatic carboxylic acids 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*-phenyl benzoate, etc., silver gallate, silver tannate, silver phthalate, silver terephthalate, silver salicylate, silver phenylacetate, silver pyromellitate, a silver salt of 3-carboxymethyl-4-methyl-4-thiazoline-2-thione or the like as described in U.S. Pat. No. 3,785,830, and silver salt of an aliphatic carboxylic acid containing a thioether group as described in U.S. Pat. No. 3,330,663, etc.

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-(ethylglycolamido) benzothiazole, a silver salt of thioglycolic acid such as a silver salt of an *S*-alkyl thioglycolic 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 a thioamide, a silver salt of 5-carboxylic-1-methyl-2-phenyl-4-thiopyridine, a silver salt of mercaptotriazine, a silver salt of 2-mercaptobenzoxazole, a silver salt as described in U.S. Pat. No. 4,123,274, for example, a silver salt of 1,2, 4-mercaptothiazole derivative such as a silver salt of 3-amino-

5-benzylthio-1,2,4-thiazole, a silver salt of thione compound such as a silver salt of 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione as disclosed in U.S. Pat. No. 3,301,678.

Furthermore, a silver salt of a compound containing an imino group may be used. Preferred examples of these compounds include silver salts of benzothiazole and derivatives thereof, for example, silver salts of benzothiazoles such as silver methylbenzotriazolate, etc., silver salt of halogen-substituted benzotriazoles, such as silver 5-chlorobenzotriazolate, etc., silver salts of carboimidobenzotriazole, etc., silver salt of 1,2,4-triazoles or 1-*H*-tetrazoles as described in U.S. Pat. No. 4,220,709, silver salts of imidazoles and imidazole derivatives, and the like. Various silver acetylide compounds can also be used, for instance, as described in U.S. Pat. Nos. 4,761,361 and 4,775,613.

It is also found convenient to use silver half soaps, of which an equimolar blend of silver behenate and behenic acid, prepared by precipitation from aqueous solution of the sodium salt of commercial behenic acid and analyzing about 14.5 percent silver, represents a preferred example. Transparent sheet materials made on transparent film backing require a transparent coating and for this purpose the silver behenate full soap, containing not more than about four or five percent of free behenic acid and analyzing about 25.2 percent silver may be used.

The method used for making silver soap dispersions 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. Pat. No. 3,985,565.

The light-sensitive silver halides may be advantageously spectrally sensitized with various known dyes including cyanine, merocyanine, styryl, hemicyanine, oxonol, hemioxonol and xanthene dyes. Useful cyanine dyes include those having a basic nucleus, such as a thiazoline nucleus, an oxazoline nucleus, a pyrroline nucleus, a pyridine nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and an imidazole nucleus. Useful merocyanine dyes which are preferred include those having not only the above described basic nuclei but also acid nuclei, such as a thiohydantoin nucleus, a rhodanine nucleus, an oxazolidinedione nucleus, a thiazolidinedione nucleus, a barbituric acid nucleus, a thiazolinone nucleus, a malononitrile nucleus and a pyrazolone nucleus. In the above described cyanine and merocyanine dyes, those having imino groups or carboxyl groups are particularly effective. Practically, the sensitizing dyes to be used in the present invention may be properly selected from known dyes such as those described in U.S. Pat. Nos. 3,761,279, 3,719,495, and 3,877,943, British Pat Nos. 1,466,201, 1,469,117 and 1,422,057, and can be located in the vicinity of the photocatalyst according to known methods. Spectral sensitizing dyes may be typically used in amounts of about  $10^{-4}$  mol to about 1 mol per 1 mol of silver halide.

The reducing agent for the organic silver salt may be any material, preferably organic material, that can reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful but hindered phenol reducing agents are preferred. The reducing agent should be present as 1 to 10 percent by weight of the imaging layer. In multilayer constructions, if the reducing agent is added to a layer other than an emulsion layer, slightly higher proportions, of from about 2 to 15 percent tend to be more desirable.

A wide range of reducing agents has been disclosed in dry silver systems including amidoximes such as phenylamidoxime, 2-thienylamidoxime and *p*-phenoxyphenylamidoxime, azines (e.g., 4-hydroxy-3,5-dimethoxybenzaldehydeazine); a combination of aliphatic carboxylic acid aryl hydrazides and ascorbic acid, such as 2,2'-bis(hydroxymethyl)propionyl- $\beta$ -phenylhydrazide in combination with ascorbic acid; a combination of polyhydroxybenzene and hydroxylamine, a reductone and/or a hydrazine (e.g., a combination of hydroquinone and bis(ethoxyethyl)hydroxylamine, piperidinohexose reductone or formyl-4-methylphenylhydrazine); hydroxamic acids such as phenylhydroxamic acid, *p*-hydroxyphenylhydroxamic acid, and  $\beta$ -alaninehydroxamic acid; a combination of azines and sulfonamidophenols, (e.g., phenothiazine and 2,6-dichloro-4-benzenesulfonamidophenol);  $\alpha$ -cyanophenylacetic acid derivatives such as ethyl- $\alpha$ -cyano-2-methylphenylacetate, ethyl  $\alpha$ -cyanophenylacetate; bis- $\beta$ -naphthols as illustrated by 2,2'-dihydroxyl-1-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, and bis(2-hydroxy-1-naphthyl)methane; a combination of bis- $\beta$ -naphthol and a 1,3-dihydroxybenzene derivative, (e.g., 2,4-dihydroxybenzophenone or 2,4-dihydroxyacetophenone); 5-pyrazolones such as 3-methyl-1-phenyl-5-pyrazolone; reductones as illustrated by dimethylaminohexose reductone, anhydrodihydroaminohexose reductone, and anhydrodihydropiperidonehexose reductone; sulfonamido-phenol reducing agents such as 2,6-dichloro-4-benzenesulfonamidophenol, and *p*-benzenesulfonamidophenol; 2-phenylindane-1,3-dione and the like; chromans such as 2,2-dimethyl-7-*t*-butyl-6-hydroxychroman; 1,4-dihydropyridines such as 2,6-dimethoxy-3,5-dicarboethoxy-1,4-dihydropyridine; bisphenols (e.g., bis(2-hydroxy-3-*t*-butyl-5-methylphenyl)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); ascorbic acid derivatives (e.g., 1-ascorbyl palmitate, ascorbyl stearate); and unsaturated aldehydes and ketones, such as benzil and biacetyl; 3-pyrazolidones and certain indane-1,3-diones.

In addition to the aforementioned ingredients it may be advantageous to include additives known as "toners" that improve the image. Toner materials may be present, for example, in amounts from 0.1 to 10 percent by weight of all silver bearing components. Toners are well known materials in the photothermographic art as shown in U.S. Pat. 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, and a quinazolinone, 3-phenyl-2-pyrazoline-5-one, 1-phenylurazole, quinazoline, and 2,4-thiazolidinedione; naphthalimides (e.g., *N*-hydroxy-1,8-naphthalimide); cobalt complexes (e.g., cobaltic hexammine trifluoroacetate); mercaptans as illustrated by 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, (e.g., (*N,N*-dimethylaminomethyl)phthalimide, and *N,N*-(dimethylaminomethyl)naphthalene-2,3-dicarboximide); and a combination of blocked pyrazoles, isothiuronium derivatives and certain photobleaching agents (e.g., a combination of *N,N'*-hexamethylene bis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoctane)bis(isothiuronium trifluoroacetate) and 2-(tribromomethylsulfonyl)benzothiazole); and merocyanine dyes such as 3-ethyl-5[(3-ethyl-2-benzothiazolinyldene)-1-methylethylidene]-2-thio-2,4-oxazolidinedione; phthalazinone and 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 phthalazinone plus sulfinic acid derivatives (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, and tetrachlorophthalic anhydride); quinazolinones, 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 (e.g., 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 asymmetric triazines (e.g., 2,4-dihydroxypyrimidine, 2-hydroxy-4-aminopyrimidine), azauracils, and tetrazapentalene derivatives (e.g., 3,6-dimercapto-1,4-diphenyl-1*H*,4*H*-2,3*a*,5,6*a*-tetrazapentalene, and 1,4-di(*o*-chlorophenyl)-3,6-dimercapto-1*H*,4*H*-2,3*a*,5,6*a*-tetrazapentalene).

A number of methods are known in the art for obtaining color images with dry silver systems including: a combination of silver benzotriazole, well known magenta, yellow and cyan dye-forming couplers, aminophenol developing agents, a base release agent such as guanidinium trichloroacetate and silver bromide in poly(vinyl butyral) as described in U.S. Pat. Nos. 4,847,188 and 5,064,742; preformed dye release systems such as those described in U.S. Pat. No. 4,678,739; a combination of silver bromide, sulfonamidophenol reducing agent, silver behenate, poly(vinyl butyral), an amine such as *n*-octadecylamine and 2-equivalent or 4-equivalent cyan, magenta or yellow dye-forming couplers; leuco dye bases which oxidize to form a dye image (e.g., Malachite Green, Crystal Violet and para-rosaniline); a combination of *in situ* silver halide, silver behenate, 3-methyl-1-phenylpyrazolone and *N,N*-dimethyl-*p*-phenylenediamine hydrochloride; incorporating phenolic leuco dye reducing agents such as 2(3,5-di-*t*-butyl)-4-hydroxyphenyl)-4,5-diphenylimidazole, and bis(3,5-di-*t*-butyl)-4-hydroxyphenyl)phenylmethane, incorporating azomethine dyes or azo dye reducing agents; silver dye bleach processes (for example, an element comprising silver behenate, behenic acid, poly(vinyl butyral), poly(vinylbutyral)peptized silver bromide emulsion, 2,6-dichloro-4-benzenesulfonamidophenol, 1,8-(3,6-diazaoctane)bis(isothiuronium-*p*-toluenesulfonate) and an azo dye can be exposed and heat processed to obtain a negative silver image with a uniform distribution of dye, and then laminated to an acid activator sheet comprising polyacrylic acid, thiourea and *p*-toluenesulfonic acid and heated to obtain well defined positive dye images); and amines such as aminoacetanilide (yellow dye-forming), 3,3'-dimethoxybenzidine (blue dye-forming) or sulfanilide (magenta dye forming) that react with the oxidized form of incorporated reducing agents such as 2,6-dichloro-4-benzenesulfonamidophenol to form dye images. Neutral dye images can be obtained by the addition of amines such as behenylamine and *p*-anisidine.

Leuco dye oxidation in such silver halide systems for color formation is disclosed in U.S. Pat. Nos. 4,021,240, 4,374,821, 4,460,681 and 4,883,747.

Silver halide emulsions containing the stabilizers of this invention can be protected further against the additional production of fog and can be stabilized against loss of sensitivity during shelf storage. Suitable antifoggants, stabilizers, and stabilizer precursors which can be used alone or in combination, include thiazolium salts as described in U.S. Pat. Nos. 2,131,038 and 2,694,716; azaindenes as described in U.S. Pat. Nos. 2,886,437 and 2,444,605; mercury salts as described in U.S. Pat. No. 2,728,663; urazoles as described in U.S. Pat. No. 3,287,135; sulfocatechols as described in U.S. Pat. No. 3,235,652; oximes as described in British Pat. No. 623,448; nitrones; nitroindazoles; polyvalent metal salts as described in U.S. Pat. No. 2,839,405; thiouronium salts as described in U.S. Pat. No. 3,220,839; and palladium, platinum and gold salts described in U.S. Pat. Nos. 2,566,263 and 2,597,915; halogen-substituted organic compounds as described in U.S. Pat. Nos. 4,108,665 and 4,442,202; triazines as described in U.S. Pat. Nos. 4,128,557; 4,137,079; 4,138,265; and

4,459,350; and phosphorous compounds as described in U.S. Pat. No. 4,411,985.

Stabilized emulsions of the invention can contain plasticizers and lubricants such as polyalcohols (e.g., glycerin and diols of the type described in U.S. Pat. No. 2,960,404); fatty acids or esters such as those described in U.S. Pat. No. 2,588,765 and U.S. Pat. No. 3,121,060; and silicone resins such as those described in British Pat. No. 955,061.

The photothermographic elements of the present invention may include image dye stabilizers. Such image dye stabilizers are illustrated by British Pat. No. 1,326,889; U.S. Pat. Nos. 3,432,300; 3,698,909; 3,574,627; 3,573,050; 3,764,337 and 4,042,394.

Photothermographic elements containing emulsion layers stabilized according to the present invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in U.S. Pat. Nos. 3,253,921; 2,274,782; 2,527,583 and 2,956,879. If desired, the dyes can be mordanted, for example, as described in U.S. Pat. No. 3,282,699.

Photothermographic elements containing emulsion layers stabilized as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in U.S. Pat. No. 2,992,101 and U.S. Pat. No. 2,701,245.

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

The binder may be selected from any of the well-known natural or synthetic resins such as gelatin, polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, and the like. Copolymers and terpolymers are of course included in these definitions. The preferred photothermographic silver containing polymers are polyvinyl butyral, butyl ethyl cellulose, methacrylate copolymers, maleic anhydride ester copolymers, polystyrene, and butadiene-styrene copolymers.

Optionally, these polymers may be used in combinations of two or more thereof. Such a polymer 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. As a guide in the case of carrying at least an organic silver salt, it can be said that a preferable ratio of the binder to the organic silver salt ranges from 15:1 to 1:2, and particularly from 8:1 to 1:1.

Photothermographic emulsions containing a stabilizer according to the present invention may be coated on a wide variety of supports. Typical supports include polyester film, subbed polyester film, poly(ethylene terephthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related or resinous materials, as well as glass, paper metal and the like. Typically, a flexible support is employed, especially a paper support, which may be partially acetylated or coated with baryta and/or an  $\alpha$ -olefin polymer, particularly a polymer of an  $\alpha$ -olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like. Substrates may be transparent or opaque.

Substrates with a backside resistive heating layer may also be used in color photothermographic imaging systems such as shown in U.S. Pat. Nos. 4,460,681 and 4,374,921.

Photothermographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in U.S. Pat. No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in U.S. Pat. No. 2,761,791 and British Pat. No. 837,095.

Additional layers may be incorporated into photothermographic articles of the present invention such as dye receptive layers for receiving a mobile dye image, an opacifying layer when reflection prints are desired, a protective topcoat layer and a primer layer as is known in the photothermographic art. Additionally, it may be desirable in some instances to coat different emulsion layers on both sides of a transparent substrate, especially when it is desirable to isolate the imaging chemistries of the different emulsion layers.

The present invention will be illustrated in detail in the following examples, but the embodiment of the present invention is not limited thereto.

## EXAMPLES

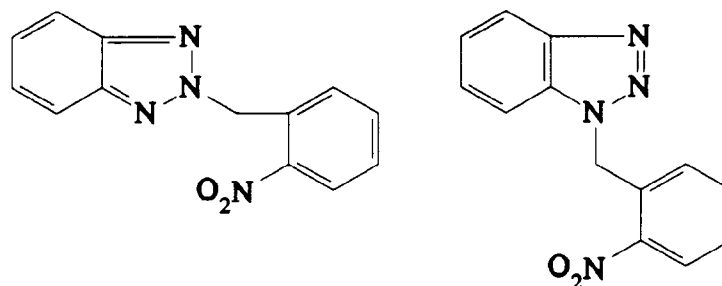
The first three examples are typical synthetic procedures for compounds of the invention. Examples 4 through 8 illustrate the utility of the invention in photothermographic imaging constructions. The scope of the invention is not limited to the examples herein.

TLC means "thin layer chromatography".

All materials used in the following examples were readily available from standard commercial sources such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise noted.

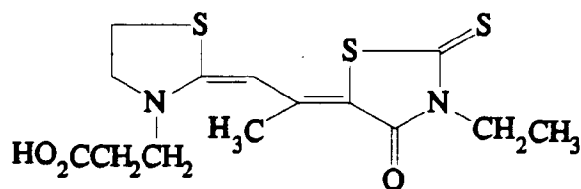
Densitometry measurements were made on a custom built computer scanned densitometer and are believed to be comparable to measurements obtainable from commercially available densitometers.

The structure of compounds I-A and I-B; II, IIA, and IIB; IIIA, IIIB, and IIIC are shown below:

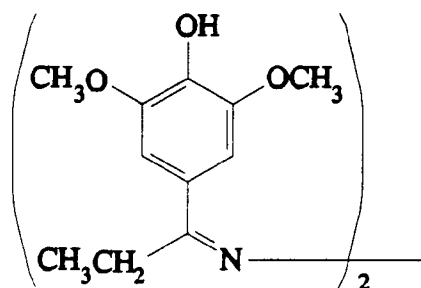


I-A

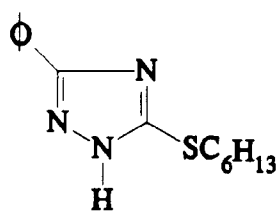
I-B



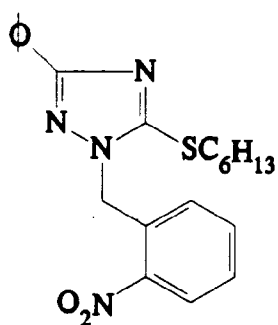
Sensitizing Dye A



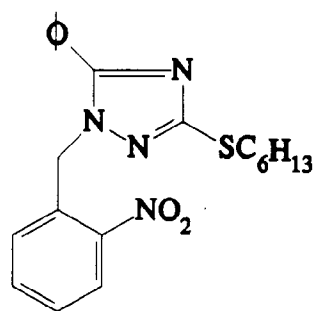
Leuco Dye B



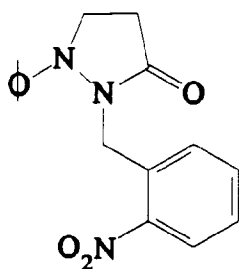
II



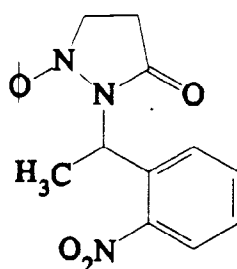
II-A



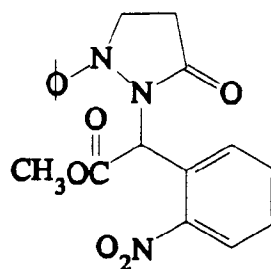
II-B



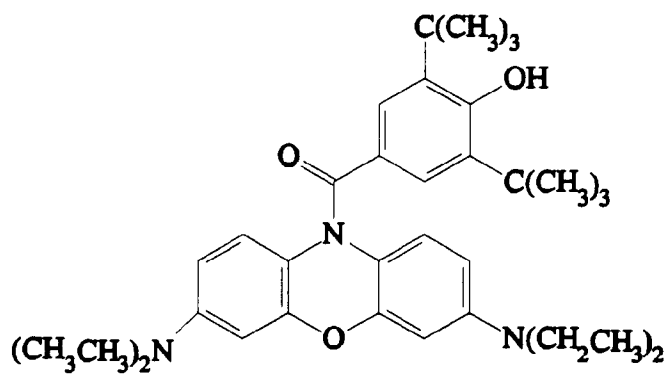
III-A



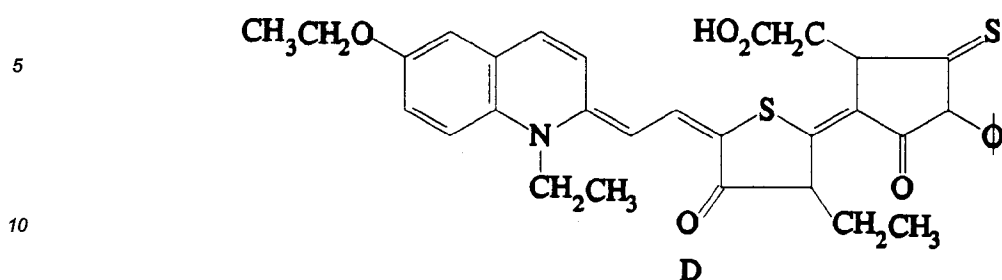
III-B



III-C



C



### Example 1

15 This example describes a preparation generally useful for this class of compounds and particularly shown as the preparation of 1- and 2-(*o*-nitrobenzyl)benzotriazole (**I-A** and **I-B**, respectively)

2-Nitrobenzyl bromide (9.1 g) and 5 g benzotriazole were stirred together with 4.24 g triethylamine in 25 mL dichloromethane. The reaction mixture was allowed to stir for 5 hours, then extracted with dilute sodium carbonate solution and dried with magnesium sulfate, filtered, and evaporated. The crude product (8.1 g) was recrystallized from methanol/ethyl acetate. TLC (on silica) showed two components, **I-A** (minor) and **I-B** (major). The crude product was used for examples that follow.

### Example 2

25 This example demonstrates the preparation of compounds **II-A** and **II-B**.

To a stirred solution of 5.00 g 3-(*n*-hexylthio)-5-phenyl-1,2,4-triazole (**II**), 4.13 g *o*-nitrobenzyl bromide, and 0.310 g tetra-*n*-butylammonium bromide in 200 mL dichloromethane was added a solution of 4.57 g of potassium carbonate in water. After vigorous stirring for five days, the layers were separated. The aqueous layer was washed with dichloromethane and the combined organic layers washed with brine (3x100 mL) and dried with sodium sulfate, filtered and concentrated *in vacuo* to give 7.4 g of a light yellow oil. Chromatography on a silica gel flash column (4.6 x 15 cm dry packed and eluted with 50:50 dichloromethane-hexane) gave 4.45 g **II-A** and 1.22 g of a mixture of **II-A** and **II-B** containing ca. 18% **II-A**. As the isomers **II-A** and **II-B** were equally effective, separation was not necessary.

### Example 3

35 This example demonstrates the preparation of compound **III-A**.

To a suspension of 4.32 g 1-phenyl-3-pyrazolidinone in 30 mL anhydrous ethanol under nitrogen was added 19 mL of 1.07 M sodium ethoxide in ethanol, and 3.08 g 2-nitrobenzyl bromide was added. After about 100 minutes, TLC (in ether) showed the reaction complete. The solvent was removed *in vacuo* overnight. The residue was taken up in ethyl acetate, washed with aqueous sodium bicarbonate and water, and evaporated. A viscous oil (5.74 g) was obtained. The crude product was flash chromatographed with silica gel in ether. After evaporation of solvent, 3.75 g **III-A** was obtained, which crystallized on standing.

### Example 4

50 A silver premix was prepared as follows: a dispersion of silver behenate half soap was made at 10% solids in toluene and acetone by homogenization. To 223.3 g of the silver half soap dispersion was added 0.34 g of polyvinyl butyral. After 15 minutes of mixing, 7.6 mL of a solution of 0.963 g mercuric acetate in 19.0 g methanol, and 21.2 mL of a solution of 1.0 g calcium bromide in 49.0 g ethanol were added. Then 14.5 mL of a solution of 1.45 g calcium bromide in 48.5 g ethanol was added 60 minutes later. After 60 minutes of mixing 41.2 g of polyvinylbutyral was added.

To 29.3 g of the silver premix described above was added 1.47 mL of a solution of 0.021 g sensitizing dye **A** in 50 mL methanol.

After 30 minutes a magenta color-forming leuco dye **B** solution was added as shown below.

| Component                                                           | Amount  |
|---------------------------------------------------------------------|---------|
| Leuco Dye B                                                         | 0.61 g  |
| Phthalazinone                                                       | 0.916 g |
| Tetrahydrofuran                                                     | 22.4 g  |
| Methyl Ethyl Ketone                                                 | 33.6 g  |
| VAGH™ (Union Carbide)<br>(a vinyl acetate/vinyl chloride copolymer) | 2.2 g   |
| Polyvinylbutyral                                                    | 9.8 g   |

The leuco dye **B** is disclosed in U.S. Pat. No. 4,795,697.

A topcoat solution was prepared consisting of 23% by weight polystyrene resin, and 3.1 wt % Acryloid B-66™ (Monsanto) in approximately 50:50 mixture of toluene and methyl ethyl ketone.

To 10.0g of the magenta silver coating solution was added 0.4 mL or 0.9 mL of the mixture of **I-A** and **I-B** from Example 1, at a concentration of 0.25 g mixture in 5.0 mL of tetrahydrofuran, or 0.3 mL of benzotriazole (BZT) at a concentration of 0.34 g in 5 mL ethanol, or 0.4 mL or 0.9 mL of *o*-nitrobenzyl alcohol (BA) at a concentration of 0.14 g in 5.0 mL ethanol.

The magenta silver layer and topcoat were each coated at a wet thickness of 2 mils, and dried for 5 minutes at 82°C. The samples were exposed for 10<sup>-3</sup> seconds through a 58 Wratten filter and a 0 to 3 continuous wedge and developed by heating to approximately 138°C for 6 seconds.

The density of magenta color for each sample was measured using a green filter of a computer densitometer.

The initial sensitometric data were:

| Stabilizer                                  | D <sub>min</sub> | D <sub>max</sub> | Speed <sup>1</sup> | Contrast <sup>2</sup> |
|---------------------------------------------|------------------|------------------|--------------------|-----------------------|
| Control (0.0 mL)                            | 0.10             | 1.68             | 2.19               | 1.25                  |
| 0.3 mL BZT                                  | 0.10             | 0.11             | **                 | **                    |
| 0.4 mL BA                                   | 0.10             | 1.72             | 2.20               | 1.24                  |
| 0.9 mL BA                                   | 0.10             | 1.78             | 2.22               | 1.31                  |
| 0.4 mL <b>I-A</b> + <b>I-B</b> <sup>3</sup> | 0.10             | 1.77             | 2.16               | 1.26                  |
| 0.9 mL <b>I-A</b> + <b>I-B</b>              | 0.10             | 1.73             | 2.20               | 1.31                  |

\*\* In this and subsequent tables, means the value was not obtainable (i.e., no image)

<sup>1</sup> Log exposure corresponding to density of 0.6 above D<sub>min</sub>.

<sup>2</sup> Average contrast measured by the slope of the line joining density points 0.3 and 0.9 above D<sub>min</sub>.

<sup>3</sup> This is an approximate molar equivalent of the BZT parent stabilizer.

Post-processing stability was measured by exposing imaged samples to 1200 ft-candles of illumination (daylight fluorescent bulbs) for 6 and 24 hours at 65% relative humidity and 26.7 °C.

| Stabilizer       | 6 hours             |                     | 24 hours            |                     |
|------------------|---------------------|---------------------|---------------------|---------------------|
|                  | $\Delta D_{\min}^1$ | $\Delta D_{\max}^1$ | $\Delta D_{\min}^1$ | $\Delta D_{\max}^1$ |
| Control (0.0 mL) | + .17               | - .19               | + .24               | - .54               |
| 0.3 mL BZT       | + .11               | **                  | + .11               | **                  |
| 0.4 mL BA        | + .13               | - .25               | + .22               | - .66               |
| 0.9 mL BA        | + .11               | - .23               | + .21               | - .78               |
| 0.4 mL I-A + I-B | + .11               | - .23               | + .11               | - .66               |
| 0.9 mL I-A + I-B | + .09               | - .21               | + .08               | - .77               |

<sup>1</sup>  $\Delta D = D_{\text{Final}} - D_{\text{Initial}}$ . D values represent reflectance optical density through a green filter.

At this concentration of the primary stabilizer benzotriazole,  $D_{\min}$  post-processing improvements were observed, but significant desensitization of the silver halide emulsion had occurred. With the use of the masked benzotriazoles I-A + I-B, the benzotriazole activity was adequately blocked to minimize any initial desensitization effects and yet release of BZT occurred at the appropriate time for  $D_{\min}$  post processing improvements similar to the unblocked BZT stabilizer. 2-Nitrobenzyl alcohol alone (BA) also contributes some post processing stabilization at 6 hours, but the effect is minimal after prolonged exposure to 24 hours illumination.

#### Example 5

To 10.0g of a magenta silver halide coating solution similar in component composition as described in Example 4, was added 0.8 mL of an isomer mixture, compounds II-A and II-B at a concentration of 0.3 g in 5.0 mL ethanol, or 0.8 mL of the primary stabilizer 3-(*n*-hexylthio)-5-phenyl-1,2,4-triazole (II) at a concentration of 0.2 g in 5.0 mL ethanol. The silver solutions and topcoats were coated, exposed, and processed as described in Example 4. The density of magenta color for each sample was measured using a green filter of a computer densitometer. The initial sensitometric data are shown below.

| Stabilizer       | $D_{\min}$ | $D_{\max}$ | Speed <sup>1</sup> | Contrast <sup>2</sup> | Contrast <sup>3</sup> |
|------------------|------------|------------|--------------------|-----------------------|-----------------------|
| Control (0.0 mL) | .08        | 1.73       | 1.85               | 1.60                  | 1.80                  |
| 0.8 mL IIA + IIB | .08        | 1.54       | 1.86               | 1.63                  | 1.43                  |
| 0.8 mL II        | .08        | 1.09       | 2.72               | 1.11                  | ***                   |

<sup>1</sup> Log exposure corresponding to density of 0.6 above  $D_{\min}$ .

<sup>2</sup> Average contrast measured by the slope of the line joining density points 0.3 and 0.9 above  $D_{\min}$ .

<sup>3</sup> Average contrast measured by the slope of the line joining density points 0.6 and 1.20 above  $D_{\min}$ .

The post-processing print stability was measured as described in Example 4, and the results are shown below.

|                    | 6 hours           |                   | 24 hours          |                   |
|--------------------|-------------------|-------------------|-------------------|-------------------|
|                    | $\Delta D_{\min}$ | $\Delta D_{\max}$ | $\Delta D_{\min}$ | $\Delta D_{\max}$ |
| Control (0.0 mL)   | + .16             | - .14             | + .21             | - .50             |
| 0.8 mL II-A + II-B | + .12             | - .11             | + .13             | - .48             |
| 0.8mL II           | + .13             | - .19             | + .14             | - .48             |

At this concentration of the primary stabilizer II,  $D_{\min}$  post-processing improvements were observed with significant desensitization of the silver halide emulsion. With the addition of an equivalent molar amount of II-A + II-B, the parent compound was adequately blocked to minimize most desensitization and yet release of the primary stabilizer II occurred at the appropriate time after processing for  $D_{\min}$  post-processing stabilization similar to the unblocked II stabilizer.

#### Example 6

A silver premix was prepared as follows: a dispersion of silver behenate half soap was made at 10% solids in toluene and ethanol by homogenization and contained 1.5% by weight polyvinyl butyral. To 71g of this silver half soap dispersion was added 200g of ethanol. After 15 minutes of mixing, 2.6 mL of a mercuric bromide solution (0.19g in 10 mL methanol) was added. Then an additional 2.6 mL of mercuric bromide solution (0.19g in 10 mL methanol) was added 15 minutes later. After 60 minutes of mixing 25g of polyvinyl butyral was added.

To 82.7g of the prepared silver premix described above was added a cyan color-forming leuco dye solution as shown below.

| Component                                                      | Amount |
|----------------------------------------------------------------|--------|
| Leuco Dye C                                                    | 0.82g  |
| Toluene                                                        | 11.7g  |
| Ethyl methacrylate copolymer<br>(Acryloid™ B72, Rohm and Haas) | 2.3g   |
| FC-431™ (a fluorocarbon surfactant, 3M)                        | 0.2 g  |
| Ethanol                                                        | 1.21 g |

Preparation of leuco dye C is disclosed in U.S. Pat. No. 4,782,010.

After the addition of the leuco dye premix solution, 1.2 mL of the sensitizing dye D (0.016g / 13 mL methanol + 37 mL toluene), shown above, was added and allowed to sensitize for 30 minutes.

A topcoat solution was prepared containing approximately 17% Scripset 640™ (Monsanto, styrene/maleic anhydride copolymer), 1.1% Syloid 244™ (Monsanto, colloidal silica), 1.37% phthalic acid, 0.14% benzotriazole, and 0.44% of a fluorocarbon surfactant in an approximate 50:50 mixture of methanol and ethanol.

To 15.0 g aliquots of the topcoat solution described above was added 0.182% or 0.455% by weight compound III-A, or 0.1% or 0.25% by weight 1-phenyl-3-pyrazolidinone (P).

The cyan silver layer and topcoat were each coated at a wet thickness of 2 mils and 1.5 mils, respectively and dried for 3 minutes at 82°C. The samples were exposed for 10<sup>-3</sup> seconds through a 25 Wratten filter and a 0 to 3 continuous wedge and developed by heating to approximately 138° C for 6 seconds.

The density of the cyan color for each sample was measured using a red filter of a computer densitometer. Post-processing stability was measured by exposing imaged samples to 1200 ft. candles of illumination for 6 and 24 hours at 65% relative humidity and 26.7°C. The initial sensitometric data are shown below.

|               | D <sub>min</sub> | Dmax | Speed <sup>1</sup> | Contrast <sup>2</sup> | Contrast <sup>3</sup> |
|---------------|------------------|------|--------------------|-----------------------|-----------------------|
| Control (0.0) | .17              | 2.08 | 1.57               | 1.44                  | 1.37                  |
| 0.1% P        | .77              | **   | **                 | **                    | **                    |
| 0.25% P       | 1.14             | **   | **                 | **                    | **                    |
| 0.182% III-A  | .18              | 1.93 | 1.58               | 1.43                  | 1.42                  |
| 0.455% III-A  | .19              | 2.10 | 1.47               | 1.62                  | 1.69                  |

<sup>1</sup> Log exposure corresponding to density of 0.6 above  $D_{\min}$ .

<sup>2</sup> Average contrast measured by the slope of the line joining density points 0.3 and 0.9 above  $D_{\min}$ .

<sup>3</sup> Average contrast measured by the slope of the line joining density points 0.6 and 1.20 above  $D_{\min}$ .

The post-processing print stability results are shown below.

|               | 6 hours           |                   | 24 hours          |                   |
|---------------|-------------------|-------------------|-------------------|-------------------|
|               | $\Delta D_{\min}$ | $\Delta D_{\max}$ | $\Delta D_{\min}$ | $\Delta D_{\max}$ |
| Control (0.0) | +.32              | -.05              | +.76              | -.02              |
| 0.182% III-A  | +.30              | +0.4              | +.69              | +.08              |
| 0.455% III-A  | +.30              | +.04              | +.67              | +.03              |

The addition of 1-phenyl-3-pyrazolidinone increased the initial  $D_{\min}$  significantly, but the addition of the blocked 1-phenyl-3-pyrazolidinone III-A, at a molar amount equivalent to the parent compound gave negligible effects on initial sensitometry. Small  $D_{\min}$  post-processing improvements were observed with III-A, though 1-phenyl-3-pyrazolidinone alone did not significantly stabilize the post-processed image.

#### Example 7

To 15.0g aliquots of the topcoat solution described in Example 6 was added 0.192% or 0.67% by weight compound III-B, which has the structure shown above.

The silver solutions and topcoats were coated, exposed, and processed as described in Example 6. The initial sensitometric data are shown below.

| Stabilizer          | D <sub>min</sub> | D <sub>max</sub> | Speed <sup>1</sup> | Contrast <sup>2</sup> |
|---------------------|------------------|------------------|--------------------|-----------------------|
| Control (0.0)       | .15              | 1.81             | 1.90               | 1.43                  |
| 0.192% <b>III-B</b> | .15              | 1.92             | 1.78               | 1.69                  |
| 0.67% <b>III-B</b>  | .15              | 1.90             | 1.74               | 1.90                  |

<sup>1</sup> Log exposure corresponding to a density of 0.6 above D<sub>min</sub>.

<sup>2</sup> Average contrast measured by the slope of the line joining density points 0.3 and 0.9 above D<sub>min</sub>.

The post-processing print stability was measured at 100 ft. candles of illumination for 7 and 14 days at 73% relative humidity and 70°C. These results are shown below.

|                     | 7 days            |                   | 14 days           |                   |
|---------------------|-------------------|-------------------|-------------------|-------------------|
|                     | ΔD <sub>min</sub> | ΔD <sub>max</sub> | ΔD <sub>min</sub> | ΔD <sub>max</sub> |
| Control (0.0)       | +.43              | +.12              | +.64              | +.16              |
| 0.192% <b>III-B</b> | +.36              | +.07              | +.50              | +.07              |
| 0.67% <b>III-B</b>  | +.35              | +.09              | +.50              | +.06              |

As described in Example 6 the parent compound 1-phenyl-3-pyrazolidinone greatly increased initial D<sub>min</sub>, but an equivalent molar amount of the blocked 1-phenyl-3-pyrazolidinone **III-B** adequately blocked the activity of the 1-phenyl-3-pyrazolidinone to minimize initial sensitometry effects. Modest post-processing D<sub>min</sub> improvements were observed.

#### Example 8

To a 15.0 g aliquot of topcoat solution described in Example 6 was added 0.77% by weight compound **III-C**.

The silver solutions and topcoats were coated, exposed and processed as described in Example 6. The initial sensitometric data are shown below.

| Stabilizer         | D <sub>min</sub> | D <sub>max</sub> | Speed <sup>1</sup> | Contrast <sup>2</sup> |
|--------------------|------------------|------------------|--------------------|-----------------------|
| Control (0.0)      | .16              | 2.33             | 1.91               | 3.23                  |
| 0.77% <b>III-C</b> | .17              | 2.21             | 1.84               | 3.25                  |

<sup>1</sup> Log exposure corresponding to density of 0.6 above D<sub>min</sub>.

<sup>2</sup> Average contrast measured by the slope of the line joining 0.3 and 0.9 above D<sub>min</sub>.

The post-processing stability was measured as described in Example 7 and the results are shown below.

| Stabilizer       | $\Delta D_{\min}$ | $\Delta D_{\min}$ |
|------------------|-------------------|-------------------|
|                  | 1200 foot-candles |                   |
|                  | 6 hours           | 24 hours          |
| Control (0.0)    | +.29              | +.70              |
| 0.77% III-C      | +.27              | +.67              |
| 100 foot-candles |                   |                   |
|                  | 7 days            | 14 days           |
| Control (0.0)    | +.45              | +.67              |
| 0.77% III-C      | +.37              | +.51              |

As described in Example 6 the parent compound 1-phenyl-3-pyrazolidinone greatly increased initial  $D_{\min}$ , but an equivalent molar amount of the blocked 1-phenyl-3-pyrazolidinone, III-C, adequately blocked the activity of the parent compound to give minimal effects on the initial sensitometry. Modest post-processing  $D_{\min}$  improvements were observed at both intensities of illumination.

#### Example 9

This example illustrates the effectiveness of a nitrobenzyl-protected stabilizer in a mercury-free formulation.

To 200 g of a silver half soap dispersion containing preformed silver bromide crystals at 55° C was added 32 g of polyvinyl butyral. After 30 minutes of mixing, three portions of 55 mg of pyridinium hydrobromide perbromide in 2 mL ethanol each were added at 60 minute intervals. Finally, 1.3 mL 10 wt % calcium bromide in ethanol was added 30 minutes later. The mixture was incubated overnight, then 17 mL of a solution of 21 mg of sensitizing dye A in 100 mL methanol was added and stirred for 30 minutes.

To 7.0 g of the above silver dispersion was added 12.5 g of the below described magenta color-forming leuco dye B.

| Component                                | Amount |
|------------------------------------------|--------|
| Leuco Dye B                              | 0.9g   |
| Phthalazinone                            | 1.8g   |
| Tetrahydrofuran                          | 80.0g  |
| VAGH (Union Carbide)                     | 2.7g   |
| (vinyl acetate/vinyl chloride copolymer) |        |
| Polyvinylbutyral                         | 7.6g   |

A topcoat solution was prepared consisting of 15 g of 4.6% by weight cellulose acetate resin in approximately 1/2/4 mixture of methanol, methyl ethyl ketone, and acetone, with 25 mg of 2,5-bis(tribromomethyl)-1-thia-3,4-diazole.

To 19.5g of the magenta silver coating solution was added 20 to 50 mg of the mixture of compounds I-A and I-B, as a methanol solution.

The magenta silver layer and topcoat were each coated at a wet thickness of 2 mils, and dried for 4 minutes at 77° C. The samples were exposed for 10<sup>-3</sup> seconds through a 58 Wratten filter and a 0 to 3 continuous wedge and developed by heating to approximately 136° C for 14 seconds.

The density of magenta color for each sample was measured using a green filter of a computer densitometer. Post-processing stability was measured by exposing imaged samples to 1200 ft-candles of illumination (daylight fluorescent bulbs) for 6 and 24 hours at 65% relative humidity and 26.7° C. The initial sensitometric data are shown below.

|                  | $D_{\min}$ | $D_{\max}$ | Speed <sup>1</sup> | Contrast <sup>2</sup> |
|------------------|------------|------------|--------------------|-----------------------|
| Control (0.0 mL) | .11        | 2.19       | 1.23               | 3.90                  |
| 20 mg I-A + I-B  | .12        | 2.20       | 1.22               | 3.89                  |
| 30 mg I-A + I-B  | .11        | 2.20       | 1.20               | 3.76                  |
| 40 mg I-A + I-B  | .13        | 2.22       | 1.22               | 4.01                  |
| 50 mg I-A + I-B  | .12        | 2.21       | 1.22               | 3.84                  |

<sup>1</sup> Log exposure corresponding to density of 0.6 above  $D_{\min}$ .

<sup>2</sup> Average contrast measured by the slope of the line joining density points 0.3 and 0.9 above  $D_{\min}$ .

<sup>3</sup> This is an approximate molar equivalent of the BZT parent stabilizer.

The post processing print stability of these constructions was measured at 1200 ft candles and the results are shown below.

| Stabilizer       | 6 hours                        |       | 24 hours                       |       |
|------------------|--------------------------------|-------|--------------------------------|-------|
|                  | $\Delta D_{\min}$ <sup>1</sup> | %Fade | $\Delta D_{\min}$ <sup>1</sup> | %Fade |
| Control (0.0 mL) | +.16                           | 11%   | +.26                           | 40%   |
| 20 mg I-A + I-B  | +.10                           | 13%   | +.14                           | 44%   |
| 30 mg I-A + I-B  | +.09                           | 14%   | +.15                           | 44%   |
| 40 mg I-A + I-B  | +.07                           | 12%   | +.11                           | 46%   |
| 50 mg I-A + I-B  | +.08                           | 15%   | +.11                           | 46%   |

<sup>1</sup> Final  $D_{\min}$  - Initial  $D_{\min}$ . Refers to reflectance optical density through a green filter.

Substantial improvements in red and blue filter  $\Delta D_{\min}$  were also seen with I-A + I-B. Note that addition of this stabilizer gives no adverse effects on sensitometry.

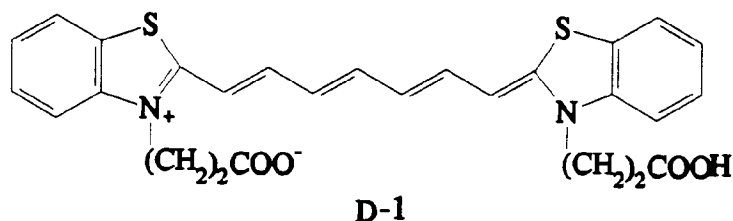
#### Examples 10-13

A silver halide-silver behenate dry soap was prepared by the procedures described in U.S. Pat. No. 3,839,049. The silver halide totalled 9% of the total silver while silver behenate comprised 9% of the total silver. The silver halide was a 0.055 micron silver bromiodide emulsion with 2% iodide.

A photothermographic emulsion was prepared by homogenizing 300 g of the silver halide-silver behenate dry soap described above with 525 g toluene, 1675 g 2-butanone and 50 g poly(vinylbutyral) (B-76, Monsanto).

The homogenized photothermographic emulsion (500 g) and 100 g 2-butanone were cooled to 55°F with stirring. Additional poly(vinylbutyral) 75.7 g (B-76) was added and stirred for 20 minutes. Pyridinium hydrobromide perbromide (PHP, 0.45 g) was added and stirred for 2 hours. The addition of 3.25 ml of a calcium bromide

solution (1 g of  $\text{CaBr}_2$  and 10 ml of methanol) was followed by 30 minutes of stirring. The temperature was raised to 70°F and the following were added in 15 minute increments with stirring: 3.0 g (2-(4-chlorobenzoyl)benzoic acid, IR dye solution (D-1 dye; 10.5 mg D-1 in 6g dimethylformamide), 185 mg of 2-mercaptobenzimidazole in 5g methanol, 16.4 g of developer 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, and 1.7 g 2-(tribromomethylsulfone)benzothiazole.



The photothermographic emulsion was divided into 40g portions. The control was coated at this stage without any additions (control) as were Examples 12 and 13. Examples 10 and 11 contained equal molar levels of the parent compound (BZT) and the blocked derivative (I-A + I-B) respectively.

The photothermographic emulsions were coated on 3 mil ( $0.76 \times 10^{-4}\text{m}$ ) polyester base by means of a knife coater and dried at 175°F for four minutes. The dry coating weight was 23 g/m<sup>2</sup>.

An active, protective topcoat solution was prepared with the following ingredients:

|         |                               |
|---------|-------------------------------|
| 256.0g  | acetone                       |
| 123.0 g | 2-butanone                    |
| 50.0 g  | methanol                      |
| 20.2 g  | cellulose acetate             |
| 2.89 g  | phthalazine                   |
| 1.55 g  | 4-methylphthalic acid         |
| 1.01 g  | tetrachlorophthalic acid      |
| 1.50 g  | tetrachlorophthalic anhydride |

The bulk topcoat was split into 20 g portions. Equal molar levels of BZT and I-A + I-B were added to the topcoat solutions for examples 12 and 13. The topcoat solutions were coated over the silver layer at a dry weight of 3.0 g/m<sup>2</sup>. The layer was dried at 175°F for four minutes.

The coated materials were then exposed with a laser sensitometer incorporating a 780 nm diode. After exposure, the film strips were processed at 260°F for ten seconds. The images obtained were evaluated by a densitometer. Sensitometric results include Dmin, Dmax, Spd (relative speed at a density of 1.0 above Dmin versus a control with no added test compound set at 100) and average contrast (cont measured from a density of 0.25 to 2.0 above Dmin). The processed film strips were tested for print stability by taping the strips to a view box (type employed by radiologists). The film strips were placed on the view box with the raw polyester side next to the view box and the silver and topcoat side out. The view box remained on during the four day test period. The Dmin values were read after the four day print stability test and are reported in Table 1.

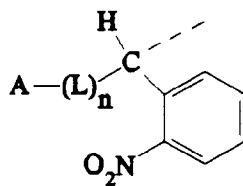
The results compiled in Table 1 show that both the parent compound BZT and the blocked version I-A + I-B greatly improve the print stability. The blocked benzotriazole, I-A + I-B, would be preferred due to the smaller reduction in initial sensitivity.

Table I

| Ex      | Test Compound |         | Moles test compound per mole silver | Dmin | Dmax | Cont | Rel Speed | $\Delta$ Spd (logE units) | Print Stability $\Delta$ Dmin |
|---------|---------------|---------|-------------------------------------|------|------|------|-----------|---------------------------|-------------------------------|
|         | Name          | Layer   |                                     |      |      |      |           |                           |                               |
| Control | None          | -       | -                                   | 0.10 | 2.90 | 4.75 | 100       | -                         | +0.07                         |
| 10      | BZT           | silver  | 0.052                               | 0.11 | 2.48 | 3.63 | 26        | -0.58                     | 0                             |
| 11      | I-A + I-B     | silver  | 0.052                               | 0.10 | 2.87 | 4.48 | 110       | +0.04                     | +0.01                         |
| 12      | BZT           | topcoat | 0.052                               | 0.10 | 2.28 | 3.89 | 46        | -0.34                     | +0.01                         |
| 13      | I-A + I-B     | topcoat | 0.052                               | 0.10 | 2.90 | 4.49 | 100       | 0                         | 0                             |

### Claims

1. A photothermographic composition comprising a photographic silver halide, an organic silver salt, and a reducing agent for the organic silver salt, and a stabilizer having a nucleus of the formula:



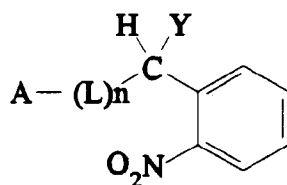
wherein:

**A** represents any monovalent group for which the corresponding compound **AH** functions as a post-processing stabilizer,

**L** is a  $-\text{CO}_2^-$  or a  $-\text{CH}_2\text{O}-$  group that is lost during or after the deblocking step, with **A** bonded to a carbon atom of this group, and

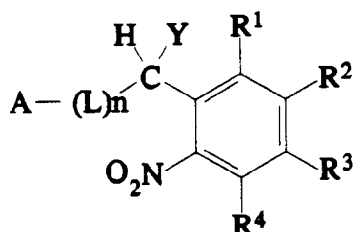
**n** is 0 or 1.

2. The composition of Claim 1 wherein said stabilizer has a central nucleus of the formula



and **Y** is selected from the group consisting of hydrogen, alkyl, alkoxycarbonyl, alkenyl, aryl, hydroxy, mercapto, amino, amido, thioamido, carbamoyl, thiocarbamoyl, cyano, nitro, sulfo, carboxyl, fluoro, formyl, sulfoxyl, sulfonyl, hydrodithio, ammonio, phosphonio, silyl, and silyloxy groups having up to 18 carbon atoms.

3. The composition of Claim 1 wherein **AH** is selected from the group consisting of benzimidazoles, triazoles, benzotriazoles, tetrazoles, triazines, thiazolines, 3-pyrazolidinones, indazoles, hypoxanthines, and imidazoles.
4. The composition of Claim 2 wherein **AH** is selected from the group consisting of benzimidazoles, triazoles, benzotriazoles, tetrazoles, 1-phenyl-3-pyrazolidinones and imidazoles.
5. The composition of Claim 2 wherein **Y** is selected from the group consisting of H, alkyl, and alkoxycarbonyl.
6. The composition of Claims 1, 2 or 3 adhered to a substrate is at least one layer.
7. A photothermographic composition comprising one layer or two adjacent layers coated on a substrate wherein the photothermographic composition comprises a photographic silver halide, an organic silver salt, and a reducing agent for the organic silver salt, and a compound having the formula:



wherein:

**A** represents any monovalent group for which the corresponding compound **AH** is a post-processing stabilizer, and

**Y**, **R<sup>1</sup>**, **R<sup>2</sup>**, **R<sup>3</sup>**, and **R<sup>4</sup>** independently represent a group selected from hydrogen, alkyl, alkenyl, aryl, hydroxy, mercapto, amino, amido, thioamido, carbamoyl, thiocarbamoyl, cyano, nitro, sulfo, carboxyl, flu-

oro, chloro, bromo, formyl, sulfoxyl, sulfonyl, hydrodithio, ammonio, phosphonio, silyl, and silyloxy groups having up to 18 carbon atoms, and wherein any two of **R**<sup>1</sup>, **R**<sup>2</sup>, **R**<sup>3</sup>, and **R**<sup>4</sup> may together form a fused ring structure with the central benzene ring, and

**L** is a -CO<sub>2</sub><sup>-</sup> or a -CH<sub>2</sub>O- group, wherein A is bonded to the carbon atom of L, and

**n** is 0 or 1.

8. The composition of Claim 7 wherein **AH** is selected from the group consisting of benzimidazoles, imidazoles, triazoles, benzotriazoles, piperidones, purines, indazoles, thiazolines, 3-pyrazolidinones, triazines, tetrazaindenes, hypoxanthines, and tetrazoles.

9. The composition of Claims 7 or 8 wherein **Y** is selected from the group consisting of hydrogen, alkyl, and alkoxy carbonyl.

10. The composition of Claims 2, 3 or 7 wherein **n** is 0.