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(54) Title: THERMALLY DEVELOPABLE COMPOSITIONS AND IMAGING MATERIALS

(57) **Abstract:** Thermally developable compositions, such as thermographic and photothermographic emulsions, include certain ascorbic acid derivatives as reducing agents for the reducible silver ions in the non photosensitive source of silver. These compositions can be used to prepare thermographic and photothermographic materials having improved post-processing stability. Such materials can have thermally developable imaging layers on one or both sides of the support and be arranged in association with one or more phosphor intensifying screens in imaging assemblies. These imaging assemblies can be exposed to X-radiation and thereby excited to form a latent image in the photothermographic material that can eventually be used for medical diagnosis.

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## THERMALLY DEVELOPABLE COMPOSITIONS AND IMAGING MATERIALS

### FIELD OF THE INVENTION

5        This invention relates to thermally developable compositions and imaging materials (both thermographic and photothermographic materials) comprising certain ascorbic acid compounds as the reducing agents for the non-photosensitive source of silver ions. Imaging materials containing these compounds have improved post-processing stability.

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### BACKGROUND OF THE INVENTION

Silver-containing photothermographic imaging materials (that is, thermally developable photosensitive imaging materials) that are imaged with actinic radiation and then developed using heat and without liquid processing have 15 been known in the art for many years. Such materials are used in a recording process wherein an image is formed by imagewise exposure of the photothermographic material to specific electromagnetic radiation (for example, X-radiation, or ultraviolet, visible, or infrared radiation) and developed by the use of thermal energy. These materials, also known as "dry silver" materials, generally comprise 20 a support having coated thereon: (a) a photocatalyst (that is, a photosensitive compound such as silver halide) that upon such exposure provides a latent image in exposed grains that are capable of acting as a catalyst for the subsequent formation of a silver image in a development step, (b) a relatively or completely 25 non-photosensitive source of reducible silver ions, (c) a reducing composition (usually including a developer) for the reducible silver ions, and (d) a hydrophilic or hydrophobic binder. The latent image is then developed by application of thermal energy.

In photothermographic materials, exposure of the photographic silver halide to light produces small clusters containing silver atoms  $(Ag^0)_n$ . The 30 imagewise distribution of these clusters, known in the art as a latent image, is generally not visible by ordinary means. Thus, the photosensitive material must be further developed to produce a visible image. This is accomplished by the

reduction of silver ions that are in catalytic proximity to silver halide grains bearing the silver-containing clusters of the latent image. This produces a black-and-white image. The non-photosensitive silver source is catalytically reduced to form the visible black-and-white negative image while much of the silver halide, 5 generally, remains as silver halide and is not reduced.

In photothermographic materials, the reducing agent for the 10 reducible silver ions, often referred to as a "developer," may be any compound that, in the presence of the latent image, can reduce silver ion to metallic silver and is preferably of relatively low activity until it is heated to a temperature sufficient to cause the reaction. A wide variety of classes of compounds have been disclosed in the literature that function as developers for photothermographic materials. At elevated temperatures, the reducible silver ions are reduced by the reducing agent. In photothermographic materials, upon heating, this reaction occurs preferentially in the regions surrounding the latent image. This reaction 15 produces a negative image of metallic silver having a color that ranges from yellow to deep black depending upon the presence of toning agents and other components in the imaging layer(s).

### **Differences Between Photothermography and Photography**

20 The imaging arts have long recognized that the field of photothermography is clearly distinct from that of photography. Photothermographic materials differ significantly from conventional silver halide photographic materials that require processing with aqueous processing solutions.

25 In photothermographic imaging materials, a visible image is created by heat as a result of the reaction of a developer incorporated within the material. Heating at 50°C or more is essential for this dry development. In contrast, conventional photographic imaging materials require processing in aqueous processing baths at more moderate temperatures (from 30°C to 50°C) to provide a visible image.

30 In photothermographic materials, only a small amount of silver halide is used to capture light and a non-photosensitive source of reducible silver ions (for example a silver carboxylate or a silver benzotriazole) is used to generate

the visible image using thermal development. Thus, the imaged photosensitive silver halide serves as a catalyst for the physical development process involving the non-photosensitive source of reducible silver ions and the incorporated reducing agent. In contrast, conventional wet-processed, black-and-white 5 photographic materials use only one form of silver (that is, silver halide) that, upon chemical development, is itself at least partially converted into the silver image, or that upon physical development requires addition of an external silver source (or other reducible metal ions that form black images upon reduction to the corresponding metal). Thus, photothermographic materials require an amount of 10 silver halide per unit area that is only a fraction of that used in conventional wet-processed photographic materials.

In photothermographic materials, all of the "chemistry" for imaging is incorporated within the material itself. For example, such materials include a developer (that is, a reducing agent for the reducible silver ions) while 15 conventional photographic materials usually do not. Even in so-called "instant photography," the developer chemistry is physically separated from the photosensitive silver halide until development is desired. The incorporation of the developer into photothermographic materials can lead to increased formation of various types of "fog" or other undesirable sensitometric side effects. Therefore, 20 much effort has gone into the preparation and manufacture of photothermographic materials to minimize these problems.

Moreover, in photothermographic materials, the unexposed silver halide generally remains intact after development and the material must be stabilized against further imaging and development. In contrast, silver halide is 25 removed from conventional photographic materials after solution development to prevent further imaging (that is in the aqueous fixing step).

Because photothermographic materials require dry thermal processing, they present distinctly different problems and require different materials in manufacture and use, compared to conventional, wet-processed silver 30 halide photographic materials. Additives that have one effect in conventional silver halide photographic materials may behave quite differently when incorporated in photothermographic materials where the chemistry is significantly

more complex. The incorporation of such additives as, for example, stabilizers, antifoggants, speed enhancers, supersensitizers, and spectral and chemical sensitizers in conventional photographic materials is not predictive of whether such additives will prove beneficial or detrimental in photothermographic

5 materials. For example, it is not uncommon for a photographic antifoggant useful in conventional photographic materials to cause various types of fog when incorporated into photothermographic materials, or for supersensitizers that are effective in photographic materials to be inactive in photothermographic materials.

10 These and other distinctions between photothermographic and photographic materials are described in *Imaging Processes and Materials (Nebblette's Eighth Edition)*, noted above, *Unconventional Imaging Processes*, E. Brinckman et al. (Eds.), The Focal Press, London and New York, 1978, pp. 74-75, in Zou et al., *J. Imaging Sci. Technol.* **1996**, *40*, pp. 94-103, and in

15 M. R. V. Sahyun, *J. Imaging Sci. Technol.* **1998**, *42*, 23.

### Problem to be Solved

Photothermographic materials have not achieved wide use in X-radiography because they have generally had relatively low photographic speed

20 or exhibited haze associated with the various conventional imaging components.

Photothermographic materials have been described in the art to include various non-photosensitive sources of reducible silver ions including silver salts of benzotriazole and silver salts of its derivatives [see for example, U.S. Patent 6,576,410 (Zou et al.)].

25 The reduction of the silver ions in silver benzotriazole to silver metal in photothermographic materials generally requires a relatively strong reducing agent. A typical developer choice is ascorbic acid that has been shown to provide useful photospeed, adequate D<sub>max</sub>, and low D<sub>min</sub>. Derivatives (such as esters) of ascorbic acid have also been described as reducing agents for silver ions

30 in organic silver salts. For example, ascorbic acid palmitate and dipalmitate are described for this purpose in U.S. Patents 4,543,309 (Hirabayashi et al.) and 4,451,561 (Hirabayashi et al.) and ascorbic acid stearate, myristate, and laurate are

described for this purpose in U.S. Patents 3,832,186 (Masuda et al.) and 3,881,938 (Masuda et al.) and FR 1,542,505 (Okubo et al.).

There is continuing work in the art to develop thermally developable materials using silver benzotriazole and other organic silver salts that 5 require relatively strong reducing agents. Because some imaging systems include components that may lead to image instability, especially in aqueous-based imaging materials, there is a continuing need to find the most suitable silver ion reducing agents in order to obtain optimal sensitometric properties and to improve post-processing light stability of the imaged materials.

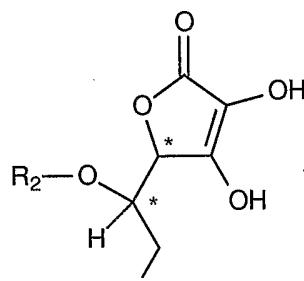
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### SUMMARY OF THE INVENTION

The present invention provides a thermally-developable composition comprising a binder, and in reactive association, a non-photosensitive source of reducible silver ions that includes a compound containing an imino group, and a reducing agent for the non-photosensitive source of reducible silver ions, 15

the reducing agent being a compound, or mixture thereof,

represented by the following Structure (I):



20

(I)

wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an acyl group having 11 or fewer carbon atoms, provided that at least one of R<sub>1</sub> and R<sub>2</sub> is an acyl group.

25 This invention also provides a black-and-white photothermographic material comprising a support and having on at least one side thereon one or more thermally developable imaging layers comprising a binder, and in reactive

association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, a reducing agent for the non-photosensitive reducible silver ions, and optionally an outermost protective layer disposed over the one or more thermally 5 developable imaging layers,

wherein the reducing agent is a compound, or mixture thereof, represented by the Structure (I) noted above.

In preferred embodiments of this invention, a black-and-white aqueous-based photothermographic material comprises a transparent support 10 having on at least one side thereof:

a) one or more thermally developable imaging layers each comprising a hydrophilic binder that is gelatin, a gelatin derivative, a poly(vinyl alcohol), or a cellulosic material, or is a water-dispersible polymeric latex, and in reactive association,

15 a preformed photosensitive silver bromide, silver iodobromide, or a mixture thereof, provided predominantly as tabular grains,

a non-photosensitive source of reducible silver ions that includes one or more organic silver salts at least one of which is predominantly a silver salt of benzotriazole,

20 a reducing agent for the non-photosensitive source of reducible silver ions, and

b) optionally, an outermost protective layer disposed over the one or more thermally developable imaging layers, and

wherein the reducing agent is selected from the list of compounds 25 in TABLE I noted below, or is a mixture thereof.

In additional preferred embodiments, a black-and-white photothermographic material comprises a support having on a frontside thereof,

30 a) one or more frontside thermally developable imaging layers comprising a hydrophilic polymer binder or water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound

containing an imino group, a reducing agent for the non-photosensitive source reducible silver ions, and

the material comprising on the backside of the support, one or more backside thermally developable imaging layers comprising a hydrophilic polymer binder or a water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, and a reducing agent for the non-photosensitive source reducible silver ions, and

10 b) optionally, an outermost protective layer disposed over the one or more thermally developable imaging layers on either or both sides of the support, and

wherein the one or more thermally developable imaging layers, or the one or more protective layers if present, on both sides of the support have the same or different composition, and

15 the reducing agents on both sides of the support are the same or different and each reducing agent is a compound, or mixture thereof, represented by the Structure (I) noted above.

This invention also provides a method of forming a visible image comprising:

20 A) imagewise exposing the photothermographic material of this invention to form a latent image,

B) simultaneously or sequentially, heating the exposed photothermographic material to develop the latent image into a visible image.

25 Where the noted method is carried out using a thermally developable material comprising a transparent support, the image-forming method can further comprise:

C) positioning the exposed and thermally-developed material with the visible image therein between a source of imaging radiation and an imageable material that is sensitive to the imaging radiation, and

30 D) exposing the imageable material to the imaging radiation through the visible image in the exposed and thermally-developed material to provide an image in the imageable material.

Thermographic materials of this invention can be similarly used to provide an image, but the latent image is formed using thermal energy and development occurs simultaneously with imaging.

The images formed in both thermographic and photothermographic 5 materials of this invention can be used for medical diagnosis.

An imaging assembly of the present invention comprises a photothermographic material of the present invention that is arranged in association with one or more phosphor intensifying screens. A method of forming a black-and-white image can then comprise exposing the imaging assembly to

10 X-radiation.

We have discovered that the specific ascorbic acid derivatives described herein by Structure I provide improved post-processing stability of images obtained in thermally developable materials that include reducible silver ions in silver salts that contain an imino group, such as silver benzotriazole.

15

#### **DETAILED DESCRIPTION OF THE INVENTION**

The thermally developable materials of this invention can be used in black-and-white or color photothermography and in electronically generated black-and-white or color hardcopy recording. They can be used in microfilm 20 applications, in radiographic imaging (for example digital medical imaging), X-ray radiography, and in industrial radiography. Furthermore, the absorbance of these materials between 350 and 450 nm is desirably low (less than 0.5), to permit their use in the graphic arts area (for example, imagesetting and phototypesetting), in the manufacture of printing plates, in contact printing, in duplicating 25 ("duping"), and in proofing.

The photothermographic materials of this invention are particularly useful for medical imaging of human or animal subjects in response to visible or X-radiation for use in medical diagnosis. Such applications include, but are not limited to, thoracic imaging, mammography, dental imaging, orthopedic imaging, 30 general medical radiography, therapeutic radiography, veterinary radiography, and auto-radiography. Increased sensitivity to X-radiation can be imparted through the use of phosphors. When used with X-radiation, the photothermographic materials

of this invention may be used in combination with one or more phosphor intensifying screens, with phosphors incorporated within the photothermographic emulsion, or with a combination thereof.

The photothermographic materials of this invention can be made  
5 sensitive to radiation of any suitable wavelength. Thus, in some embodiments, the materials are sensitive at ultraviolet, visible, near infrared, or infrared wavelengths of the electromagnetic spectrum. In these embodiments, the materials are preferably sensitive to radiation greater than 350 nm (such as sensitivity to, from 350 nm to 450 nm). Increased sensitivity to a particular region of the spectrum is  
10 imparted through the use of various sensitizing dyes.

The photothermographic materials of this invention are also useful for non-medical uses of visible or X-radiation (such as X-ray lithography and industrial radiography). In these and other imaging applications, it is particularly desirable that the photothermographic materials be "double-sided."

15 In some embodiments of the thermally developable materials of this invention, the components needed for imaging can be in one or more imaging or emulsion layers on one side ("frontside") of the support. The layer(s) that contain the photosensitive photocatalyst (such as a photosensitive silver halide) for photothermographic materials or the non-photosensitive source of reducible  
20 silver ions, or both, are referred to herein as the emulsion layer(s). In photothermographic materials, the photocatalyst and non-photosensitive source of reducible silver ions are in catalytic proximity and preferably are in the same emulsion layer. Various non-imaging layers can also be disposed on the "backside" (non-emulsion or non-imaging side) of the materials, including,  
25 conductive layers, antihalation layer(s), protective layers, antistatic layers, and transport enabling layers.

Various non-imaging layers can also be disposed on the "frontside" or imaging or emulsion side of the support, including protective topcoat layers, primer layers, interlayers, opacifying layers, antistatic layers, antihalation layers,  
30 acutance layers, auxiliary layers, and other layers readily apparent to one skilled in the art.

For some embodiments it may be useful that the thermally developable materials be “double-sided” or “duplitized” and have the same or different emulsion coatings (or imaging layers) on both sides of the support. In such constructions each side can also include one or more protective topcoat layers, primer layers, interlayers, antistatic layers, acutance layers, antihalation layers, auxiliary layers, conductive layers, anti-crossover layers, and other layers readily apparent to one skilled in the art.

When the photothermographic materials of this invention are heat-developed as described below in a substantially water-free condition after, or 10 simultaneously with, imagewise exposure, a silver image (preferably a black-and-white silver image) is obtained.

### Definitions

As used herein:

15 In the descriptions of the thermally developable materials of the present invention, “a” or “an” component refers to “at least one” of that component [for example, the ascorbic acid derivatives of Structure (I)].

Heating in a substantially water-free condition as used herein, means heating at a temperature of from 50°C to 250°C with little more than 20 ambient water vapor present. 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 material. Such a condition is described in T. H. James, *The Theory of the Photographic Process*, Fourth Edition, Eastman 25 Kodak Company, Rochester, NY, 1977, p. 374.

“Photothermographic material(s)” means a construction comprising at least one photothermographic emulsion layer or a photothermographic set of emulsion layers (wherein the photosensitive silver halide and the source of 30 reducible silver ions are in one layer and the other essential components or desirable additives are distributed, as desired, in the same layer or in an adjacent coated layer. These materials also include multilayer constructions in which one or more imaging components are in different layers, but are in “reactive

association.” For example, one layer can include the non-photosensitive source of reducible silver ions and another layer can include the reducing agent and/or photosensitive silver halide.

“Thermographic material(s)” can be similarly constructed but are 5 intentionally non-photosensitive (thus no photosensitive silver halide is intentionally added).

When used in photothermography, the term, “imagewise exposing” or “imagewise exposure” means that the material is imaged using any exposure means that provides a latent image using electromagnetic radiation. This includes, 10 for example, by analog exposure where an image is formed by projection onto the photosensitive material as well as by digital exposure where the image is formed one pixel at a time such as by modulation of scanning laser radiation.

When used in thermography, the term “imagewise exposing” or “imagewise exposure” means that the material is imaged using any suitable 15 thermal energy imaging source such as a thermal print head.

“Catalytic proximity” or “reactive association” means that the materials are in the same layer or in adjacent layers so that they readily come into contact with each other during thermal imaging and development.

“Emulsion layer,” “imaging layer,” or “photothermographic (or 20 “thermographic”) emulsion layer,” means a layer of a photothermographic (or thermographic) material that contains the photosensitive silver halide (not present in thermographic materials) and/or non-photosensitive source of reducible silver ions. It can also mean a layer of the material that contains, in addition to the photosensitive silver halide and/or non-photosensitive source of reducible ions, 25 additional essential components and/or desirable additives such as the reducing agent(s). These layers are usually on what is known as the “frontside” of the support but they can be on both sides of the support.

In addition, “frontside” also generally means the side of a 30 thermally developable material that is first exposed to imaging radiation, and “backside” generally refers to the opposite side of the thermally developable material.

“Photocatalyst” means a photosensitive compound such as silver halide that, upon exposure to radiation, provides a compound that is capable of acting as a catalyst for the subsequent development of the thermally developable material.

5               Many of the materials used herein are provided as a solution. The term “active ingredient” means the amount or the percentage of the desired material contained in a sample. All amounts listed herein are the amount of active ingredient added.

10               “Ultraviolet region of the spectrum” refers to that region of the spectrum less than or equal to 410 nm, and preferably from 100 nm to 410 nm, although parts of these ranges may be visible to the naked human eye. More preferably, the ultraviolet region of the spectrum is the region of from 190 nm to 405 nm.

15               “Visible region of the spectrum” refers to that region of the spectrum of from 400 nm to 700 nm.

              “Short wavelength visible region of the spectrum” refers to that region of the spectrum of from 400 nm to about 450 nm.

              “Red region of the spectrum” refers to that region of the spectrum of from 600 nm to 700 nm.

20               “Infrared region of the spectrum” refers to that region of the spectrum of from 700 nm to 1400 nm.

              “Non-photosensitive” means not intentionally light sensitive.

              “Transparent” means capable of transmitting visible light or imaging radiation without appreciable scattering or absorption.

25               The sensitometric term “absorbance” is another term for optical density (OD).

              The sensitometric terms “photospeed,” “speed,” or “photographic speed” (also known as sensitivity), absorbance, contrast, D<sub>min</sub>, and D<sub>max</sub> have conventional definitions known in the imaging arts. In photothermographic materials, D<sub>min</sub> is considered herein as image density achieved when the photothermographic material is thermally developed without prior exposure to

radiation. It is the average of eight lowest density values on the exposed side of the fiducial mark. D<sub>max</sub> is the maximum density of film in the imaged area.

“Speed-2” is Log<sub>10</sub>E + 4 corresponding to the density value of 1.0 above D<sub>min</sub> where E is the exposure in ergs/cm<sup>2</sup>.

5 As used herein, the phrase “organic silver coordinating ligand” refers to an organic molecule capable of forming a bond with a silver atom. Although the compounds so formed are technically silver coordination compounds they are also often referred to as silver salts.

10 In the compounds described herein, no particular double bond geometry (for example, *cis* or *trans*) is intended by the structures drawn unless otherwise specified. Similarly, in compounds having alternating single and double bonds and localized charges their structures are drawn as a formalism. In reality, both electron and charge delocalization exists throughout the conjugated chain.

15 As is well understood in this art, for the chemical compounds herein described, substitution is not only tolerated, but is often advisable and various substituents are anticipated on the compounds used in the present invention unless otherwise stated. Thus, when a compound is referred to as “having the structure” of, or as “a derivative” of, a given formula, any substitution that does not alter the bond structure of the formula or the shown atoms within 20 that structure is included within the formula, unless such substitution is specifically excluded by language.

25 As a means of simplifying the discussion and recitation of certain substituent groups, the term “group” refers to chemical species that may be substituted as well as those that are not so substituted. Thus, the term “alkyl group” is intended to include not only pure hydrocarbon alkyl chains, such as methyl, ethyl, *n*-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, and carboxy. For example, alkyl group includes ether and thioether groups (for example 30 CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>- and CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-), hydroxyalkyl (such as 1,2-dihydroxyethyl), haloalkyl, nitroalkyl, alkylcarboxy, carboxyalkyl, carboxamido, sulfoalkyl, and other groups readily apparent to one skilled in the

art. 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.

5      *Research Disclosure* is a publication of Kenneth Mason Publications Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ England (also available from Emsworth Design Inc., 147 West 24th Street, New York, N.Y. 10011).

10     Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, examples, and claims provided in this application.

### **The Photocatalyst**

15     The photothermographic materials of the present invention include one or more photocatalysts in the photothermographic emulsion layer(s). Useful photocatalysts are typically photosensitive silver halides such as silver bromide, silver iodide, silver chloride, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide, and others readily apparent to one skilled in the art. Mixtures of silver halides can also be used in any suitable proportion. Silver bromide and silver bromoiodide are more preferred silver halides, with the latter silver halide 20 having up to 10 mol% silver iodide based on total silver halide.

25     In some embodiments, higher amounts of iodide may be present in the photosensitive silver halide grains up to the saturation limit of iodide as described in copending and commonly assigned U.S. Serial No. 10/246,265 (filed September 18, 2002 by Maskasky and Scaccia).

30     The silver halide grains may have any crystalline habit or morphology including, but not limited to, cubic, octahedral, tetrahedral, orthorhombic, rhombic, dodecahedral, other polyhedral, tabular, laminar, twinned, or platelet morphologies and may have epitaxial growth of crystals thereon. If desired, a mixture of grains with different morphologies can be employed. Silver halide grains having cubic and tabular morphology (or both) are preferred. More preferably, the silver halide grains are predominantly (at least 50% based on total silver halide) present as tabular grains.

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 or more silver halides, and a discrete 5 shell of one of more different silver halides. Core-shell silver halide grains useful in photothermographic materials and methods of preparing these materials are described for example in U.S. Patent 5,382,504 (Shor et al.). Iridium and/or copper doped core-shell and non-core-shell grains are described in U.S. Patent 5,434,043 (Zou et al.) and U.S. Patent 5,939,249 (Zou).

10 In some instances, it may be helpful to prepare the photosensitive silver halide grains in the presence of a hydroxytetraazaindene or an N-heterocyclic compound comprising at least one mercapto group as described in U.S. Patent 6,413,710 (Shor et al.).

15 The photosensitive silver halide can be added to (or formed within) the emulsion layer(s) in any fashion as long as it is placed in catalytic proximity to the non-photosensitive source of reducible silver ions.

It is preferred that the silver halide grains be preformed and prepared by an *ex-situ* process, and then be added to and physically mixed with the non-photosensitive source of reducible silver ions.

20 It is also possible to form the source of reducible silver ions in the presence of *ex-situ*-prepared silver halide. In this process, the source of reducible silver ions, such as a silver salt of an imino compound, is formed in the presence of the preformed silver halide grains. Co-precipitation of the reducible source of silver ions in the presence of silver halide provides a more intimate mixture of the 25 two materials [see, for example U.S. Patent 3,839,049 (Simons)] to provide a “preformed emulsion.”

It is also effective to use an *in-situ* process in which a halide- or halogen-containing compound is added to an organic silver salt to partially convert the silver of the organic silver salt to silver halide. Inorganic halides (such 30 as zinc bromide, calcium bromide, lithium bromide, or zinc iodide) or an organic halogen-containing compound (such as N-bromosuccinimide or pyridinium hydrobromide perbromide) can be used. The details of such *in-situ* generation of

silver halide are well known and described for example in U.S. Patent 3,457,075 (Morgan et al.).

Additional methods of preparing these silver halide and organic silver salts and manners of blending them are described in *Research Disclosure*,

5 June 1978, item 17029, U.S. Patent 3,700,458 (Lindholm) and U.S. Patent 4,076,539 (Ikenoue et al.), JP Kokai 49-013224, (Fuji), JP Kokai 50-017216 (Fuji), and JP Kokai 51-042529 (Fuji).

In general, the non-tabular silver halide grains used in this invention can vary in average diameter of up to several micrometers ( $\mu\text{m}$ ) and 10 they usually have an average particle size of from 0.01 to 1.5  $\mu\text{m}$  (preferably from 0.03 to 1.0  $\mu\text{m}$ , and more preferably from 0.05 to 0.8  $\mu\text{m}$ ).

The average size of the photosensitive silver halide grains is expressed by the average diameter if the grains are spherical, and by the average 15 of the diameters of equivalent circles for the projected images if the grains are cubic, tabular, or other non-spherical shapes. Representative grain sizing methods are described by in "Particle Size Analysis," ASTM Symposium on Light Microscopy, R. P. Loveland, 1955, pp. 94-122, and in C. E. K. Mees and T. H. James, *The Theory of the Photographic Process*, Third Edition, Macmillan, New York, 1966, Chapter 2. Particle size measurements may be expressed in terms of 20 the projected areas of grains or approximations of their diameters. These will provide reasonably accurate results if the grains of interest are substantially uniform in shape.

In most preferred embodiments of this invention, the silver halide grains are provided predominantly (based on at least 50 mol % silver) as tabular 25 silver halide grains that are considered "ultrathin" and have an average thickness of at least 0.02  $\mu\text{m}$  and up to and including 0.10  $\mu\text{m}$  (preferably, an average thickness of at least 0.03  $\mu\text{m}$  and more preferably of at least 0.04  $\mu\text{m}$ , and up to and including 0.08  $\mu\text{m}$  and more preferably up to and including 0.07  $\mu\text{m}$ ).

In addition, these ultrathin tabular grains have an equivalent 30 circular diameter (ECD) of at least 0.5  $\mu\text{m}$  (preferably at least 0.75  $\mu\text{m}$ , and more

preferably at least 1  $\mu\text{m}$ ). The ECD can be up to and including 8  $\mu\text{m}$  (preferably up to and including 6  $\mu\text{m}$ , and more preferably up to and including 4  $\mu\text{m}$ ).

The aspect ratio of the useful tabular grains is at least 5:1 (preferably at least 10:1, and more preferably at least 15:1) and generally up to 5 50:1.

The grain size of ultrathin tabular grains may be determined by any of the methods commonly employed in the art for particle size measurement, such as those described above.

The ultrathin tabular silver halide grains can also be doped using 10 one or more of the conventional metal dopants known for this purpose including those described in *Research Disclosure* item 38957, September, 1996 and U.S. Patent 5,503,970 (Olm et al.). Preferred dopants include iridium (III or IV) and ruthenium (II or III) salts.

Mixtures of both *in-situ* and *ex-situ* silver halide grains may be 15 used.

The one or more light-sensitive silver halides used in the photothermographic materials of the present invention are preferably present in an amount of from 0.005 to 0.5 mole (more preferably from 0.01 to 0.25 mole, and most preferably from 0.03 to 0.15 mole) per mole of non-photosensitive source of 20 reducible silver ions.

### Chemical Sensitizers

The photosensitive silver halides used in photothermographic materials of this invention can be chemically sensitized using any useful 25 compound that contains sulfur, tellurium, or selenium, or may comprise a compound containing gold, platinum, palladium, ruthenium, rhodium, iridium, or combinations thereof, a reducing agent such as a tin halide or a combination of any of these. The details of these materials are provided for example, in T. H. James, *The Theory of the Photographic Process*, Fourth Edition, Eastman Kodak 30 Company, Rochester, NY, 1977, Chapter 5, pp. 149-169. Suitable conventional chemical sensitization procedures and compounds are also described in U.S. Patent 1,623,499 (Sheppard et al.), U.S. Patent 2,399,083 (Waller et al.), U.S.

Patent 3,297,447 (McVeigh), U.S. Patent 3,297,446 (Dunn), U.S. Patent 5,049,485 (Deaton), U.S. Patent 5,252,455 (Deaton), U.S. Patent 5,391,727 (Deaton), U.S. Patent 5,912,111 (Lok et al.), U.S. Patent 5,759,761 (Lushington et al.), U.S. Patent 6,296,998 (Eikenberry et al), EP 0 915 371 A1 (Lok et al.), and U.S. Patent 5,691,127 (Daubendiek et al.).

Certain substituted or and unsubstituted thioureas can be used as chemical sensitizers including those described in U.S. Patent 6,296,998 (Eikenberry et al.) and U.S. Patent 6,322,961 (Lam et al.), U.S. Patent 4,810,626 (Burgmaier et al.), and U.S. Patent 6,368,779 (Lynch et al.).

10 Still other useful chemical sensitizers include tellurium- and selenium-containing compounds that are described in U.S. Published Application 2002-0164549 (Lynch et al.), U.S. Patents 5,158,892 (Sasaki et al.), 5,238,807 (Sasaki et al.), 5,942,384 (Arai et al.) and 6,620,577 (Lynch et al.).

15 Noble metal sensitizers for use in the present invention include gold, platinum, palladium and iridium. Gold (+1 or +3) sensitization is particularly preferred, and described in U.S. Patents 5,858,637 (Eshelman et al.) and 5,759,761 (Lushington et al.). Combinations of gold(III) compounds and either sulfur- or tellurium-containing compounds are useful as chemical sensitizers and are described in U.S. Patent 6,423,481 (Simpson et al.).

20 In addition, sulfur-containing compounds can be decomposed on silver halide grains in an oxidizing environment. Examples of such sulfur-containing compounds include sulfur-containing spectral sensitizing dyes described in U.S. Patent 5,891,615 (Winslow et al.) and diphenylphosphine sulfide compounds represented by the Structure (PS) described in copending and 25 commonly assigned U.S.S.N. 10/731,251 (filed December 9, 2003 by Simpson, Burleva, and Sakizadeh).

30 The chemical sensitizers can be used in making the silver halide emulsions in conventional amounts that generally depend upon the average size of the silver halide grains. Generally, the total amount is at least  $10^{-10}$  mole per mole of total silver, and preferably from  $10^{-8}$  to  $10^{-2}$  mole per mole of total silver. The upper limit can vary depending upon the compound(s) used, the level of silver halide, and the average grain size and grain morphology.

### Spectral Sensitizers

The photosensitive silver halides used in the photothermographic features of the invention may be spectrally sensitized with one or more spectral 5 sensitizing dyes that are known to enhance silver halide sensitivity to ultraviolet, visible, and/or infrared radiation. 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. They may be added at any stage in chemical finishing 10 of the photothermographic emulsion, but are generally added after chemical sensitization is achieved.

Suitable sensitizing dyes such as those described in U.S. Patent 3,719,495 (Lea), U.S. Patent 4,396,712 (Kinoshita et al.), U.S. Patent 4,439,520 (Kofron et al.), U.S. Patent 4,690,883 (Kubodera et al.), U.S. Patent 4,840,882 15 (Iwagaki et al.), U.S. Patent 5,064,753 (Kohno et al.), U.S. Patent 5,281,515 (Delprato et al.), U.S. Patent 5,393,654 (Burrows et al.), U.S. Patent 5,441,866 (Miller et al.), U.S. Patent 5,508,162 (Dankosh), U.S. Patent 5,510,236 (Dankosh), U.S. Patent 5,541,054 (Miller et al.), JP Kokai 2000-063690 (Tanaka et al.), 20 JP Kokai 2000-112054 (Fukusaka et al.), JP Kokai 2000-273329 (Tanaka et al.), JP Kokai 2001-005145 (Arai), JP Kokai 2001-064527 (Oshiyama et al.), and JP Kokai 2001-154305 (Kita et al.), can be used in the practice of the invention.. Useful spectral sensitizing dyes are also described in *Research Disclosure*, item 308119, Section IV, December, 1989.

Teachings relating to specific combinations of spectral sensitizing 25 dyes also provided in U.S. Patent 4,581,329 (Sugimoto et al.), U.S. Patent 4,582,786 (Ikeda et al.), U.S. Patent, U.S. Patent 4,609,621 (Sugimoto et al.), U.S. Patent 4,675,279 (Shuto et al.), U.S. Patent 4,678,741 (Yamada et al.), U.S. Patent 4,720,451 (Shuto et al.), U.S. Patent 4,818,675 (Miyasaka et al.), U.S. Patent 4,945,036 (Arai et al.), and U.S. Patent 4,952,491 (Nishikawa et al.).

30 Also useful are spectral sensitizing dyes that decolorize by the action of light or heat as described in U.S. Patent 4,524,128 (Edwards et al.),

JP Kokai 2001-109101 (Adachi), JP Kokai 2001-154305 (Kita et al.), and JP 2001-183770 (Hanyu et al.).

Dyes may also be selected for the purpose of supersensitization to attain much higher sensitivity than the sum of sensitivities that can be achieved by 5 using each dye alone.

An appropriate amount of spectral sensitizing dye added is generally  $10^{-10}$  to  $10^{-1}$  mole, and preferably,  $10^{-7}$  to  $10^{-2}$  mole per mole of silver halide.

#### 10 Non-Photosensitive Source of Reducible Silver Ions

The non-photosensitive source of reducible silver ions used in the thermally developable materials of this invention can be any metal-organic compound that contains reducible silver(I) ions. Such compounds are generally organic silver salts of coordination ligands that are comparatively stable to light 15 and form a silver image when heated to 50°C or higher in the presence of an exposed silver halide (for photothermographic materials) and a reducing agent.

Silver salts of nitrogen-containing heterocyclic compounds are preferred, and one or more silver salts of compounds containing an imino group are particularly preferred, especially in the aqueous-based materials that are 20 preferred in this invention. Representative compounds of this type include, but are not limited to, 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 such as phenylmercaptotetrazole as described in U.S. Patent 4,220,709 (deMauriac), and silver salts of imidazole and 25 imidazole derivatives as described in U.S. Patent 4,260,677 (Winslow et al.). Particularly useful silver salts of this type are the silver salts of benzotriazole, substituted derivatives thereof, or mixtures of two or more of these salts. A silver salt of benzotriazole is most preferred in the photothermographic emulsions and materials of this invention.

30 Other silver salts can be used if present in “minor” amounts (less than 50 mol %) based on the total moles of organic silver salts.

Silver salts of heterocyclic compounds containing mercapto or thione groups and derivatives thereof can also be used. Such heterocyclic nuclei include, but are not limited to, triazoles, oxazoles, thiazoles, thiazolines, imidazoles, diazoles, pyridines, and triazines as described in U.S. Patent 5 4,123,274 (Knight et al.) and U.S. Patent 3,785,830 (Sullivan et al.). Examples of other useful silver salts of mercapto or thione substituted compounds that do not contain a heterocyclic nucleus include silver salts of thioglycolic acids, silver salts of dithiocarboxylic acids, and silver salts of thioamides.

Silver salts of organic acids including silver salts of long-chain 10 aliphatic or aromatic carboxylic acids may also be included in minor amounts. The chains typically contain 10 to 30, and preferably 15 to 28, carbon atoms. Silver behenate is a preferred silver carboxylate, alone or mixed with other silver carboxylates.

Sources of reducible silver ions can also be core-shell silver salts as 15 described in U.S. Patent 6,355,408 (Whitcomb et al.), that is cited herein by reference wherein a core has one or more silver salts and a shell has one or more different silver salts.

Other useful sources of non-photosensitive reducible silver ions are the silver dimer compounds that comprise two different silver salts as described in 20 U.S. Patent 6,566,045 (Whitcomb).

Still other useful sources of non-photosensitive reducible silver ions in the practice of this invention are the silver core-shell compounds comprising a primary core comprising one or more photosensitive silver halides, or one or more non-photosensitive inorganic metal salts or non-silver containing 25 organic salts, and a shell at least partially covering the primary core, wherein the shell comprises one or more non-photosensitive silver salts, each of which silver salts comprises a organic silver coordinating ligand. Such compounds are described in copending and commonly assigned U.S. Serial No. 10/208,603 (filed July 30, 2002 by Bokhonov, Burleva, Whitcomb, Howlader, and Leichter).

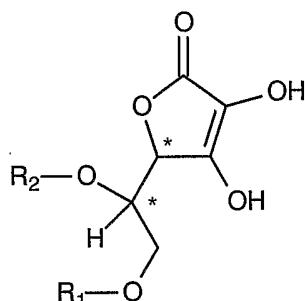
30 The one or more non-photosensitive sources of reducible silver ions are preferably present in an amount of 5% by weight to 70% by weight, and more preferably, 10% to 50% by weight, based on the total dry weight of the

emulsion layers. Alternatively, the amount of the sources of reducible silver ions is generally present in an amount of from 0.001 to 0.2 mol/m<sup>2</sup> of the dry photo-thermographic material (preferably from 0.01 to 0.05 mol/m<sup>2</sup>).

5 The total amount of silver (from all silver sources) in the photo-thermographic materials of this invention is generally at least 0.002 mol/m<sup>2</sup> and preferably from 0.01 to 0.05 mol/m<sup>2</sup>. The amount of silver in the thermographic materials of this invention is generally 0.02 mol/m<sup>2</sup>.

### Reducing Agents

10 The reducing agents (or “developers”) useful in this invention are ascorbic acid compounds (or derivatives) that are represented by the following Structure (I):



15 (I)

wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen and/or the same or different acyl groups [ R<sub>3</sub>-(C=O)- or R<sub>3</sub>-L-(C=O)- ], provided that R<sub>1</sub> and R<sub>2</sub> are not both hydrogen. The acyl groups each have 11 or fewer carbon atoms, and preferably 20 each acyl group is branched and/or contains at least one ring. The acyl groups may be substituted with functional groups such as ethers, halogens, esters and amides.

R<sub>3</sub> of the acyl group may be hydrogen, or a substituted or unsubstituted alkyl group having 10 or fewer carbon atoms (such as methyl, ethyl, 25 *iso*-propyl, *t*-butyl, and benzyl), substituted or unsubstituted aryl having 6 to 10 carbon atoms in the carbocyclic ring (such as phenyl, 4-methylphenyl, 4-methoxyphenyl, and naphthyl), substituted or unsubstituted alkenyl having 10 or fewer

carbon atoms in the chain (such as ethenyl, hexenyl, and 1-methylpropenyl), or a substituted or unsubstituted heterocyclic group having 5 to 7 nitrogen, oxygen, sulfur, and carbon atoms in the heterocyclic ring (such as tetrahydrofuryl and benzthiazoyl). L may be oxy, thio, or -NR<sub>4</sub>-, wherein R<sub>4</sub> is defined in the same way as R<sub>3</sub>.

At least one of R<sub>1</sub> and R<sub>2</sub> is an acyl group and the other of R<sub>1</sub> and R<sub>2</sub> is preferably hydrogen. Preferably, R<sub>3</sub> is *tert*-butyl, R<sub>4</sub> is hydrogen, and L is nitrogen.

Mixtures of these compounds can be used if desired in any specific proportion.

Compounds of Structure I have two chiral centers (indicated by \*). Therefore four isomers are possible and compounds of Structure I may be derived from D- or L-ascorbic acid or from D- or L-isoascorbic acid.

Representative examples of compounds having Structure I are shown below in TABLE I.

TABLE I

Compound	Derived From	R <sub>1</sub>	R <sub>2</sub>
I-1	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-2	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-3	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-4	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-5	D-isoascorbic acid	H	<i>t</i> -Butyl-(C=O)-
I-6	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	H
I-7	L-ascorbic acid	Ph-(C=O)-	H
I-8	L-ascorbic acid	1-Adamantyl-(C=O)-	H
I-9	L-ascorbic acid	1-Adamantylmethyl-(C=O)-	H
I-10	L-ascorbic acid	1-Methylcyclohexyl-(C=O)-	H
I-11	L-ascorbic acid	2-Adamantylmethyl-(C=O)	H

I-12	L-ascorbic acid	2,2-Dimethylpropyl-(C=O)-	H
I-13	L-ascorbic acid	Cyclohexyl-(C=O)-	H
I-14	L-ascorbic acid	1,1-Dimethylpropyl-(C=O)-	H
I-15	L-ascorbic acid	1-Ethylpropyl-(C=O)-	H
I-16	L-ascorbic acid	2,4,4-Trimethylpentyl-(C=O)-	H
I-17	L-ascorbic acid	2-Methylpropyl-(C=O)-	H
I-18	L-ascorbic acid	Cyclopentyl-(C=O)-	H
I-19	L-ascorbic acid	Diethylamino-(C=O)	H
I-20	L-ascorbic acid	Diethylamino-(C=O)-	Diethylamino-(C=O)-
I-21	L-ascorbic acid	Phenyl-NH-(C=O)-	H
I-22	L-ascorbic acid	Hexyl-NH-(C=O)-	Hexyl-NH-(C=O)-
I-23	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	Ethyl-(C=O)-
I-24	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-
I-25	L-ascorbic acid	Ethyl-O-(C=O)-	H
I-26	L-ascorbic acid	Phenyl-O-(C=O)-	H
I-27	L-ascorbic acid	4-HO-Phenyl-(C=O)-	H
I-28	L-ascorbic acid	2-norbornylmethyl-(C=O)-	H
I-29	L-ascorbic acid	3,4-(HO) <sub>2</sub> -Phenyl-(C=O)-	H
I-30	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	<i>i</i> -Propyl-(C=O)-
I-31	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-

Compounds I-1, I-2, I-7, and I-9 are preferred.

Compounds of Structure I may be prepared by known methods.

5 For example, 5- and/or 6-substituted esters of ascorbic acid may be prepared by the reaction of ascorbic acid and a carboxylic acid in sulfuric acid as described by H. Tanaka and R. Yamamoto, *Yakugaku Zasshi*, **1966**, 86(5), 376-83. In particular, compound I-1 has been prepared using this method by K.R. Bharucha et al.

*J. Agric. Food Chem.*, **1980**, 28(6), 1274-181. The preparation of 5- or 6-acyl ascorbic acid derivatives has also been accomplished through the use of enzymes as described, for example, in T. Maugard et al., *Biotechnology Progress*, **2000**, 16(3), 358-362, Y. Watanabe et al., *Food Sci. Technol. Res.*, **1999**, 5(2), 188-192, 5 U.S. Patent 5,079,153 (Enomoto et al.), and WO 03/018,003 (Rath et al.). Alternatively, 2-O,3-O-dibenzyl-ascorbic acid can be prepared as described by R. Dallacker and F. Sanders, *Chemiker-Zeitung*, **1985**, 109(6), 197-202. Acylation of this material and removal of the benzyl groups by hydrogenation affords 5-acyl, 6-acyl, or 5,6-diacyl ascorbic acid derivatives. Mixed acyl derivatives can be 10 prepared in this manner. 5,6-Diacyl ascorbic acid derivatives have also been prepared using methods described in JP 49-87655 (Shionogi & Co. Ltd.), and U.S. Patent 4,822,898 (Kamaya et al.).

15 Minor (less than 20 mol % of total moles of reducing agents) of conventional reducing agents [such as ascorbic acid or ascorbic acid derivatives not represented by Structure (I) or hindered phenols] can be used in combination with the reducing agents of Structure (I) if desired, but it is preferred that the materials of this invention contain the compounds of Structure (I) as the exclusive reducing agents.

20 If desired, co-developers and contrast enhancing agents may be used in combination with the ascorbic acid and reductone reducing agents described herein. Useful co-developer reducing agents include for example, those described in U.S. Patent 6,387,605 (Lynch et al.).

25 Additional classes of reducing agents that may be used as co-developers are trityl hydrazides and formyl phenyl hydrazides as described in U.S. Patent 5,496,695 (Simpson et al.), 2-substituted malondialdehyde compounds as described in U.S. Patent 5,654,130 (Murray), and 4-substituted isoxazole compounds as described in U.S. Patent 5,705,324 (Murray). Additional developers are described in U.S. Patent 6,100,022 (Inoue et al.).

30 Yet another class of co-developers includes substituted acrylonitrile compounds that are identified as HET-01 and HET-02 in U.S. Patent 5,635,339 (Murray) and CN-01 through CN-13 in U.S. Patent 5,545,515 (Murray et al.).

Various contrast enhancing agents may be used in some photothermographic materials with specific co-developers. Examples of useful contrast enhancing agents include, but are not limited to, hydroxylamines (including hydroxylamine and alkyl- and aryl-substituted derivatives thereof), alkanolamines 5 and ammonium phthalamate compounds as described in U.S. Patent 5,545,505 (Simpson), hydroxamic acid compounds as described in U.S. Patent 5,545,507 (Simpson et al.), N-acylhydrazine compounds as described in U.S. Patent 5,558,983 (Simpson et al.), and hydrogen atom donor compounds as described in U.S. Patent 5,637,449 (Harring et al.).

10 The reducing agent (or mixture thereof) of Structure (I) is generally present in the thermally developable compositions of this invention in an amount of from 0.3 to 1.0 mol/mol of total silver. In the thermally developable materials of this invention, these reducing agents are generally present in an amount of from 0.002 to 0.05 mol/m<sup>2</sup> (preferably from 0.006 to 0.03 mol/m<sup>2</sup>).

15

### Other Addenda

20 The thermally developable materials of this invention can also include one or more compounds that are known in the art as "toners." Toners are compounds that when added to the imaging layer shift the color of the developed silver image from yellowish-orange to brown-black or blue-black, and/or act as development accelerators to speed up thermal development. "Toners" or derivatives thereof that improve the black-and-white image are highly desirable components of the thermally developable materials of this invention.

25 Thus, compounds that either act as toners or react with a reducing agent to provide toners can be present in an amount of 0.01% by weight to 10% (preferably from 0.1% to 10% by weight) based on the total dry weight of the layer in which they are included. The amount can also be defined as being within the range of from  $1 \times 10^{-5}$  to 1.0 mol per mole of non-photosensitive source of 30 reducible silver in the photothermographic material. The toner compounds may be incorporated in one or more of the thermally developable layers as well as in adjacent layers such as a protective overcoat layer or underlying "carrier" layer.

Toners can be located on both sides of the support if thermally developable layers are present on both sides of the support.

Compounds useful as toners are described, for example, in U.S. Patent 3,074,809 (Owen), U.S. Patent 3,080,254 (Grant, Jr.), U.S. Patent 5 3,446,648 (Workman), U.S. Patent 3,844,797 (Willems et al.), U.S. Patent 3,847,612 (Winslow), U.S. Patent 3,951,660 (Hagemann et al.), U.S. Patent 4,082,901 (Laridon et al.), U.S. Patent 4,123,282 (Winslow), U.S. Patent 5,599,647 (Defieuw et al.), U.S. Patent 3,832,186 (Masuda et al.), and GB 1,439,478 (AGFA).

10 Particularly useful toners are mercaptotriazoles as described in copending and commonly assigned U.S. Serial No. 10/193,443 (filed July 11, 2002 by Lynch, Zou, and Ulrich), the heterocyclic disulfide compounds described in copending and commonly assigned U.S. Serial No. 10/384,244 (filed March 7, 2003 by Lynch and Ulrich), the triazine-thione compounds described in copending 15 and commonly assigned U.S. Serial No. 10/341,754 (filed January 14, 2003 by Lynch, Ulrich, and Skoug).

Also useful as toners are phthalazine and phthalazine derivatives [such as those described in U.S. Patent 6,146,822 (Asanuma et al.)], phthalazinone, and phthalazinone derivatives as well as phthalazinium compounds 20 [such as those described in U.S. Patent 6,605,418 (Ramsden et al.)].

The photothermographic materials of this invention can also contain other additives such as shelf-life stabilizers, antifoggants, contrast enhancing agents, development accelerators, acutance dyes, post-processing stabilizers or stabilizer precursors, thermal solvents (also known as melt formers), 25 humectants, and other image-modifying agents as would be readily apparent to one skilled in the art.

To further control the properties of photothermographic materials (for example, contrast,  $D_{min}$ , speed, or fog) in infrared sensitive materials, it may be preferable to add one or more heteroaromatic mercapto compounds or 30 heteroaromatic disulfide compounds of the formulae  $Ar-S-M^1$  and  $Ar-S-S-Ar$ , wherein  $M^1$  represents a hydrogen atom or an alkali metal atom and  $Ar$  represents a heteroaromatic ring or fused heteroaromatic ring containing one or more of

nitrogen, sulfur, oxygen, selenium, or tellurium atoms. Useful heteroaromatic mercapto compounds are described as supersensitizers in EP 0 559 228 B1 (Philip et al.).

The photothermographic materials of the present invention can be further protected against the production of fog and can be stabilized against loss of sensitivity during storage. Suitable antifoggants and stabilizers that can be used alone or in combination include thiazolium salts as described in U.S. Patent 2,131,038 (Brooker et al.) and U.S. Patent 2,694,716 (Allen), azaindenes as described in U.S. Patent 2,886,437 (Piper), triazaindolizines as described in U.S. Patent 2,444,605 (Heimbach), urazoles as described in U.S. Patent 3,287,135 (Anderson), sulfocatechols as described in U.S. Patent 3,235,652 (Kennard), oximes as described in GB 623,448 (Carrol et al.), polyvalent metal salts as described in U.S. Patent 2,839,405 (Jones), thiuronium salts as described in U.S. Patent 3,220,839 (Herz), palladium, platinum, and gold salts as described in U.S. Patent 2,566,263 (Tirelli) and U.S. Patent 2,597,915 (Damshroder), compounds having  $-\text{SO}_2\text{CBr}_3$  groups as described for example in U.S. Patent 5,594,143 (Kirk et al.) and U.S. Patent 5,374,514 (Kirk et al.), and 2-(tribromomethylsulfonyl)-quinoline compounds as described in U.S. Patent 5,460,938 (Kirk et al.).

Stabilizer precursor compounds capable of releasing stabilizers upon application of heat during development can also be used as described in U.S. Patent 5,158,866 (Simpson et al.), U.S. Patent 5,175,081 (Krepski et al.), U.S. Patent 5,298,390 (Sakizadeh et al.), and U.S. Patent 5,300,420 (Kenney et al.).

In addition, certain substituted-sulfonyl derivatives of benzotriazoles (for example alkylsulfonylbenzotriazoles and arylsulfonylbenzotriazoles) have been found to be useful for post-processing print stabilizing as described in U.S. Patent 6,171,767 (Kong et al.).

Other useful antifoggants/stabilizers are described in U.S. Patent 6,083,681 (Lynch et al.). Still other antifoggants are hydrobromic acid salts of heterocyclic compounds (such as pyridinium hydrobromide perbromide) as described in U.S. Patent 5,028,523 (Skoug), benzoyl acid compounds as described in U.S. Patent 4,784,939 (Pham), substituted propenenitrile compounds as described in U.S. Patent 5,686,228 (Murray et al.), silyl blocked compounds as

described in U.S. Patent 5,358,843 (Sakizadeh et al.), vinyl sulfones as described in U.S. Patent 6,143,487 (Philip, et al.), diisocyanate compounds as described in EP 0 600 586A1 (Philip et al.), and tribromomethylketones as described in EP 0 600 587A1 (Oliff et al.).

5           The photothermographic materials may also include one or more polyhalo antifoggants that include one or more polyhalo substituents including but not limited to, dichloro, dibromo, trichloro, and tribromo groups. The antifoggants can be aliphatic, alicyclic or aromatic compounds, including aromatic heterocyclic and carbocyclic compounds. Particularly useful antifoggants of this 10 type are polyhalo antifoggants, such as those having a  $-\text{SO}_2\text{C}(\text{X}')_3$  group wherein X' represents the same or different halogen atoms.

Another class of useful antifoggants includes those compounds described in U.S. Patent 6,514,678 (Burgmaier et al.).

15           Advantageously, the photothermographic materials of this invention also include one or more thermal solvents (also called "heat solvents," "thermosolvents," "melt formers," "melt modifiers," "eutectic formers," "development modifiers," "waxes," or "plasticizers").

20           By the term "thermal solvent" in this invention is meant an organic material which becomes a plasticizer or liquid solvent for at least one of the imaging layers upon heating at a temperature above 60°C. Useful for that purpose are polyethylene glycols having a mean molecular weight in the range of 1,500 to 20,000 described in U.S. Patent 3,347,675 (Henn et al.), urea, methyl sulfonamide and ethylene carbonate as described in U.S. Patent 3,667,959 (Bojara et al.), and compounds described as thermal solvents in *Research Disclosure*, December 25 1976, item 15027, pp. 26-28. Other representative examples of such compounds include, but are not limited to, niacinamide, hydantoin, 5,5-dimethylhydantoin, salicylanilide, phthalimide, N-hydroxyphthalimide, N-potassium-phthalimide, succinimide, N-hydroxy-1,8-naphthalimide, phthalazine, 1-(2H)-phthalazinone, 2-acetylphthalazinone, benzanilide, 1,3-dimethylurea, 1,3-diethylurea, 30 1,3-diallylurea, *meso*-erythritol, D-sorbitol, tetrahydro-2-pyrimidone, glycouril, 2-imidazolidone, 2-imidazolidone-4-carboxylic acid, and benzenesulfonamide.

Combinations of these compounds can also be used including, for example, a combination of succinimide and 1,3-dimethylurea.

It may be advantageous to include a base-release agent or base precursor in the photothermographic materials. Representative base-release 5 agents or base precursors include guanidinium compounds, such as guanidinium trichloroacetate, and other compounds that are known to release a base but do not adversely affect photographic silver halide materials, such as phenylsulfonyl acetates as described in U.S. Patent 4,123,274 (Knight et al.).

## 10 **Phosphors**

In some embodiments, it is also effective to incorporate X-radiation-sensitive phosphors in the chemically sensitized photothermographic emulsions and materials of this invention as described in U.S. Patents 6,573,033 (Simpson et al.) and 6,440,649 (Simpson et al.).

15 Any conventional or useful storage or prompt-emitting phosphor can be used, singly or in mixtures, in the practice of this invention.

The one or more phosphors used in the practice of this invention are present in the photothermographic materials in an amount of at least 0.1 mole per mole, and preferably from 0.5 to 20 mole, per mole of total silver in the photothermographic material. Generally, the amount of total silver is at least 0.002 20 mol/m<sup>2</sup>.

Because of the size of the phosphors used in the invention, generally the layers in which they are incorporated (usually one or more emulsion 25 layers) have a dry coating weight of at least 5 g/m<sup>2</sup>, and preferably from 5 g/m<sup>2</sup>, to about 200 g/m<sup>2</sup>. Most preferably, the one or more phosphors and the photosensitive silver halide are incorporated within the same imaging layer that has a dry coating weight within the noted preferred range.

## **Binders**

30 The photosensitive silver halide (if present), the non-photosensitive source of reducible silver ions, the reducing agent, antifoggant(s), toner(s), and any other additives used in the present invention are added to and coated in one or

more binders using a suitable solvent. Thus, organic solvent-based or aqueous-based formulations are used to prepare the thermographic and photo-thermographic materials of this invention. Mixtures of different types of hydrophilic and/or hydrophobic binders can also be used. Preferably, hydrophilic 5 binders and water-dispersible polymeric latexes are used to provide aqueous-based materials in this invention.

Examples of useful hydrophilic binders include, but are not limited to, proteins and protein derivatives, gelatin and gelatin derivatives (hardened or unhardened), cellulosic materials, acrylamide/methacrylamide polymers, 10 acrylic/methacrylic polymers, polyvinyl pyrrolidones, polyvinyl alcohols, poly(vinyl lactams), polymers of sulfoalkyl acrylate or methacrylates, hydrolyzed polyvinyl acetates, polyamides, polysaccharides, and other naturally occurring or synthetic vehicles commonly known for use in aqueous-based photographic emulsions (see for example *Research Disclosure*, item 38957, noted above).

15 Particularly useful hydrophilic binders are gelatin, gelatin derivatives, polyvinyl alcohols, and cellulosic materials. Gelatin and its derivatives are most preferred, and comprise at least 75 weight % of total binders when a mixture of binders is used.

20 Aqueous dispersions of water-dispersible polymeric latexes may also be used, alone or with hydrophilic or hydrophobic binders described herein. Such dispersions are described in, for example, U.S. Patent 4,504,575 (Lee), U.S. Patent 6,083,680 (Ito et al), U.S. Patent 6,100,022 (Inoue et al.), U.S. Patent 6,132,949 (Fujita et al.), U.S. Patent 6,132,950 (Ishigaki et al.), U.S. Patent 6,140,038 (Ishizuka et al.), U.S. Patent 6,150,084 (Ito et al.), U.S. Patent 25 6,312,885 (Fujita et al.), U.S. Patent 6,423,487 (Naoi).

25 In some embodiments, the components needed for imaging can be added to one or more binders that are predominantly (at least 50% by weight of total binders) hydrophobic in nature. Examples of typical hydrophobic binders include polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, cellulose acetate butyrate, polyolefins, polyesters, polystyrenes, polyacrylonitrile, 30 polycarbonates, methacrylate copolymers, maleic anhydride ester copolymers, butadiene-styrene copolymers, and other materials readily apparent to one skilled

in the art. Copolymers (including terpolymers) are also included in the definition of polymers. The polyvinyl acetals (such as polyvinyl butyral and polyvinyl formal), cellulose ester polymers, and vinyl copolymers (such as polyvinyl acetate and polyvinyl chloride) are preferred. Particularly suitable binders are polyvinyl butyral resins that are available under the name BUTVAR® from Solutia, Inc.(St. Louis, MO) and PIOLOFORM® from Wacker Chemical Company (Adrian, MI) and cellulose ester polymers.

5 Hardeners for various binders may be present if desired. Useful hardeners are well known and include diisocyanate compounds as described for example, in EP 0 600 586B1 (Philip et al.) and vinyl sulfone compounds as described in U.S. Patent 6,143,487 (Philip et al.), and EP 0 640 589A1 (Gathmann et al.), aldehydes and various other hardeners as described in U.S. Patent 10 6,190,822 (Dickerson et al.).

15 Where the proportions and activities of the photothermographic materials require a particular developing time and temperature, the binder(s) should be able to withstand those conditions. Generally, it is preferred that the binder does not decompose or lose its structural integrity at 120°C for 60 seconds. It is more preferred that it does not decompose or lose its structural integrity at 177°C for 60 seconds.

20 The polymer binder(s) is used in an amount sufficient to carry the components dispersed therein. Preferably, a binder is used at a level of 10% by weight to 90% by weight, and more preferably at a level of 20% by weight to 70% by weight, based on the total dry weight of the layer in which it is included. The amount of binders on opposing sides of the support in double-sided materials may 25 be the same or different.

### Support Materials

The photothermographic materials of this invention comprise a polymeric support that is preferably a flexible, transparent film that has any 30 desired thickness and is composed of one or more polymeric materials. They are required to exhibit dimensional stability during thermal development and to have suitable adhesive properties with overlying layers. Useful polymeric materials for

making such supports include, but are not limited to, polyesters (such as polyethylene terephthalate and polyethylene naphthalate), cellulose acetate and other cellulose esters, polyvinyl acetal, polyolefins, polycarbonates, and polystyrenes. Preferred supports are composed of polymers having good heat 5 stability, such as polyesters and polycarbonates. Support materials may also be treated or annealed to reduce shrinkage and promote dimensional stability.

It is also useful to use supports comprising dichroic mirror layers as described in U.S. Patent 5,795,708 (Boutet).

Also useful are transparent, multilayer, polymeric supports 10 comprising numerous alternating layers of at least two different polymeric materials that preferably reflect at least 50% of actinic radiation in the range of wavelengths to which the photothermographic material is sensitive. Such polymeric supports are described in U.S. Patent 6,630,283 (Simpson et al.).

Support materials can contain various colorants, pigments, 15 antihalation or acutance dyes if desired. For example, blue-tinted supports are particularly useful for providing images useful for medical diagnosis. Support materials may be treated using conventional procedures (such as corona discharge) to improve adhesion of overlying layers, or subbing or other adhesion-promoting layers can be used.

20

### **Photothermographic Formulations**

An organic solvent-based coating formulation for the emulsion 25 layer(s) can be prepared by mixing the emulsion components with one or more hydrophobic binders in a suitable solvent system that usually includes an organic solvent, such as toluene, 2-butanone (methyl ethyl ketone), acetone, or tetrahydrofuran.

Alternatively and preferably, the emulsion components are prepared in a formulation containing a hydrophilic binder (such as gelatin, a 30 gelatin-derivative, or a cellulosic material) or a water-dispersible polymer in the form of a latex in water or water-organic solvent mixtures to provide aqueous-based coating formulations.

The materials of the invention can contain plasticizers and lubricants such as poly(alcohols) and diols as described in U.S. Patent 2,960,404 (Milton et al.), fatty acids or esters as described in U.S. Patents 2,588,765 (Robijns) and 3,121,060 (Duane), and silicone resins as described in GB 955,061 (DuPont). The materials can also contain inorganic or organic matting agents as described in U.S. Patents 2,992,101 (Jolley et al.) and 2,701,245 (Lynn). Polymeric fluorinated surfactants may also be useful in one or more layers as described in U.S. Patent 5,468,603 (Kub).

10 U.S. Patent 6,436,616 (Geisler et al.), describes various means of modifying photothermographic materials to reduce what is known as the “woodgrain” effect, or uneven optical density.

15 The materials of this invention can include one or more antistatic agents in any of the layers on either or both sides of the support. Conductive components include soluble salts, evaporated metal layers, or ionic polymers as described in U.S. Patent 2,861,056 (Minsk) and U.S. Patent 3,206,312 (Sterman et al.), insoluble inorganic salts as described in U.S. Patent 3,428,451 (Trevoy), electroconductive underlayers as described in U.S. Patent 5,310,640 (Markin et al.), electronically-conductive metal antimonate particles as described in U.S. Patent 5,368,995 (Christian et al.), and electrically-conductive metal-containing 20 particles dispersed in a polymeric binder as described in EP 0 678 776 A1 (Melpolder et al.). Particularly useful conductive particles are the non-acicular metal antimonate particles described in copending and commonly assigned U.S. Serial No. 10/304,224 (filed on November 27, 2002 by LaBelle, Sakizadeh, Ludemann, Bhave, and Pham).

25 Still other conductive compositions include one or more fluoro-chemicals each of which is a reaction product of  $R_f-CH_2CH_2-SO_3H$  with an amine wherein  $R_f$  comprises 4 or more fully fluorinated carbon atoms as described in U.S. Published Application 2003-0198901 (Sakizadeh et al.).

30 Additional conductive compositions include one or more fluoro-chemicals described in more detail in copending and commonly assigned U.S. Serial No. 10/265,058 (filed October 4, 2002 by Sakizadeh, LaBelle, and Bhave).

Layers to promote adhesion of one layer to another are also known, as described in U.S. Patent 5,891,610 (Bauer et al.), U.S. Patent 5,804,365 (Bauer et al.), U.S. Patent 4,741,992 (Przezdziecki), and U.S. Patent 5,928,857 (Geisler et al.).

5 Layers to reduce emissions from the film may also be present, including the polymeric barrier layers described in U.S. Patent 6,352,819 (Kenney et al.), U.S. Patent 6,352,820 (Bauer et al.), U.S. Patent 6,420,102 (Bauer et al.), and U.S. Patent 6,667,148 (Rao et al.), and U.S. Serial No. 10/351,814 (filed January 27, 2003 by Hunt).

10 The formulations described herein (including the thermally developable formulations) can be coated by various coating procedures including wire wound rod coating, dip coating, air knife coating, curtain coating, slide coating, or extrusion coating using hoppers of the type described in U.S. Patent 2,681,294 (Beguin). Layers can be coated one at a time, or two or more layers can  
15 be coated simultaneously by the procedures described in U.S. Patent 2,761,791 (Russell), U.S. Patent 4,001,024 (Dittman et al.), U.S. Patent 4,569,863 (Keopke et al.), U.S. Patent 5,340,613 (Hanzalik et al.), U.S. Patent 5,405,740 (LaBelle), U.S. Patent 5,415,993 (Hanzalik et al.), U.S. Patent 5,525,376 (Leonard), U.S. Patent 5,733,608 (Kessel et al.), U.S. Patent 5,849,363 (Yapel et al.), U.S. Patent 20 5,843,530 (Jerry et al.), U.S. Patent 5,861,195 (Bhave et al.), and GB 837,095 (Ilford). A typical coating gap for the emulsion layer can be from 10 to 750  $\mu\text{m}$ , and the layer can be dried in forced air at a temperature of from 20°C to 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, from 0.5 to 5.0 or more, as  
25 measured by a MacBeth Color Densitometer Model TD 504.

For example, after or simultaneously with application of the emulsion formulation to the support, a protective overcoat formulation can be applied over the emulsion formulation.

30 Preferably, two or more layer formulations are applied simultaneously to a film support using slide coating, the first layer being coated on top of the second layer while the second layer is still wet, using the same or different solvents.

In other embodiments, a “carrier” layer formulation comprising a single-phase mixture of the two or more polymers described above may be applied directly onto the support and thereby located underneath the emulsion layer(s) as described in U.S. Patent 6,355,405 (Ludemann et al.). The carrier layer 5 formulation can be applied simultaneously with application of the emulsion layer formulation.

Mottle and other surface anomalies can be reduced in the materials by incorporation of a fluorinated polymer as described for example in U.S. Patent 5,532,121 (Yonkoski et al.) or by using particular drying techniques as described, 10 for example in U.S. Patent 5,621,983 (Ludemann et al.).

While the first and second layers can be coated on one side of the film support, manufacturing methods can also include forming on the opposing or backside of the polymeric support, one or more additional layers, including a conductive layer, antihalation layer, or a layer containing a matting agent (such as 15 silica), or a combination of such layers. Alternatively, one backside layer can perform all of the desired functions.

It is also contemplated that the thermally developable materials of this invention can include emulsion layers on both sides of the support and/or an antihalation underlayer beneath at least one emulsion layer.

20 To promote image sharpness, photothermographic materials of the present invention can contain one or more layers containing acutance and/or antihalation dyes. These dyes are chosen to have absorption close to the exposure wavelength and are designed to absorb scattered light. One or more antihalation compositions may be incorporated into one or more antihalation backing layers, 25 underlayers, or overcoats. Additionally, one or more acutance dyes may be incorporated into one or more frontside layers.

Dyes useful as antihalation and acutance dyes include squaraine dyes described in U.S. Patent 5,380,635 (Gomez et al.), U.S. Patent 6,063,560 (Suzuki et al.), and EP 1 083 459A1 (Kimura), indolenine dyes described in EP 0 30 342 810A1 (Leichter), and cyanine dyes described in U.S. Published Application 2003-0162134 (Hunt et al.).

It may also be useful to employ compositions including acutance or antihalation dyes that will decolorize or bleach with heat during processing, as described in, for example, U.S. Patent 5,135,842 (Kitchin et al.), U.S. Patent 5,266,452 (Kitchin et al.), U.S. Patent 5,314,795 (Helland et al.), U.S. Patent 5 6,306,566, (Sakurada et al.), JP Kokai 2001-142175 (Hanyu et al.), and JP Kokai 2001-183770 (Hanye et al.). Useful bleaching compositions are described in JP Kokai 11-302550 (Fujiwara), JP Kokai 2001-109101 (Adachi), JP Kokai 2001-51371 (Yabuki et al.), and JP Kokai 2000-029168 (Noro).

Other useful heat-bleachable backside antihalation compositions 10 can include a radiation absorbing compound such as an oxonol dye and various other compounds used in combination with a hexaarylbiimidazole (also known as a “HABI”), or mixtures thereof. HABI compounds are described in U.S. Patent 4,196,002 (Levinson et al.), U.S. Patent 5,652,091 (Perry et al.), and U.S. Patent 5,672,562 (Perry et al.). Examples of such heat-bleachable compositions are 15 described for example in U.S. Patent 6,455,210 (Irving et al.), U.S. Patent 6,514,677 (Ramsden et al.), and U.S. Patent 6,558,880 (Goswami et al.).

Under practical conditions of use, these compositions are heated to provide bleaching at a temperature of at least 90°C for at least 0.5 seconds (preferably, at a temperature of from 100°C to 200°C for from 5 to 20 seconds).

20 In some embodiments, the thermally developable materials of this invention include a surface protective layer over one or more imaging layers on one or both sides of the support. In other embodiments, the materials include a surface protective layer on the same side of the support as the one or more emulsion layers and a layer on the backside that includes an antihalation and/or 25 conductive antistatic composition. A separate backside surface protective layer can also be included in these embodiments.

### **Imaging/Development**

The photothermographic materials of the present invention can be 30 imaged in any suitable manner consistent with the type of material, using any suitable imaging source (typically some type of radiation or electronic signal). In some embodiments, the materials are sensitive to radiation in the range of from at

least 300 nm to 1400 nm, and preferably from 300 nm to 850 nm because of the use of appropriate spectral sensitizing dyes. In one preferred embodiment, the materials are sensitive to radiation of from 350 nm to 450 nm.

5 Imaging can be achieved by exposing the photothermographic materials of this invention to a suitable source of radiation to which they are sensitive, including ultraviolet radiation, visible light, near infrared radiation and infrared radiation to provide a latent image. Suitable exposure means are well known and include incandescent or fluorescent lamps, xenon flash lamps, lasers, laser diodes, light emitting diodes, infrared lasers, infrared laser diodes, infrared 10 light-emitting diodes, infrared lamps, or any other ultraviolet, visible, or infrared radiation source readily apparent to one skilled in the art such as described in *Research Disclosure*, item 38957 (noted above).

15 In some embodiments, the photothermographic materials of the present invention can be imaged using an X-radiation imaging source and one or more prompt-emitting or storage X-ray sensitive phosphor screens adjacent to the photothermographic material. The phosphors emit suitable radiation to expose the photothermographic material.

20 In other embodiments, the photothermographic materials of the present invention can be imaged directly using an X-radiation imaging source to provide a latent image.

In still other embodiments, the photothermographic materials of the present invention can be imaged using an X-radiation imaging source and one or more X-ray sensitive prompt emitting or storage phosphors incorporated within the photothermographic material.

25 Imaging of the thermographic materials of this invention is carried out using a suitable imaging source of thermal energy such as a thermal print head.

30 Thermal development conditions will vary, depending on the construction used but will typically involve heating the thermally sensitive material at a suitably elevated temperature, for example, at from 50°C to 250°C for a sufficient period of time, generally from 1 to 120 seconds. Heating can be accomplished using any suitable heating means. A preferred heat development

procedure for photothermographic materials described herein includes heating at from 130°C to 170°C for from 10 to 25 seconds. A particularly preferred development procedure is heating at 150°C for 15 to 25 seconds.

## 5 Use as a Photomask

In some embodiments, the photothermographic and thermographic materials of the present invention are sufficiently transmissive in the range of from 350 to 450 nm in non-imaged areas to allow their use in a method where there is a subsequent exposure of an ultraviolet or short wavelength visible radiation sensitive imageable medium. The heat-developed materials absorb ultraviolet or short wavelength visible radiation in the areas where there is a visible image and transmit ultraviolet or short wavelength visible radiation where there is no visible image. The materials may then be used as a mask and positioned between a source of imaging radiation (such as an ultraviolet or short wavelength visible radiation energy source) and an imageable material that is sensitive to such imaging radiation, such as a photopolymer, diazo material, photoresist, or photosensitive printing plate. Exposing the imageable material to the imaging radiation through the visible image in the exposed and heat-developed photothermographic material provides an image in the imageable material. These embodiments of the imaging method of this invention are carried out using Steps A through D noted above in the Summary of the Invention.

## Imaging Assemblies

In preferred embodiments, the photothermographic materials of this invention are used in association with one or more phosphor intensifying screens and/or metal screens in what is known as "imaging assemblies." Double-sided X-radiation sensitive photothermographic materials are preferably used in combination with two adjacent intensifying screens, one screen in the "front" and one screen in the "back" of the material. The front and back screens can be appropriately chosen depending upon the type of emissions desired, the desired photicity, emulsion speeds, and percent crossover. A metal (such as copper or lead) screen can also be included if desired.

There are a wide variety of phosphors known in the art that can be formulated into phosphor intensifying screens as described in hundreds of publications including U.S. Patent 6,573,033 (noted above) and references cited therein.

5 Imaging assemblies can be prepared by arranging a suitable photo-thermographic material in association with one or more phosphor intensifying screens, and one or more metal screens in a suitable holder (often known as a cassette), and appropriately packaging them for transport and imaging uses.

10 The following examples are provided to illustrate the practice of the present invention and the invention is not meant to be limited thereby.

#### Materials and Methods for the Examples:

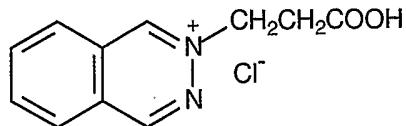
15 All materials used in the following examples can be prepared using known synthetic procedures or are readily available from standard commercial sources, such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified. All percentages are by weight unless otherwise indicated.

Densitometry measurements were carried out on an X-Rite® Model 301 densitometer that is available from X-Rite Inc. (Grandville, MI).

20 Vinol 523 is partially hydrolyzed (87 to 89%) poly(vinyl alcohol). It was obtained from Air Products and Chemicals, Inc. (Allentown, PA).

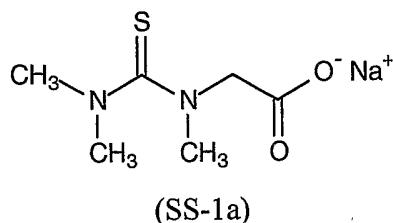
ZONYL® FSN is a nonionic fluorosurfactant that is available from E. I. DuPont de Nemours & Co. (Wilmington, DE). It is a fluorinated poly-ethyleneoxide alcohol.

25 Compound A-1 is described in U.S. Patent 6,605,418 (noted above) and is believed to have the following structure.



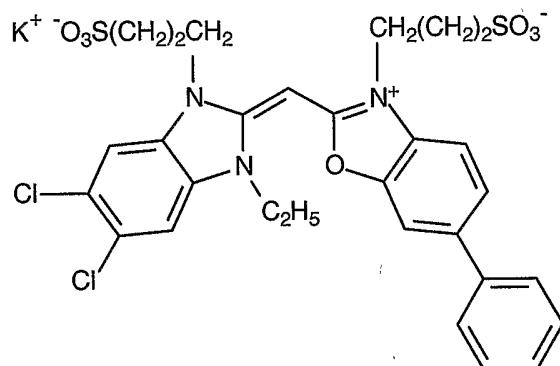
(A-1)

Compound SS-1a is described in U.S. Patent 6,296,998 (Eikenberry et al.) and is believed to have the following structure.



5

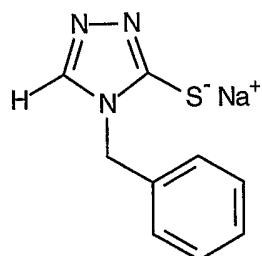
Blue sensitizing dye SSD-1 is believed to have the following structure.



(SSD-1)

10

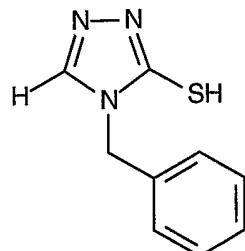
Compound T-1 is the sodium salt of 2,4-dihydro-4-(phenylmethyl)-3H-1,2,4-triazole-3-thione and is believed to have the following structure. It is drawn as the sodium salt of the thiol form but may also exist as the sodium salt of the thione tautomer.



15

(T-1)

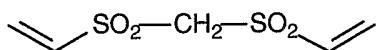
Compound T-2 is 2,4-dihydro-4-(phenylmethyl)-3H-1,2,4-triazole-3-thione. It is believed to have the following structure. It is drawn as the thiol form but may also exist as the thione tautomer.



5

(T-2)

Bisvinyl sulfonyl methane (VS-1) is 1,1'-(methylenebis(sulfonyl))-bis-ethene and is believed to have the following structure.



10

(VS-1)

### Preparation of Ascorbic Acid Compounds of Structure I

**Synthetic Preparation 1: 2-O,3-O-Dibenzyl-L-ascorbic acid,**

**15 5-O,6-O-bis(2-methylpropionate) and 2-O,3-O-dibenzyl-L-ascorbic acid,**  
**5-O,6-O-bis(2,2-dimethylpropionate).**

To a solution of 10.42 g (29.24 mmol) of 2-O,3-O-dibenzyl-L-ascorbic acid in 60 ml of dry pyridine cooled to 5 °C under nitrogen with magnetic stirring was added 7.79 g (73.10 mmol) of isobutyryl chloride via syringe over 15 min. The mixture was warmed to room temperature, held 18 hr, poured into water, extracted into ethyl acetate, washed 4 times with 1 M hydrochloric acid solution and once with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. HPLC/MS and NMR indicated the desired product. 2-O,3-O-Dibenzyl-L-ascorbic acid, 5-O,6-O-bis(2,2-dimethylpropionate) was also prepared in an analogous manner substituting 2,2-dimethylpropionyl chloride for isobutyryl chloride.

**Synthetic Preparation 2: L-ascorbic acid, 5-O,6-O-bis(2-methylpropionate)  
(Compound I-30) and L-ascorbic acid, 5-O,6-O-bis(2,2-dimethylpropionate)  
(Compound I-3).**

The product obtained in Synthetic Preparation 1 (29 mmol) was dissolved in 50 ml of ethanol and 30 ml of cyclohexene, and 200 mg of 10 % palladium on carbon added under nitrogen with magnetic stirring. After heating at reflux for 5 hr the mixture was filtered through infusorial earth, washing the earth with ethanol. Concentration *in vacuo* of the filtrate gave 11.84 g of crude product. This was crystallized from 20 ml of ethyl acetate and 50 ml of hexanes to give 2.85 g of product (Compound I-30), mp 118-120 °C. HPLC/MS and NMR agreed with the assigned structure.

L-ascorbic acid, 5-O,6-O-bis(2,2-dimethylpropionate) (Compound I-3) was obtained in an analogous manner starting with 2-O,3-O-dibenzyl-L-ascorbic acid, 5-O,6-O-bis(2,2-dimethylpropionate).

**15 Synthetic Preparation 3: 2-O,3-O-dibenzyl-6-O-phenylaminocarbonyl-L-ascorbic acid.**

To an ice-cold solution of 5.21 g (14.6 mmol) of 2-O,3-O-dibenzyl-L-ascorbic acid in 35 ml of dry pyridine under nitrogen with magnetic stirring was added 2.26 g (19.0 mmol) of phenylisocyanate. After 20 hr at room temperature, it was concentrated *in vacuo* to give a mixture (HPLC/MS) of starting material, mono adducts, diphenylurea, and bis adduct. This was column chromatographed on a 5x26 cm silica gel column packed in hexanes and gradient eluted from 5 to 50 % ethyl acetate. After 4 liters of elutant (around 30 % ethyl acetate) 4 g of material that was 80 % desired, 15 % diphenylurea, and 5 % of bis adduct were obtained. Recrystallization from methanol multiple times gave 2.04 g of material which was > 95 % of the desired 2-O,3-O-dibenzyl-6-O-phenylaminocarbonyl-L-ascorbic acid by HPLC/MS and NMR.

**Synthetic Preparation 4: 6-O-phenylaminocarbonyl-L-ascorbic acid  
(Compound I-21).**

30 A solution of 2.04 g of the material obtained in Synthetic Preparation 3 in 4 ml of cyclohexene and 6.5 ml of ethanol was heated to reflux

under nitrogen with magnetic stirring with 130 mg of 10 % palladium on carbon for 1.3 hr. After filtration through infusorial earth and washing with ethanol, the filtrate was concentrated *in vacuo*. Separately, a 1.47 g sample of 2-O,3-O-dibenzyl-6-O-phenylaminocarbonyl-L-ascorbic acid which also 5 contained 25 % diphenylurea was treated in the same manner. After filtration and concentration it was dissolved in ethyl acetate, extracted into 9 ml of 1M sodium hydroxide solution, acidified with 10 ml of 1M hydrochloric acid solution, ethyl acetate extracted 3 times, dried over sodium sulfate, filtered, and concentrated *in vacuo* to give 1.23 g of oil. The materials were combined and recrystallized from 10 ethyl acetate/hexanes to give 1.87 g 6-O-phenylaminocarbonyl-L-ascorbic acid (Compound I-21), mp 171 – 172°C with bubbling and decomposition. The structure was confirmed by HPLC/MS and NMR.

**Example 1 – Preparation of Aqueous-Based Photothermographic Materials:**

15 Aqueous-based photothermographic materials of this invention were prepared in the following manner.

Preparation of Silver Benzotriazole Dispersion:

20 Solution A was prepared in a stirred reaction vessel by dissolving 85 g of lime-processed gelatin and 25 g of phthalated gelatin in 2000 g of deionized water.

25 Solution B containing 185 g of benzotriazole, 1405 g of deionized water, and 680 g of a 2.5 molar solution of sodium hydroxide was prepared. The mixture in the reaction vessel was adjusted to a pAg of 7.25 and a pH of 8.0 by addition of 2.5 molar sodium hydroxide solution as needed, and maintaining it at temperature of 36°C.

30 Solution C containing 228.5 g of silver nitrate and 1222 g of deionized water was added to the reaction vessel at an accelerated flow rate defined by: Flow =  $16(1 + 0.002t^2)$  ml/min (where t is the time in minutes), and the pAg was maintained at 7.25 by simultaneous addition of Solution B. This process was terminated when Solution C was exhausted, at which point Solution D containing 80 g of phthalated gelatin and 700 g of deionized water at 40°C was added to the reaction vessel. The mixture was then stirred and the pH

was adjusted to 2.5 with 2 molar sulfuric acid to coagulate the silver salt emulsion. The coagulum was washed twice with 5 liters of deionized water, and redispersed by adjusting pH to 6.0 and pAg to 7.0 with 2.5 molar sodium hydroxide solution and Solution B. The resulting dispersion contained fine particles of silver  
5 benzotriazole.

Preparation of Tabular Grain Silver Halide Emulsions:

A reaction vessel equipped with a stirrer was charged with 6 liters of water containing 4.21 g of lime-processed bone gelatin, 4.63 g of sodium bromide, 37.65 mg of potassium iodide, an antifoamant, and 1.25 ml of 0.1 molar sulfuric acid. The solution was held at 39°C for 5 minutes. Simultaneous additions were then made of 5.96 ml of 2.5378 molar silver nitrate and 5.96 ml of 2.5 molar sodium bromide over 4 seconds. Following nucleation, 0.745 ml of a 4.69% solution of sodium hypochlorite was added. The temperature was increased to 54°C over 9 minutes. After a 5-minute hold, 100 g of oxidized 10 methionine lime-processed bone gelatin in 1.412 liters of water containing additional antifoamant at 54°C were then added to the reactor. The reactor temperature was held for 7 minutes, after which 106 ml of a 5 molar sodium 15 chloride solution containing 2.103 g of sodium thiocyanate was added. The reaction was continued for 1 minute.

20 During the next 38 minutes, the first growth stage took place wherein solutions of 0.6 molar AgNO<sub>3</sub>, 0.6 molar sodium bromide, and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal uniform iodide level of 4.2 mole %. The flow rates during this growth segment were increased from 9 to 42 ml/min (silver nitrate) and from 0.8 to 25 3.7 ml/min (silver iodide). The flow rates of the sodium bromide were allowed to fluctuate as needed to maintain a constant pBr. At the end of this growth segment 78.8 ml of 3.0 molar sodium bromide were added and held for 3.6 minutes.

20 During the next 75 minutes the second growth stage took place wherein solutions of 3.5 molar silver nitrate and 4.0 molar sodium bromide and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal iodide level of 4.2 mole %. The flow rates during this segment were

increased from 8.6 to 30 ml/min (silver nitrate) and from 4.5 to 15.6 ml/min (silver iodide). The flow rates of the sodium bromide were allowed to fluctuate as needed to maintain a constant pBr.

During the next 15.8 minutes, the third growth stage took place  
5 wherein solutions of 3.5 molar silver nitrate, 4.0 molar sodium bromide, and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal iodide level of 4.2 mole %. The flow rates during this segment were 35 ml/min (silver nitrate) and 15.6 ml/min (silver iodide). The temperature was decreased to 47.8°C during this segment.

10 During the next 32.9 minutes, the fourth growth stage took place wherein solutions of 3.5 molar silver nitrate and 4.0 molar sodium bromide and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal iodide level of 4.2 mole %. The flow rates during this segment were held constant at 35 ml/min (silver nitrate) and 15.6 ml/min (silver iodide). The  
15 temperature was decreased to 35°C during this segment.

A total of 12 moles of silver iodobromide (4.2% bulk iodide) were formed. The resulting emulsion was coagulated using 430.7 g of phthalated lime-processed bone gelatin and washed with de-ionized water. Lime-processed bone gelatin (269.3 g) was added along with a biocide and pH and pBr were adjusted to  
20 6 and 2.5 respectively.

The resulting emulsion was examined by Scanning Electron Microscopy. Tabular grains accounted for greater than 99% of the total projected area. The mean ECD of the grains was 2.369  $\mu\text{m}$ . The mean tabular thickness was 0.062  $\mu\text{m}$ .

25 This emulsion was spectrally sensitized with 1.0 mmol of blue sensitizing dye SSD-1 per mole of silver halide. Chemical sensitization was carried out using 0.0055 mmol of sulfur sensitizer (compound SS-1a) per mole of silver halide at 60°C for 10 minutes.

Preparation of Photothermographic Materials:

30 Solution A: Silver benzotriazole and gelatin (35% gelatin/65% water) were placed in a beaker and heated to 50°C for 15 minutes to melt the

material. A 5% aqueous solution of 3-methylbenzothiazolium iodide was added. Mixing for 15 minutes was followed by cooling to 40°C. The sodium salt of benzotriazole was added and the mixture was stirred for 15 minutes. Compound T-1 was then added. Mixing for 15 minutes was followed by addition of 2.5 N 5 sulfuric acid to adjust the pH to 5.5. ZONYL® FSN surfactant was then added.

Solution B: A portion of the tabular-grain silver halide emulsion prepared above was placed in a beaker and melted at 40°C.

Solution C: Solution C was prepared by adding the dry materials to water and heating to 40°C.

10 Solution D: Solution D was prepared by adding the dry materials to water and heating to 55°C. The finished solution was allowed to cool to 40°C before use.

15 Solutions A, B, and C were mixed immediately before coating to form a photothermographic emulsion formulation. Solutions A, B, and D were mixed immediately before coating to form a photothermographic emulsion formulation. Each formulation was coated as a single layer on a 7 mil (178 µm) transparent, blue-tinted poly(ethylene terephthalate) film support using a knife coater to form an imaging layer having the dry composition shown in the following TABLE II. Samples were dried at 120°F (48.9°C) for 7 minutes.

20 Control sample (Sample 1-1-C) contained ascorbic acid while the inventive example (Sample 1-2) had Compound I-1 as the developer. The inventive developer, Compound I-1, was added in an equivalent molar amount to that of ascorbic acid used in control sample 1-1-C.

TABLE II

Solution	Component	Dry Coating Weight (g/m <sup>2</sup> )
A	Silver (from Ag benzotriazole salt)	1.82
A	Lime processed gelatin	1.10
A	3-Methylbenzothiazolium Iodide	0.09

A	Sodium benzotriazole	0.10
A	Mercaptotriazole compound T-1	0.07
A	ZONYL® FSN surfactant	0.06
B	Silver (from AgBrI emulsion)	0.38
C	Succinimide	0.13
C	Dimethylurea	0.16
C	Compound A-1	0.06
C	Compound VS-1	0.09
C	Ascorbic Acid	2.10
D	Succinimide	0.13
D	Dimethylurea	0.16
D	Compound A-1	0.06
D	Compound VS-1	0.09
D	Compound I-1 (TABLE I)	3.15

Evaluation of Photothermographic Materials:

The resulting photothermographic films were imagewise exposed for  $10^{-2}$  seconds using an EG&G flash sensitometer equipped with a P-16 filter and a 0.7 neutral density filter. Following exposure, the films were developed by heating on a heated drum for 18 seconds at 150°C to generate continuous tone wedges. These samples provided initial D<sub>min</sub>, D<sub>max</sub>, and Relative Speed.

The speeds are reported as “relative speed.” “Relative Speed-2” was determined at a density value of 1.00 above D<sub>min</sub>. Speed values were normalized. Sample 1-1, which contained ascorbic acid, was assigned a relative speed value of 100.

Densitometry measurements were made on a custom built computer-scanned densitometer and meeting ISO Standards 5-2 and 5-3 and are believed to be comparable to measurements from commercially available

densitometers. Density of the wedges was then measured with a computer densitometer using a filter appropriate to the sensitivity of the photothermographic material to obtain graphs of density versus log exposure (that is, D log E curves). D<sub>min</sub> is the density of the non-exposed areas after development and it is the 5 average of the eight lowest density values.

Post-processing light stability was evaluated using two test procedures. The first test was performed on a Picker light box, where the developed samples were subjected to 600 foot-candles of light (6456 lux) and a temperature of 108°F (42.2°C) for 24 hours. The change in D<sub>min</sub> ( $\Delta D_{min}$ ) was 10 calculated by subtracting the initial D<sub>min</sub> from the D<sub>min</sub> after completion of the 24 hour test. The D<sub>min</sub> values were read with an X-Rite, point densitometer. The results are tabulated in TABLE III below.

Developed samples were also evaluated for post-processing light stability. Samples were placed in a controlled environment at 70°F (21°C) and 15 50% RH (relative humidity) for 24 hours while being subjected to 100 foot-candles (1076 lux) of light. A metal bar was placed over a portion of each sample, and the protected portion was used as a reference region. The change in D<sub>min</sub> ( $\Delta D_{min}$ ) was calculated by subtracting the D<sub>min</sub> of the reference region from the D<sub>min</sub> of the sample that had been exposed for 24 hours. The D<sub>min</sub> values were 20 read with an X-Rite, point densitometer.

The results, shown below in TABLE III, record the initial sensitometry and post-processing light stability measurements. The reduction in change of D<sub>min</sub> ( $\Delta D_{min}$ ) demonstrates that the use of the specific ascorbic acid derivatives as reducing agents according to this invention, provide photothermographic materials with improved post-processing light stability.

TABLE III

Sample	Reducing Agent	D <sub>min</sub>	D <sub>max</sub>	Relative Speed-2	Light Box Test (ΔD <sub>min</sub> )	70/50 Test (ΔD <sub>min</sub> )	Invention (I) or Comparison (C)
1-1-C	Ascorbic Acid	0.291	2.69	100	0.43	0.74	C
1-2	I-1	0.293	2.53	95	0.03	0.14	I

**Example 2 Evaluation of Ascorbic Acid Derivatives:**

A tabular-grain silver halide emulsion was prepared as described in Example 1. This emulsion was spectrally sensitized with 1.0 mmol of blue sensitizing dye SSD-1 per mole of silver halide. Chemical sensitization was 5 carried out using 0.0055 mmol of gold sensitizer (potassium tetrachloroaurate) per mole of silver halide and 0.0055 mmol of sulfur sensitizer (compound SS-1a) per mole of silver halide at 60°C for 10 minutes.

**Preparation of a Photothermographic Emulsion Layer:**

Solution B: A portion of the tabular-grain silver halide emulsion 10 was placed in a beaker and melted at 40°C.

Solution E: Silver benzotriazole and gelatin (35% gelatin/65% water), were placed in a beaker and heated to 50°C for 20 minutes to melt the material. A 5% aqueous solution of 3-methylbenzothiazolium iodide was added. Mixing for 15 minutes was followed by cooling to 40°C. The solution was 15 finished with the addition of ZONYL® FSN surfactant.

Solutions B and E were mixed immediately before coating to form a silver emulsion formulation. Multiple coatings of the identical silver emulsion formulation were prepared. Each equivalent formulation was coated as a single layer on a 7 mil (178 µm) transparent, blue-tinted poly(ethylene terephthalate) 20 film support using a knife coater to form a layer having the dry composition shown in the following TABLE IV. Samples were dried at 120°F (48.9°C) for 7.5 minutes.

TABLE IV

Solution	Component	Dry Coating Weight (g/m <sup>2</sup> )
B	Silver (from AgBrI emulsion)	0.38
E	Silver (from Ag benzotriazole salt)	1.82
E	Lime processed gelatin	1.10
E	3-Methylbenzothiazolium Iodide	0.09
E	ZONYL® FSN surfactant	0.06

Preparation of Developer Layer Incorporating Ascorbic Acid Derivatives:

Solution F: Solution F was prepared by adding the dry materials to 5 methanol.

Solution G: Solution G was prepared by dissolving Vinol 523 in water with heating.

Solutions F and G were mixed with agitation resulting in a solution containing 50% methanol and 50% water. Benzotriazole and ascorbic acid 10 compound (materials H in TABLE V below) were added as solids to the combined solution and dissolved. The ascorbic acid derivative reducing agents described for this invention and ascorbic acid (comparison), were added at the same molar equivalent.

Each solution was coated on top of a sample of the previously 15 coated silver lower layer prepared above. The coating was performed using a knife coater to form a layer having the dry composition shown in the following TABLE V. Samples were dried at 120°F (48.9°C) for 7.5 minutes.

TABLE V

Solution	Component	Dry Coating Weight (g/m <sup>2</sup> )
F	Mercaptotriazole compound T-2	0.07
F	Compound VS-1	0.15
F	Succinimide	0.21
F	Dimethylurea	0.21
F	Compound A-1	0.09
G	Vinol 523	2.82
H	Benzotriazole	0.75
H	Reducing agent: Ascorbic acid or ascorbic acid derivative	0.017 mol/m <sup>2</sup>

Evaluation of Photothermographic Materials:

The resulting photothermographic materials were imagewise exposed and developed as described in Example 1. Developed samples were evaluated for post-processing light stability after being placed in a controlled environment at 70°F (21°C) and 50% RH (relative humidity) for 24 hours while being subjected to 100 foot-candles of light (1076 lux) as described in Example 1.

The changes in the minimum density ( $\Delta D_{min}$ ), shown below in TABLE VI, demonstrate that compounds of this invention helped reduce the  $\Delta D_{min}$  over time and provide increased print stability.

TABLE VI

Example	Reducing Agent	$\Delta D_{min}$
2-1-C	L-Ascorbic Acid (Comparison)	0.61
2-2	I-1 (TABLE I)	0.17
2-3	I-3 (TABLE I)	0.08
2-4	I-5 (TABLE I)	0.21
2-5	I-6 (TABLE I)	0.41
2-6	I-7 (TABLE I)	0.12
2-7	I-8 (TABLE I)	0.02
2-8	I-9 (TABLE I)	0.05
2-9	I-10 (TABLE I)	0.12
2-10	I-12 (TABLE I)	0.15
2-11	I-13 (TABLE I)	0.17
2-12	I-14 (TABLE I)	0.17
2-13	I-15 (TABLE I)	0.37
2-14	I-16 (TABLE I)	0.38
2-15	I-17 (TABLE I)	0.47
2-16	I-18 (TABLE I)	0.35
2-17	I-27 (TABLE I)	0.09
2-18	I-28 (TABLE I)	0.09
2-19	I-29 (TABLE I)	0.03
2-20	I-30 (TABLE I)	0.22
2-21	I-31 (TABLE I)	0.34

**Example 3:**

The following example demonstrates that ascorbic acid compounds within the scope of the present invention can be used as reducing agents in thermographic materials.

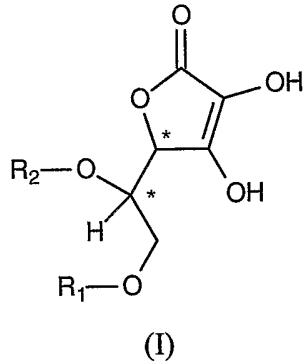
5 A 20 cm x 1 cm strip of thermographic material was prepared using the materials described in Example 1 but without photosensitive silver bromoiodide emulsion (Solution B). The strip was heated on a Reichert Heizbank heating block system (Kofler Reichert, Austria) with a temperature gradient from 68°C to 212°C for 15 seconds. Densitometry measurements were carried out on 10 an X-Rite® Model 301 densitometer. A development onset temperature of 175°C was found. A D<sub>max</sub> optical density of 3.9 was obtained. The D<sub>min</sub> optical density remained at 0.18 at temperatures below 110°C.

15 Thus, thermographic materials containing the ascorbic acid derivatives within the present invention are capable of providing images with excellent D<sub>min</sub> and D<sub>max</sub>.

## CLAIMS:

1. A thermally-developable composition comprising a binder, and in reactive association, a non-photosensitive source of reducible silver ions that includes a compound containing an imino group, and a reducing agent for said non-photosensitive source of reducible silver ions,

5 the reducing agent being a compound, or mixture thereof, represented by the following Structure (I):



wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an acyl group having 11 or fewer carbon atoms, provided that at least one of R<sub>1</sub> and R<sub>2</sub> is an acyl group.

15

2. The composition of claim 1 wherein the acyl group comprises from 2 to 11 carbon atoms.

20

3. The composition of claim 1 wherein the acyl group comprises a cyclic group or a branched alkyl group.

4. The composition of claim 1 wherein R<sub>1</sub> and R<sub>2</sub> are the same or different acyl groups.

25

5. The composition of claim 1 wherein the reducing agent comprises one or more compounds defined in Structure I and identified in the following list with the noted R<sub>1</sub> and R<sub>2</sub> groups:

Compound	Derived From	R <sub>1</sub>	R <sub>2</sub>
I-1	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-2	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-3	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-4	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-5	D-isoascorbic acid	H	<i>t</i> -Butyl-(C=O)-
I-6	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	H
I-7	L-ascorbic acid	Ph-(C=O)-	H
I-8	L-ascorbic acid	1-Adamantyl-(C=O)-	H
I-9	L-ascorbic acid	1-Adamantylmethyl-(C=O)-	H
I-10	L-ascorbic acid	1-Methylcyclohexyl-(C=O)-	H
I-11	L-ascorbic acid	2-Adamantylmethyl-(C=O)	H
I-12	L-ascorbic acid	2,2-Dimethylpropyl-(C=O)-	H
I-13	L-ascorbic acid	Cyclohexyl-(C=O)-	H
I-14	L-ascorbic acid	1,1-Dimethylpropyl-(C=O)-	H
I-15	L-ascorbic acid	1-Ethylpropyl-(C=O)-	H
I-16	L-ascorbic acid	2,4,4-Trimethylpentyl-(C=O)-	H
I-17	L-ascorbic acid	2-Methylpropyl-(C=O)-	H
I-18	L-ascorbic acid	Cyclopentyl-(C=O)-	H
I-19	L-ascorbic acid	Diethylamino-(C=O)	H
I-20	L-ascorbic acid	Diethylamino-(C=O)-	Diethylamino-(C=O)-
I-21	L-ascorbic acid	Phenyl-NH-(C=O)-	H
I-22	L-ascorbic acid	Hexyl-NH-(C=O)-	Hexyl-NH-(C=O)-
I-23	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	Ethyl-(C=O)-
I-24	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-
I-25	L-ascorbic acid	Ethyl-O-(C=O)-	H
I-26	L-ascorbic acid	Phenyl-O-(C=O)-	H

I-27	L-ascorbic acid	4-HO-Phenyl-(C=O)-	H
I-28	L-ascorbic acid	2-norbornylmethyl-(C=O)-	H
I-29	L-ascorbic acid	3,4-(HO) <sub>2</sub> -Phenyl-(C=O)-	H
I-30	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	<i>i</i> -Propyl-(C=O)-
I-31	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-

6. The composition of claim 1 wherein the reducing agent is present in an amount of from 0.3 to 1.0 mol/mol of total silver.

5

7. The composition of claim 1 further comprising a photosensitive silver halide.

8. The composition of claim 1 further comprising a preformed photosensitive silver halide provided predominantly as tabular grains, and the binder is a hydrophilic binder or a water-dispersible polymeric latex.

9. The thermally developable composition of claim 1 further comprising photosensitive preformed silver bromide or silver iodobromide grains, and wherein the binder is gelatin, a gelatin derivative, a cellulosic material, or a poly(vinyl alcohol), the non-photosensitive source of reducible silver ions includes a silver salt of benzotriazole, the reducing agent comprises one or more compounds defined in Structure I and identified in the following list with the noted R<sub>1</sub> and R<sub>2</sub> groups:

Compound	Derived From	R <sub>1</sub>	R <sub>2</sub>
I-1	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-2	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-3	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-4	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-5	D-isoascorbic acid	H	<i>t</i> -Butyl-(C=O)-
I-6	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	H

20

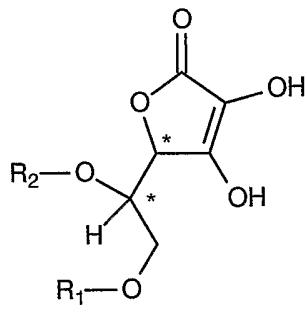
I-7	L-ascorbic acid	Ph-(C=O)-	H
I-8	L-ascorbic acid	1-Adamantyl-(C=O)-	H
I-9	L-ascorbic acid	1-Adamantylmethyl-(C=O)-	H
I-10	L-ascorbic acid	1-Methylcyclohexyl-(C=O)-	H
I-11	L-ascorbic acid	2-Adamantylmethyl-(C=O)	H
I-12	L-ascorbic acid	2,2-Dimethylpropyl-(C=O)-	H
I-13	L-ascorbic acid	Cyclohexyl-(C=O)-	H
I-14	L-ascorbic acid	1,1-Dimethylpropyl-(C=O)-	H
I-15	L-ascorbic acid	1-Ethylpropyl-(C=O)-	H
I-16	L-ascorbic acid	2,4,4-Trimethylpentyl-(C=O)-	H
I-17	L-ascorbic acid	2-Methylpropyl-(C=O)-	H
I-18	L-ascorbic acid	Cyclopentyl-(C=O)-	H
I-19	L-ascorbic acid	Diethylamino-(C=O)	H
I-20	L-ascorbic acid	Diethylamino-(C=O)-	Diethylamino-(C=O)-
I-21	L-ascorbic acid	Phenyl-NH-(C=O)-	H
I-22	L-ascorbic acid	Hexyl-NH-(C=O)-	Hexyl-NH-(C=O)-
I-23	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	Ethyl-(C=O)-
I-24	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-
I-25	L-ascorbic acid	Ethyl-O-(C=O)-	H
I-26	L-ascorbic acid	Phenyl-O-(C=O)-	H
I-27	L-ascorbic acid	4-HO-Phenyl-(C=O)-	H
I-28	L-ascorbic acid	2-norbornylmethyl-(C=O)-	H
I-29	L-ascorbic acid	3,4-(HO) <sub>2</sub> -Phenyl-(C=O)-	H
I-30	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	<i>i</i> -Propyl-(C=O)-
I-31	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-

10. A thermally developable imaging material comprising a  
5 support and having on at least one side thereon one or more thermally developable

imaging layers comprising a binder, and in reactive association, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, and a reducing agent for the non-photosensitive reducible silver ions,

wherein the reducing agent is a compound, or mixture thereof,

5 represented by the following Structure (I):



(I)

wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an acyl group having 11 or fewer

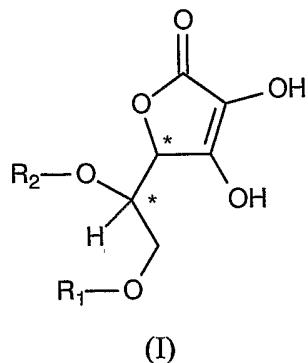
10 carbon atoms, provided that at least one of R<sub>1</sub> and R<sub>2</sub> is an acyl group.

11. The material of claim 10 that is a non-photosensitive thermographic material.

15 12. The material of claim 11 wherein the binder is a hydrophilic binder or a water-dispersible polymeric latex.

20 13. A black-and-white photothermographic material comprising a support and having on at least one side thereon one or more thermally developable imaging layers comprising a binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, a reducing agent for the non-photosensitive reducible silver ions, and optionally an outermost protective layer disposed over the one or more thermally developable imaging layers,

25 wherein the reducing agent is a compound, or mixture thereof, represented by the following Structure (I):



wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an acyl group having 11 or fewer  
5 carbon atoms, provided that at least one of R<sub>1</sub> and R<sub>2</sub> is an acyl group.

14. The material of claim 13 further comprising a phosphor in at  
least one of the thermally developable imaging layers.

10 15. The material of claim 13 wherein the non-photosensitive source  
of reducible silver ions includes a silver salt of benzotriazole or a substituted  
derivative thereof, or mixtures of such silver salts, the material is an aqueous-based  
material and comprises predominantly one or more hydrophilic binders or one or  
more water-dispersible polymeric latex binders in the one or more thermally  
15 developable imaging layers, and the photosensitive silver halide comprises one or  
more preformed photosensitive silver halides that are provided predominantly as  
tabular grains.

16. The material of claim 13 wherein the reducing agent is present  
20 in an amount of from 0.3 to 1.0 mol/mol of total silver.

17. The material of claim 13 wherein the acyl group comprises  
from 2 to 11 carbon atoms.

25 18. The material of claim 13 wherein the acyl group comprises a  
cyclic group or a branched alkyl group.

19. The material of claim 13 wherein the reducing agent comprises one or more compounds defined in Structure I and identified in the following list with the noted R<sub>1</sub> and R<sub>2</sub> groups:

Compound	Derived From	R <sub>1</sub>	R <sub>2</sub>
I-1	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-2	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-3	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-4	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-5	D-isoascorbic acid	H	<i>t</i> -Butyl-(C=O)-
I-6	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	H
I-7	L-ascorbic acid	Ph-(C=O)-	H
I-8	L-ascorbic acid	1-Adamantyl-(C=O)-	H
I-9	L-ascorbic acid	1-Adamantylmethyl-(C=O)-	H
I-10	L-ascorbic acid	1-Methylcyclohexyl-(C=O)-	H
I-11	L-ascorbic acid	2-Adamantylmethyl-(C=O)	H
I-12	L-ascorbic acid	2,2-Dimethylpropyl-(C=O)-	H
I-13	L-ascorbic acid	Cyclohexyl-(C=O)-	H
I-14	L-ascorbic acid	1,1-Dimethylpropyl-(C=O)-	H
I-15	L-ascorbic acid	1-Ethylpropyl-(C=O)-	H
I-16	L-ascorbic acid	2,4,4-Trimethylpentyl-(C=O)-	H
I-17	L-ascorbic acid	2-Methylpropyl-(C=O)-	H
I-18	L-ascorbic acid	Cyclopentyl-(C=O)-	H
I-19	L-ascorbic acid	Diethylamino-(C=O)	H
I-20	L-ascorbic acid	Diethylamino-(C=O)-	Diethylamino-(C=O)-
I-21	L-ascorbic acid	Phenyl-NH-(C=O)-	H
I-22	L-ascorbic acid	Hexyl-NH-(C=O)-	Hexyl-NH-(C=O)-
I-23	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	Ethyl-(C=O)-

I-24	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-
I-25	L-ascorbic acid	Ethyl-O-(C=O)-	H
I-26	L-ascorbic acid	Phenyl-O-(C=O)-	H
I-27	L-ascorbic acid	4-HO-Phenyl-(C=O)-	H
I-28	L-ascorbic acid	2-norbornylmethyl-(C=O)-	H
I-29	L-ascorbic acid	3,4-(HO) <sub>2</sub> -Phenyl-(C=O)-	H
I-30	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	<i>i</i> -Propyl-(C=O)-
I-31	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-

20. The material of claim 13 comprising one or more toners at least  
 5 one of which is a mercaptotriazole, triazine thione, phthalazine, or phthalazine derivative.

21. A black-and-white aqueous-based photothermographic material that comprises a transparent support having on at least one side thereof:

10 a) one or more thermally developable imaging layers each comprising a hydrophilic binder that is gelatin, a gelatin derivative, a poly(vinyl alcohol), or a cellulosic material, or is a water-dispersible polymeric latex, and in reactive association,

15 a preformed photosensitive silver bromide, silver iodobromide, or a mixture thereof, provided predominantly as tabular grains,

a non-photosensitive source of reducible silver ions that includes one or more organic silver salts at least one of which is a silver salt of benzotriazole,

a reducing agent for the non-photosensitive source of reducible silver ions, and

20 b) optionally, an outermost protective layer disposed over the one or more thermally developable imaging layers, and

wherein the reducing agent comprises one or more compounds defined in Structure I and identified in the following list with the noted R<sub>1</sub> and R<sub>2</sub> groups:

Compound	Derived From	R <sub>1</sub>	R <sub>2</sub>
I-1	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-2	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-3	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-4	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-5	D-isoascorbic acid	H	<i>t</i> -Butyl-(C=O)-
I-6	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	H
I-7	L-ascorbic acid	Ph-(C=O)-	H
I-8	L-ascorbic acid	1-Adamantyl-(C=O)-	H
I-9	L-ascorbic acid	1-Adamantylmethyl-(C=O)-	H
I-10	L-ascorbic acid	1-Methylcyclohexyl-(C=O)-	H
I-11	L-ascorbic acid	2-Adamantylmethyl-(C=O)	H
I-12	L-ascorbic acid	2,2-Dimethylpropyl-(C=O)-	H
I-13	L-ascorbic acid	Cyclohexyl-(C=O)-	H
I-14	L-ascorbic acid	1,1-Dimethylpropyl-(C=O)-	H
I-15	L-ascorbic acid	1-Ethylpropyl-(C=O)-	H
I-16	L-ascorbic acid	2,4,4-Trimethylpentyl-(C=O)-	H
I-17	L-ascorbic acid	2-Methylpropyl-(C=O)-	H
I-18	L-ascorbic acid	Cyclopentyl-(C=O)-	H
I-19	L-ascorbic acid	Diethylamino-(C=O)	H
I-20	L-ascorbic acid	Diethylamino-(C=O)-	Diethylamino-(C=O)-
I-21	L-ascorbic acid	Phenyl-NH-(C=O)-	H
I-22	L-ascorbic acid	Hexyl-NH-(C=O)-	Hexyl-NH-(C=O)-
I-23	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	Ethyl-(C=O)-
I-24	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-
I-25	L-ascorbic acid	Ethyl-O-(C=O)-	H
I-26	L-ascorbic acid	Phenyl-O-(C=O)-	H

I-27	L-ascorbic acid	4-HO-Phenyl-(C=O)-	H
I-28	L-ascorbic acid	2-norbornylmethyl-(C=O)-	H
I-29	L-ascorbic acid	3,4-(HO) <sub>2</sub> -Phenyl-(C=O)-	H
I-30	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	<i>i</i> -Propyl-(C=O)-
I-31	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-

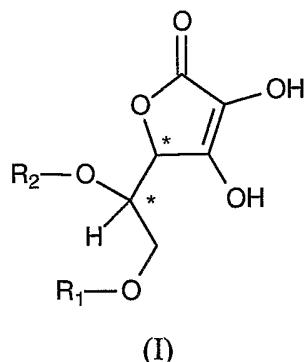
22. The material of claim 21 wherein the hydrophilic binder is  
5 gelatin or a gelatin derivative, silver benzotriazole is the predominant source of  
reducible silver ions, and the reducing agent is one or more of Compounds I-1, I-2,  
I-7, and I-9.

23. A black-and-white photothermographic material comprising a  
10 support having on a frontside thereof,

a) one or more frontside thermally developable imaging layers comprising a hydrophilic polymer binder or water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, a reducing agent for the non-photosensitive source reducible silver ions, and  
15 the material comprising on the backside of the support, one or more backside thermally developable imaging layers comprising a hydrophilic polymer binder or a water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that  
20 includes a silver salt of a compound containing an imino group, and a reducing agent for the non-photosensitive source reducible silver ions, and

b) optionally, an outermost protective layer disposed over the one or more thermally developable imaging layers on either or both sides of the support, and  
wherein the one or more thermally developable imaging layers, or the  
25 one or more protective layers if present, on both sides of the support have the same or different composition, and

the reducing agents on both sides of the support are the same or different and each reducing agent is a compound, or mixture thereof, represented by the following Structure (I):



5 wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or an acyl group having 11 or fewer carbon atoms, provided that at least one of R<sub>1</sub> and R<sub>2</sub> is an acyl group.

24. A method of forming a visible image comprising:

- A) imagewise exposing the photothermographic material of claim 13 to 10 form a latent image,
- B) simultaneously or sequentially, heating the exposed photothermographic material to develop the latent image into a visible image.

25. The method of claim 24 wherein the thermally developable material comprises a transparent support, and the image-forming method further comprises:

- C) positioning the exposed and thermally-developed material with the visible image therein between a source of imaging radiation and an imageable material that is sensitive to the imaging radiation, and
- D) exposing the imageable material to the imaging radiation through the visible image in the exposed and thermally-developed material to provide an image in the imageable material.

26. The method of claim 24 wherein the imagewise exposing is 25 carried out using visible or X-radiation.

27. The method of claim 24 wherein the thermally developable material is arranged in association with one or more phosphor intensifying screens during imaging.

28. The method of claim 24 wherein the exposed photothermographic material is used for medical diagnosis.

5

29. A method of forming a visible image comprising:

- A) imagewise exposing the photothermographic material of claim 23 to form a latent image,
- B) simultaneously or sequentially, heating the exposed photothermographic material to develop the latent image into a visible image.

10

30. An imaging assembly comprising the photothermographic material of claim 13 that is arranged in association with one or more phosphor intensifying screens.

15

31. A method of forming a black-and-white image comprising exposing the imaging assembly of claim 30 to X-radiation.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2005/001611

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03C1/498

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 881 938 A (MASUDA ET AL) 6 May 1975 (1975-05-06) cited in the application column 1, line 7 - line 10 column 2, line 9 - line 46 column 3, line 27 - line 33 column 7, line 27 - line 53 column 9, line 53 - line 64 claims 1,4,9,10 -----           -/-	1,2,7, 10,13, 17,24,26

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

### ° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

30 May 2005

Date of mailing of the international search report

06/06/2005

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2005/001611

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 4 211 839 A (SUZUKI ET AL) 8 July 1980 (1980-07-08)</p> <p>column 1, line 17 - line 25 column 2, line 2 - column 3, line 19 column 7, line 13 - column 8, line 43 column 9, line 1 - line 51 column 10, line 53 - line 60 column 14, line 5 - line 13 column 16, line 1 - line 12 claims 1,5,9,11,12</p> <p>-----</p>	1,2,5-7, 10,13, 16,17, 19,24,26
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A	<p>PATENT ABSTRACTS OF JAPAN vol. 014, no. 214 (P-1044), 7 May 1990 (1990-05-07) &amp; JP 02 048659 A (FUJI PHOTO FILM CO LTD), 19 February 1990 (1990-02-19) abstract pages 3-5, compounds AS-3, 6, 9, 10, 12, 17, 22, 25, 29 table 2, samples 104, 105, 107 table 5, samples 204, 205, 207</p> <p>-----</p>	1-31

# INTERNATIONAL SEARCH REPORT

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