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(54) **Imaging element for inhibiting image formation with cobalt(III) complexes, and method of forming an image.**

(57) An imaging element contains an energy-activatable image precursor composition comprising a cobalt III complex having releasable ligands which react with an image forming material to form a visible image. The element also contains a photoinhibitor which, on activating exposure, inhibits the release of ligands from the cobalt III complex or inhibits their image forming action. Images may be formed by imagewise activating the photoinhibitor, preferably with radiation longer than 300 nm, and thereafter activating the image precursor composition, for instance by heating. Images of a different sense may be formed by varying the exposure and activation treatments of the element.

Croydon Printing Company Ltd.

INHIBITING IMAGE FORMATION WITH COBALT(III) COMPLEXES

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a cobalt(III) complex-containing photographic element which can be made negative-working or positive-working, depending upon the nature of the exposure given.

State of the Prior Art

Cobalt(III) complexes containing releasable ligands have been utilized in non-silver redox reactions photoinitiated by means of photoreductants or spectral sensitizers, as disclosed, for example, in Research Disclosure, Volumes 126 and 130, October 1974 and February 1975, Publications Nos. 12617 and 13023, respectively, published by Industrial Opportunities Limited, Homewell, Havant Hampshire PO91EF, United Kingdom. Preferred reduction products of such a reaction are cobalt(II) and amines such as ammonia. Either of these can in turn be used to form images, the cobalt(II) being chelated by compounds capable of forming at least bidentate chelates, or the amines being reacted with dye precursors, including diazo-coupler systems, to form a dye; or the cobalt(II) or amines can be used to bleach out preincorporated dye. Such imaging processes are disclosed in Research Disclosure, Volume 126, October 1974, Publication No. 12617, part III. Amplification can be achieved by using a reducing agent precursor capable of forming a reducing agent with the aforesaid reduction products, for the reduction of remaining cobalt(III) complexes. For example, certain of said chelating compounds for cobalt(II) form, when chelated, a reducing agent, as described in Research Disclosure, Volume 135, July 1975, Publication No. 13505, and o-phthalaldehyde will react with ammonia to form a reducing agent, as disclosed in Research Disclosure, Volume 158, June 1977, Publication No. 15874. Imaging elements based upon such reactions involving cobalt(III) complexes are useful, for example, in graphic arts as room-light handling contact films, e.g., as an intermediate in the preparation of printing plates.

The cobalt complex imaging elements of the prior Research Disclosure can be either negative-working or positive-working, but the same element is not both. That is, a separate image-forming material (e.g., a dye former) is used in those instances in which the element is to be negative-working, compared to those instances in which the element is positive-working (e.g., by bleaching out a pre-existing dye). It would be highly desirable to provide an imaging element wherein the same element can be made negative or positive working, merely by controlling the processing of the element.

A further aspect of said prior cobalt complex imaging elements is that they can develop background print-up because the unexposed photoinitiator in the background areas causes increased D_{min}

(minimum density) upon handling as a result of room light activation of the photoinitiator. To avoid print-up, a peel-apart system can be used, that is, one wherein the layer of cobalt(III) complex relied upon for the imaging is removed from the image recording layer. Print-up is more difficult to avoid in integral systems, particularly when the exposed photo-reductant reduces the complex at room temperatures.

Therefore, there is a need for cobalt imaging systems which are less likely to suffer print-up when handled in room light conditions.

Metal complexes capable of releasing amines have been used prior to this invention to thermally activate image recording means such as diazo-coupler compositions. Examples are disclosed in U.S. Patent Nos. 3,469,984; 3,224,878; and 2,774,669. Because of their thermal instability, such complexes generate amines when overall heated, to cause diazo coupling or the like. There is no disclosure in this art of means for inhibiting such dye development.

<u>Canadian J. Chem</u>., Volume 54, pages 3685 through 3692 (1976), teaches that certain cobalt complexes, specifically $[(NH_3)_5Co(III)\text{dimethylsulfoxide}]^{3+}$, can be inhibited against thermal reduction by the addition of equimolar concentrations of p-toluenesulfonic acid. No suggestion is made that uch acid can be photolytically generated.

Patents relating to the background of image ormation using amines or cobalt complexes include .S. Patent Nos. 2,774,669; 3,102,811; 3,469,984; ,224,878; and Japanese Patent Publication No.74/6234.

escription of the Invention

The problem of providing an imaging element utilizing a radiation-sensitive, image precursor composition containing a cobalt(III) complex which is positive or negative-working and which avoids undesirable print-up of non-image areas is provided in accordance with the invention by an imaging element containing, in one or more operatively associated layers, an energy-activatable image precursor composition comprising at least a cobalt(III) complex having releasable ligands and an image-forming material which generates an image in response to the release of said ligands; characterized in that said imaging element contains, in chemical association with the image precursor composition, a photoinhibitor compound which inhibits the release of ligands from the cobalt(III) complex or inhibits the effect of released ligands on the image-forming material upon exposure to activating radiation.

The imaging element of the invention can be used to form a negative or positive image by subjecting said element to a first imagewise exposure to radiation of a wavelength which activates either the image precursor composition or the photoinhibitor, followed by a second uniform exposure to radiation of a wavelength which activates the component not activated by the first exposure.

Brief Description of the Drawings

Figs. 1A through 1C are schematic sectional views of an element of the invention, each view illustrating a step in a positive-working processing of the element in accordance with the invention;

Figs. 2A and 2B are sectional views similar to those of Figs. 1A through 1C, wherein a negative-working process is demonstrated; and

Fig. 3 is a sectional view similar to that of Fig. 1, but illustrating still another embodiment.

Description of the Preferred Embodiments

This invention relates to an imaging element wherein an exposure activates an image precursor composition comprising at least a cobalt(III) complex containing releasable ligands, to form an image, and wherein an inhibiting exposure photolytically generates the means for inhibiting such ligand release. More specifically, it has been discovered that a photoinhibitor such as a photolytic acid generator after suitable exposure will inhibit the release of ligands which would otherwise occur by activating exposure of the image precursor composition.

An "image precursor composition", as used herein, is a composition as described which when appropriately activated by exposure, produces an image by generating either a density or by destroying a preexisting density. Also as used herein, the precursor composition is "energy-activatable" if it is activatable by electromagnetic energy of any kind in areas where it is not inhibited by an already exposed photoinhibitor of the invention. The image precursor composition can be activated by thermal, light or electrical exposures of the type disclosed, for example, in Research Disclosure, Volume 147, July 1976, Publication No. 14719 depending upon the circumstances. Thermal exposure can occur through the use of infrared radiation or convection, but preferably it is achieved through conduction. As will be readily apparent, exposure of the image precursor composition is achieved by an energy form, such as a range of wavelengths, that is different from that used to activate the photoinhibitor. Generally the image precursor composition is activated by longer wavelength energy than will activate the photoinhibitor.

In a highly preferred form, the exposure of the image precursor composition is achieved through the use of heat or light or both together. However, as noted, if light is used or is present in a thermal exposure, preferably it is of a wavelength or an intensity that does not activate the photoinhibitor. Similarly, the light exposure used to imagewise activate the photoinhibitor to inhibit image formation can include energy of wavelengths and intensities that are incapable of activating the image precursor composition in preferance to the photoinhibitor, as shown in examples hereinafter described. To insure such discrimination, filters may be used, particularly for broad-band exposures. Preferably, if thermal energy is used to expose the image precursor composition, it is generated in a total absence of light, such as by a hot block, hot stylus, or heated rollers in a dark room.

As used herein, "photoinhibitor" means a single compound or a mixture of compounds which respond to activating radiation having a wavelength greater than about 300 nm, to inhibit the release of ligands by the cobalt(III) complex. The photoinhibitor can comprise one or more compounds which themselves have a sensitivity that responds to wavelengths longer than about 300 nm, or it can comprise a compound whose sensitivity responds only to wavelengths shorter than about 300 nm, and a spectral sensitizer which increases the native sensitivity to beyond 300 nm.

An imaging element containing the radiation-sensitive composition of the invention can comprise one or more operatively associated layers, with the image precursor composition being contained in one or more of the layers. That is, the image-forming material of the image precursor composition can either be admixed with the photoinhibitor, or it can be in a separate, adjacent layer where it responds to the ligands which are released by the cobalt(III) complex, as is more fully described hereafter. Thus, the photoinhibitor and the image precursor composition are in chemical association, that is, are either admixed together in a single layer, or are in contiguous layers either as manufactured or as processed.

Image Precursor Composition

This composition includes at least 1) a cobalt(III) complex containing releasable ligands and 2) an image-forming material capable of generating an image upon release of said ligands. If the cobalt(III) complex is thermally stable, i.e., it will not release ligands in response to an exposure which is primarily thermal in nature, then one or more destabilizer materials preferably is included, as defined and described hereafter.

An amplifier can also be included in the image precursor composition. As used herein, an "amplifier" is a reducing agent precursor composition or compound which interacts with the image precursor composition to generate additional initiators of the imaging reaction, whereby an internal gain, usually expressed as enhanced density, is achieved compared to that which results without the amplifier. Preferably, the initiators so generated are amines, and a highly useful example of an amplifier for generating such additional amine initiators is phthalaldehyde. The reason for such preference is that phthalaldehyde also functions as an image-forming material, as is hereinafter described. Alternatively, the amplifiers can be compounds which chelate with the cobalt(II) produced from cobalt(III). Such chelating compounds contain conjugated π-bonding systems capable of forming with such cobalt(II), additional reducing agents for remaining cobalt(III) complexes. Typical amplifiers of this class, and necessary restrictions concerning pKa values of the anions that can be used in the cobalt(III) complex in such circumstances, are described in Research Disclosure, Volume 135, July 1975, Publication No. 13505, the details of which are expressly incorporated herein by reference.

Any cobalt(III) complex containing releasable ligands and which is thermally stable at room temperature will function in this invention, whether or not it is thermally stable within the processing temperatures used. Such complexes on occasion have been described as being "inert". See, e.g., U.S. Patent No. 3,862,842, Columns 5 and 6. However, the ability of such complexes to remain stable, i.e., retain their original ligands when stored by themselves or in a neutral solution at room temperature until a chemically or thermally initiated reduction to cobalt(II) takes place, is so well known that the term "inert" will not be applied herein.

Such cobalt(III) complexes feature a molecule having a cobalt atom or ion surrounded by a group of atoms, ions or other molecules which are generically referred to as ligands. The cobalt atom or ion in the center of these complexes is a Lewis acid while the ligands are Lewis bases. While it is known that cobalt is capable of forming complexes in both its divalent and trivalent forms, trivalent cobalt complexes, i.e., cobalt(III) complexes, are employed in the practice of this invention, since the ligands are relatively tenaciously held in these complexes. and released when the cobalt is reduced to the (II) state.

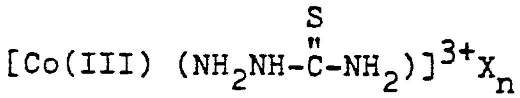
Preferred cobalt(III) complexes useful in the practice of this invention are those having a coordination number of 6. A wide variety of ligands can be used with cobalt(III) to form a cobalt (III) complex. The one of choice will depend upon whether the image-forming material described hereinafter relies upon amines to generate a dye or the destruction of dye, or upon the chelation of cobalt(II) to form a dye density. In the latter case, amine ligands or non-amine ligands can be used, whereas in the former case amine ligands are preferred as the source of initiators for the image-forming reaction. Useful amine ligands include, e.g., methylamine, ethylamine, ammines, and amino acids such as glycinato. As used herein, "ammine" refers to ammonia specifically, when functioning as a ligand, whereas "amine" is used to indicate the broader class noted above. Highly useful with all the embodiments of the image precursor composition hereinafter described are the ammine complexes. The other amine complexes achieve best results when used with particular destabilizer materials hereinafter described, for example, photoreductants.

The cobalt(III) complexes useful in the practice of this invention can be neutral compounds which are entirely free of either anions or cations. As used herein, "anion" refers to non-ligand anions, unless otherwise stated. The cobalt(III) complexes can also include one or more cations and anions as determined by the charge neutralization rule. Useful cations are those which produce readily soluble cobalt(III) complexes, such as alkali metals and quaternary ammonium cations.

A wide variety of anions can be used, and the choise depends in part on whether or not an amplifier is used which requires that the element be free of anions of acids having pKa values greater than about 3.5. Otherwise, the choice of anions is significant only to the extent that it determines whether or not the complex is thermally stable when heated to the temperature at which the composition or element is processed. As used herein, "thermally unstable" means that the complex decomposes at the temperature in question sufficiently to release enough ligands to start the intended reaction of the image precursor composition, as described herein. If a thermally unstable complex is used with the image-forming material alone as the image precursor composition, the complex is preferably unstable only at temperatures greater than about 100°C. If a thermally stable complex is to be used with a destabilizer material, the complex is preferably stable at temperatures at least as high as 130°C.

The anions which tend to render the complex thermally unstable include those that decompose readily to a radical, such as trichloroacetate; those forming unstable heavy metal salts, such as azido; and those which are themselves reducing agents, such as 2,5-dihydroxy-benzoate; N,N-dimethyl-dithiocarbamate; and 1-phenyl-tetrazolyl-5-thiolate.

Representative examples of complexes containing ligands which are reported as being thermally unstable above 100°C are listed below:



$$[\mathrm{Co(III)}\ (\mathrm{NH_2NH}\text{-}\overset{\overset{S}{\|}}{\mathrm{C}}\text{-}\mathrm{NH_2})]^{3+}X_n$$

$$[\mathrm{Co(III)}\ (\mathrm{NH_3})_3\ (\mathrm{N_3})_3]$$

$$[\mathrm{Co(III)}\ (\mathrm{NH_3})_5\ (\mathrm{C_2O_4})]^{1+}X_n$$

$$[\mathrm{Co(III)}\ (\mathrm{NH_3})_4\ (\mathrm{C_2O_4})]^{1+}X_n$$

$$[\mathrm{Co(III)}\ (\mathrm{NH_3})_2\ (\mathrm{C_2O_4})_2]^{1-}X_n$$

$[Co(III)\ (NH_3)_3\ (H_2O)\ (C_2O_4)]^{1+}X_n$

$[Co(III)\ (NH_3)_4\ (NO_2)\ (N_2H_4)]^{2+}X_n$

$[Co(III)\ (NH_3)_3\ (H_2O)_3]^{3+}X_n$

$[Co(III)\ (NH_3)_3\ Cl_3]$

wherein X is a suitable anion and n is 0 to 3 and represents the number of anions necessary to satisfy the charge neutralization rule.

Except for the special condition of thermal instability noted above, any anion can be selected if an anion is necessary for charge neutralization, provided the anion is compatible. As used herein, anions are considered "compatible" if they do not spontaneously cause a reduction of cobalt(III) complex at room temperature. As noted, a complex does not require anions if it is already neutral.

The following Table II is a partial list of particularly preferred cobalt(III) complex within the scope of the invention. The suffix (U) designates those which are thermally unstable above about 100°C.

TABLE II -- COBALT(III) COMPLEXES

hexa-ammine cobalt(III) benzilate
hexa-ammine cobalt(III) thiocyanate
hexa-ammine cobalt(III) trifluoroacetate
chloropenta-ammine cobalt(III) perchlorate
bromopenta-ammine cobalt(III) perchlorate
aquopenta-ammine cobalt(III) perchlorate
bis(methylamine) tetra-ammine cobalt(III) hexafluorophosphate
bis(dimethylglyoxime)bispyridine cobalt(III)trichloroacetate (U)
bis(dimethylglyoxime)ethylaquo cobalt(III)

cobalt(III) acetylacetonate

tris(2,2'-bipyridyl)cobalt(III) perchlorate

aquopenta(methylamine) cobalt(III) nitrate (U)

chloropenta(ethylamine) cobalt(III) perfluorobutyrate (U)

trinitrotris-ammine cobalt(III)

trinitrotris(methylamine) cobalt(III) (U)

μ-superoxodeca-ammine dicobalt(III) perchlorate (U)

penta-ammine carbonato cobalt(III) perchlorate

tris(glycinato) cobalt(III)

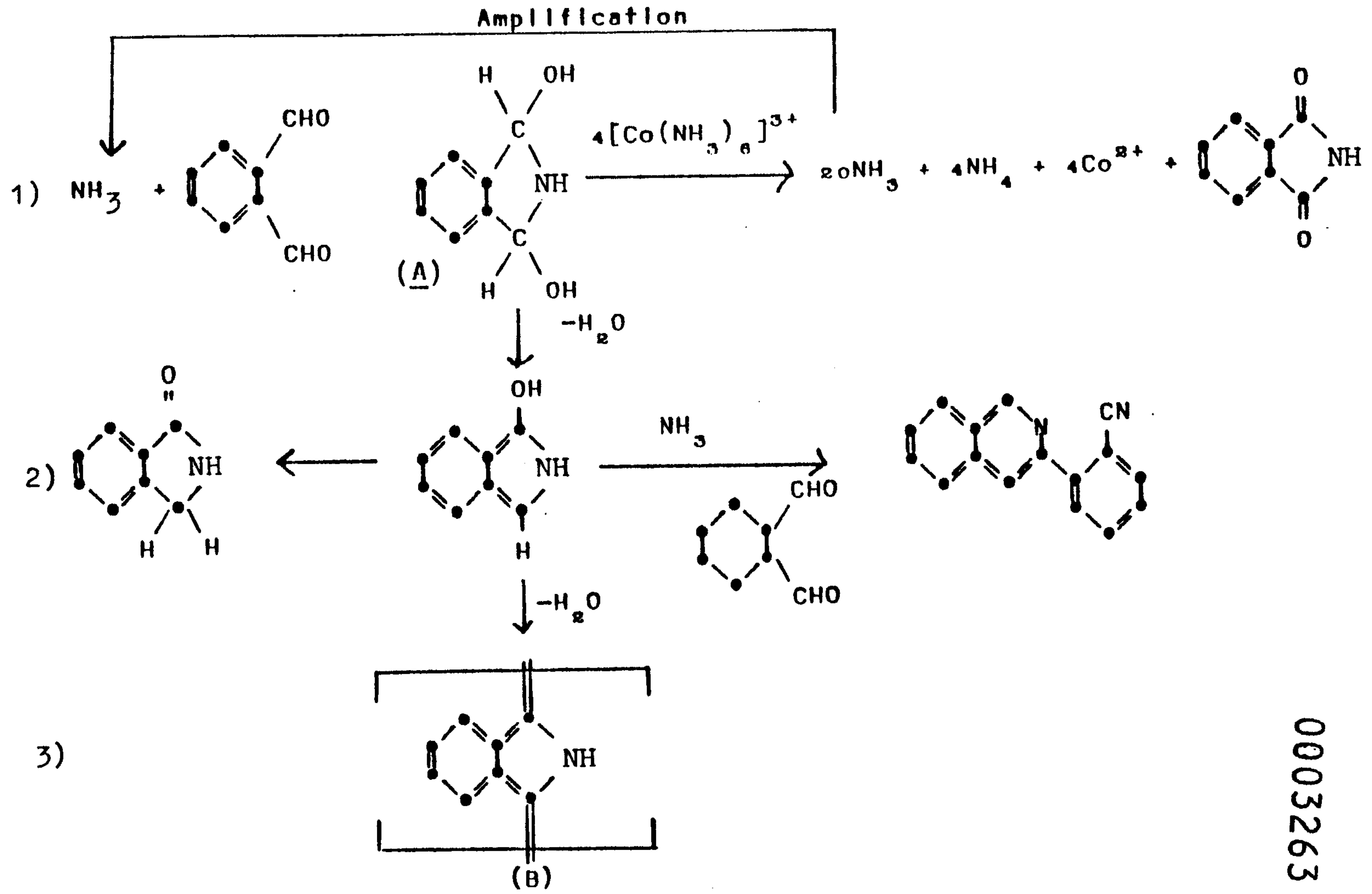
The image-forming material of the image precursor composition can comprise compounds or compositions in addition to the cobalt(III) complex and destabilizer material, if any, or it can be the same compound as is used as a destabilizer material. It can be a dye-forming material, or a dye which is bleachable. Examples of dye-forming materials which also comprise destabilizer materials used to interact with the cobalt(III) complex, as discussed hereinafter, include 4-methoxynaphthol, which forms a blue dye when oxidized, and protonated diamine destabilizer material which when associated with a conventional color coupler will form a dye when it is oxidized by the reduction of the cobalt(III) complex. Examples of image-forming materials used in addition to a destabilizer material include phthalaldehyde, also used as an amplifier; an ammonia-bleachable or color-alterable dye (cyanine dyes, styryl dyes, rhodamine dyes, azo dyes, and pyrylium dyes); a dye-precursor such as ninhydrin; or a diazo-coupler system. Details of these examples are set forth in Research Disclosure, Volume 126, October 1974, Publication No. 12617, Part III, noted above. Still another alternative is to admix with the cobalt(III) complex, chelating compounds which will react with cobalt(II) to form a dye.

Ammonia-bleachable image-forming materials will,of course, produce an absence of dye in the exposed areas. As will be readily apparent, ammonia-bleachable, image-forming materials and color-alterable image-forming materials, when incorporated into an element, preferably are used in a separate adjacent layer that is associated with the photo-inhibitor layer after the latter is exposed.

As noted above, the image precursor composition includes destabilizer materials in those instances wherein the cobalt(III) complex is thermally stable. As is implied by the term, destabilizer materials are those which render the otherwise thermally stable cobalt(III) complex susceptible to release of the ligands when appropriately exposed. The exact mechanism by which these destabilizer materials cause the release of the ligands from the cobalt complex is not understood in most instances, other than that such release does occur and cobalt(II) is produced, except where inhibited by the photo-inhibitor photoproducts. Because the mechanism of these destabilizer materials is largely uncertain, the subclasses under which various examples fall are uncertain and not necessarily mutually exclusive. To be useful, the destabilizer materials must be compatible with the cobalt(III) complex. Usually, this is not a problem, "compatible destabilizer materials" being used here to mean materials that do not interfere with the complex, such as by precipitating it or by spontaneously reducing it.

Examples of destabilizer materials useful with the complex include organo-metallics such as ferrocene and 1,1-dimethylferrocene, and tricarbonyls such as N,N-dimethylaniline chromium tricarbonyl, as well as organic materials, and may or may not require an amplifier such as phthalaldehyde. For example, destabilizer materials comprising 4-phenyl catechol and quinone photoreductants, hereinafter described, do not require the use of an amplifier compound. Other destabilizer materials will not release the ligands, when appropriately exposed, in amounts sufficient to generate observable dye in the same or an adjacent layer without the presence of an amplifier such as phthalaldehyde. Still other destabilizer materials may release sufficient ligands to cause some dye formation, and at least some of these destabilizer materials can achieve much higher density if an amplifier is included. Therefore, in many of the embodiments of the invention, phthalaldehyde comprises part of the image precursor composition, for preferred results, whether or not it actually is required to produce observable results.

The behavior of phthalaldehyde in an image precursor composition appears to involve, in the preferred embodiments, the formation with ammonia of an adduct which is a reducing agent (see structure A in equation 1 below). The adduct itself causes reduction of remaining cobalt(III) complex and releases more ligands. Such release produces an internal gain.


Amplification
1) NH3 +
CHO
CHO
H
OH
C
NH
C
H
OH
(A)
4[Co(NH3)6]3+
20NH3 + 4NH4 + 4Co2+ +
O
NH
O
-H2O
2)
O
NH
H
H
OH
NH
H
NH3
CHO
CHO
N
CN
-H2O
3)
NH
(B)

The initial NH_3 comes from the cobalt(III) complex on exposure, either because of its own thermal instability, or because of activation by a destabilizer material, by one of several mechanisms described hereafter. Phthalaldehyde also forms a dye imaging material, oligomer (B), in addition to its amplifying function as a reducing agent precursor for cobalt(III). Further explanation can be found in DoMinh et al, "Reactions of Phthalaldehyde with Ammonia and Amines", J. Org. Chem. Vol. 42, Dec. 23, 1977, p. 4217.

Useful destabilizer materials are the following thermally responsive organic materials and equivalents thereof:

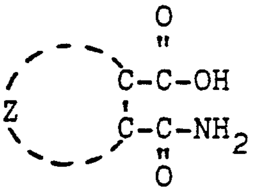
(a) 4-Phenyl catechol.

(b) Sulfonamidophenols and naphthols such as 4-phenylsulfonamido-2,6-dichlorophenol and 4-phenylsulfonamido-2-methyl-1-naphthol.

(c) Other aromatic alcohols such as 4-methoxynaphthol and 1,4-dihydroxynaphthalene.

(d) Pyrazolidones such as 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone and the like.

(e) Acids having the formula:



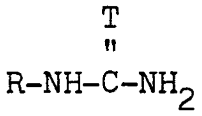
wherein:

Z represents from about 4 to about 8 carbon atoms necessary to complete 1 or more aromatic or cycloalkyl ring such as a benzene, a naphthalene or a cyclohexane ring.

Suitable examples of such acids include, for example, phthalamic acid, 2-carboxy-cyclohexylcarboxyamide and amine salts thereof, including

2-carboxy-cyclohexylcarboxyamide triethanolamine salt, and the like.

(f) Ureas having the formula:



$$R\text{-}NH\text{-}\overset{T}{\overset{\|}{C}}\text{-}NH_2$$

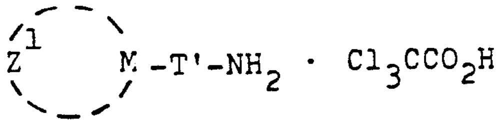
wherein:

T represents S or O; and

R represents a hydrogen atom, an o-hydroxyphenyl group or an o-carbamoylphenyl group.

Suitable compounds include: Urea, thiourea, 2-hydroxyphenyl urea and the like.

(g) Salts having the formula:



wherein:

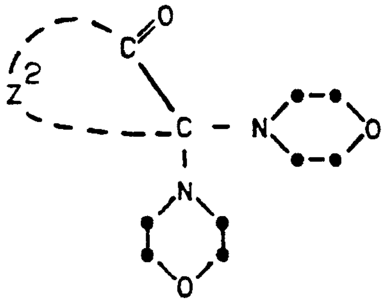
M represents a carbon or nitrogen atom

T' represents a chemical bond or an alkylene group containing from 1 to 3 carbon atoms,

and Z^1 represents from about 4 to about 6 nonmetallic atoms necessary to form an aromatic carbocyclic or heterocyclic ring.

Suitable examples of such salts including 1-(β-aminoethyl)-2-imidazolidinone trichloroacetate, 2-amino-2-thiazoline trichloroacetate, anilinium trichloroacetate and the like.

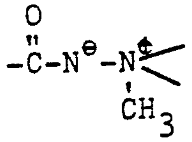
(h) Morpholine precursors having the formula:



wherein:

Z^2 represents from about 4 to about 8 non-metallic atoms required to complete one or more heterocyclic rings; one example of such precursors being 3,3-bis(morphilino)oxindole.

(i) Aminimides in polymeric or simple compound form containing the structure:



including, for example,

(N-methypiperidine) 1-naphthoylimide;

(trialkylamine) cinnamimides;

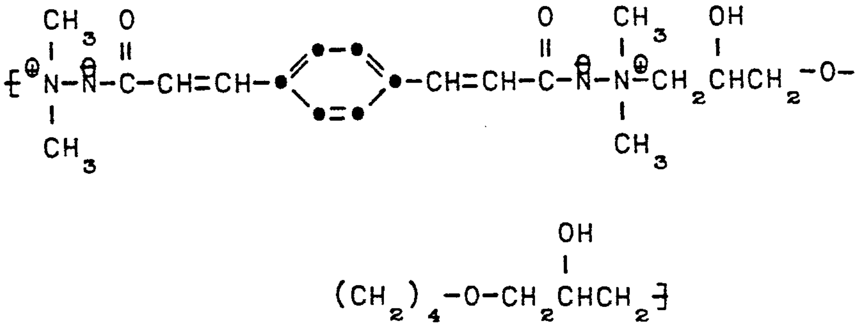
bis(dialkyl-2-hydroxypropylamine) adipimides;

(dialkyl-2-hydroxypropylamine) palmitimides or laurimides;

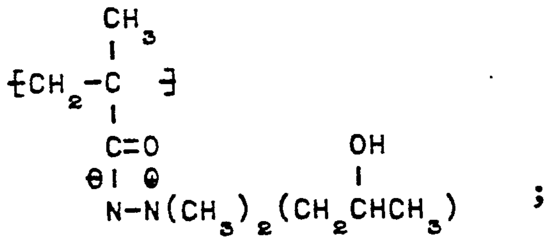
bis(trialkylamine) sebacimides or azelamides;

2,2'-(p-phenylenebis-β-acryloyl)-bis-[1-hydroxypropyl-1,1-dimethylhydrazinium] dihydroxide bis(inner salt); and

polymers having a repeating unit of the formula:



polymers having repeating units with pendant aminimide groups of the formula:

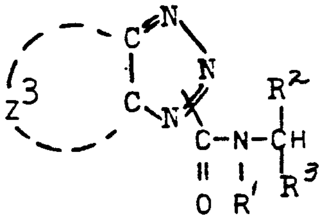


$$\left[CH_2-\underset{\substack{| \\ C=O \\ | \\ {}^{\ominus}N-\overset{\oplus}{N}(CH_3)_2(CH_2\overset{\overset{OH}{|}}{C}HCH_3)}}{\overset{\overset{CH_3}{|}}{C}} \right]$$

;

those described in U.S. Patent No. 4,016,340, issued April 5, 1977, and in Research Disclosure, Vol. 157, May 1977, Publication Nos. 15732, 15733 and 15776; (trialkylamine) arylimides such as (trimethylamine) benzimide and (trimethylamine) naphthimide, including arylimides substituted with hydroxy, lower alkyl or nitro; and trialkylamine aryl sulfonimides such as trimethylamine-p-toluenesulfonimide.

(j) Amido-triazoles having the formula:



wherein:

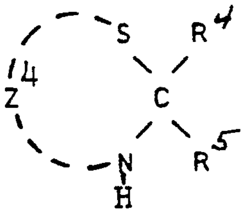
R^1 represents a hydrogen atom or an alkyl group having from 1 to about 5 carbon atoms, such as methyl, ethyl, iso-propyl and the like;

R^2 and R^3 either both represent hydrogen atoms or taken together form an aromatic, a cycloalkyl or a heterocyclic ring; and

Z^3 represents from 4 to 8 nonmetallic atoms necessary to complete one or more substituted or unsubstituted aromatic ring.

Such amido-triazoles including, for example, 5-methyl-1-(2)-N-(phenylcarbamoyl)benzotriazole, 5, 6-dichloro-1-(2)-N-(dimethyl carbamoyl) benzotirazole.

(k) Thiolate precursors having the formula:



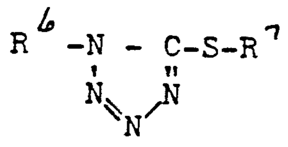
wherein:

R^4 is lower alkyl containing from 1 to 5 carbon atoms, for example, methyl, ethyl, propyl and the like;

R^5 is carbamoyl or an unsubstituted heterocyclic or aromatic ring or a substituted aromatic ring containing from about 6 to 8 nonmetallic ring atoms, for example, 2-pyridyl, phenyl, 4-nitrophenyl and the like; and

Z^4 is the nonmetallic atoms required to complete a substituted or unsubstituted heterocyclic ring containing from about 4 to about 9 atoms. Examples of such precursors include thiazolidines, such as 2-methyl-2-carboxamidothiazolidine, substituted benzothiazolines such as 2-methyl-2-[2-pyridyl]-benzothiazoline and 2-methyl-2-[4-nitrophenyl]-benzothiazoline.

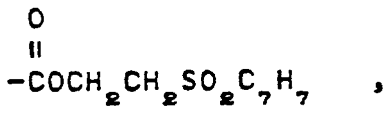
(l) Blocked mercaptotetrazoles having the formula:



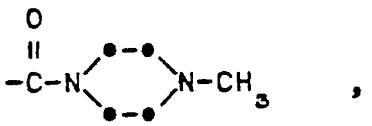
wherein:

R^6 represents a hydrogen atom or a phenyl group and,

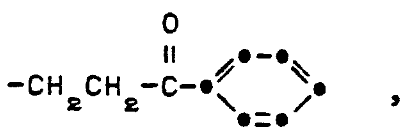
R^7 represents a heat-removable group selected from the group consisting of:



$$-\overset{O}{\overset{\|}{C}}OCH_2CH_2SO_2C_7H_7 ,$$

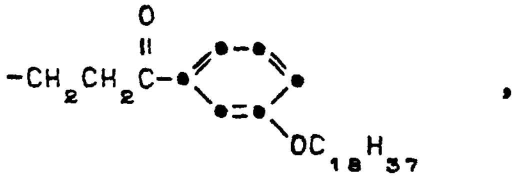


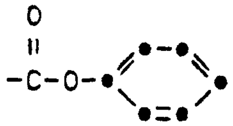
,



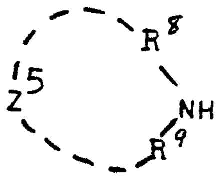
,

$-CH_2CH_2CN$,





(m) Cyclic imides having the structure:

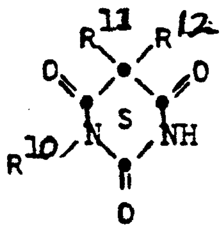


wherein:

Z^5 represents the non-metallic atoms necessary to complete one or more heterocyclic rings, and,

R^8 and R^9 are the same or different and each represents a carbonyl or methylidyne group. Such cyclic imides include, for example, succinimide, hydantoin and substituted hydantoin, phthalimide, oxazolinedione and the like.

(n) Barbiturates such as 5-n-butylbarbituric acid, and those having the structure:



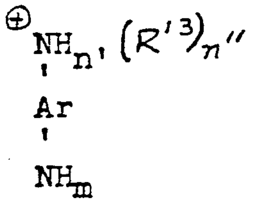
wherein:

R^{10} represents a hydrogen atom or an alkyl group having from 1 to 5 carbon atoms, such as methyl, ethyl, propyl and the like;

R^{11} represents a hydrogen atom or an alkyl group having from 1 to 5 carbon atoms such as methyl, ethyl, propyl, n-butyl and the like; and

R^{12} represents an alkyl group having from 1 to 5 carbon atoms, such as methyl, ethyl, peopyl, and the like, or an aralkyl group such as benzyl; and

(o) Protonated arylene diamines having the structure:



$$\begin{array}{l} \overset{\oplus}{N}H_{n'}(R^{13})_{n''} \\ \mid \\ Ar \\ \mid \\ NH_m \end{array}$$

wherein:

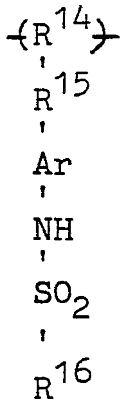
Ar represents a substituted or unsubstituted arylene group containing from 6 to about 20 carbon atoms,

R^{13} represents a hydrogen atom or an alkyl group having 1 to 3 carbon atoms,

m is 2 or 3, and,

n' and n" are each 1, 2 or 3; provided that the sum of n' and n" is 3. Useful protonated p-phenylene diamines include those which are characterized by the loss of the extra proton when heated, creating the unprotonated form which undergoes a redox reaction with the cobalt(III) complex.

(p) Polymers having repeating units with the structure:



$$\begin{array}{c} -(R^{14})- \\ \mid \\ R^{15} \\ \mid \\ Ar \\ \mid \\ NH \\ \mid \\ SO_2 \\ \mid \\ R^{16} \end{array}$$

wherein:

R^{14} represents an organic polymer chain;

R^{15} represents an organic moiety or a carbon-to-carbon bond;

Ar is arylene including substitued arylene, such as phenylene and naphthylene, wherein the substituents, if any, are electron withdrawing groups such as nitro, sulfoalkyl containing from 1 to 5 carbom atoms, halogen such as chloride, fluoride and the like, and substituted alkyl such as trihalo-substituted methyl; and

R^{16} represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms.

All of the preceding destabilizers induce the release of the ligands from the cobalt(III) complex in the presence of heat. As noted, they may or may not require the presence of an amplifier-dye former such as phthalaldehyde. Some of them, such as destabilizer materials (a) through (d), are quite clearly reducing agents per se. Some like destabilizer material (k) are heat-responsive reducing agent precursors. Some, such as destabilizer material (e) and others are heat-responsive amine precursors. They are particularly useful with amine-responsive reducing agents and reducing agent precursors such as phthalaldehyde that form reducing agents in the presence of amines. Some such as destabilizer materials (h), (i) and (j) are believed to be base precursors which form a base in the presence of heat. Destabilizer materials (a) through (d) which are direct reducing agents do not require the presence of an amplifier such as phthalaldehyde, although an amplifier is effective to increase the speed of an element or composition of the invention which incorporates these compounds.

Quinone photoreductants are yet another class of destabilizer materials which are useful in inducing the release of amines from the cobalt complex. The quinones which are particularly useful as photoreductants include ortho- and para-benzoquinones and ortho- and para-naphthoquinones. phenanthrenequinones and anthraquinones. The quinones may be unsubstituted or incorporate any substituent or combination of substituents that does not interfere with the conversion of the quinone to the corresponding reducing agent. A variety of such substituents are known in the art and include, but are not limited to, primary, secondary and tertiary alkyl, alkenyl and alkynyl, aryl, alkoxy, aryloxy, alkoxyalkyl, acyloxyalkyl, aryloxyalkyl, aroyloxyalkyl, aryloxyalkoxy, alkylcarbonyl, carboxy, primary and secondary amino, aminoalkyl, amidoalkyl, anilino, piperidino, pyrrolidino, morpholino, nitro, halide and other similar substituents. Aryl substituents are preferably phenyl substituents. Alkyl, alkenyl and alkynyl substituents, whether present as sole substituents or in combination with other atoms, typically contain 20 or fewer (preferably 6 or fewer) carbon atoms.

A preferred class of photoreductants are internal hydrogen source quinones; that is, quinones incorporating labile hydrogen atoms. These quinones are more easily photo-reduced than quinones which do not incorporate labile hydrogen atoms.

Particularly preferred internal hydrogen source quinones are 5,8-dihydro-1,4-naphthoquinones having at least one hydrogen atom in each of the 5- and 8-ring positions. Other preferred incorporated hydrogen source quinones are those which have a hydrogen atom bonded to a carbon atom to which is also bonded the oxygen atom of an oxy substituent or a nitrogen atom of an amine substituent with the further provision that the carbon-to-hydrogen bond is the third or fourth bond removed from at least one quinone carbonyl doubled bond. As employed in the discussion of photoreductants herein, the term "amine substituent" is inclusive of amide and imine substituents.

Further details and a list of useful quinone photoreductants of the type described above are set forth in Research Disclosure, Volume 126, October 1974, Publication No. 12617, published by Industrial Opportunities Limited, Homewell, Havant Hampshire PO91EF, United Kingdom, the contents of which are hereby expressly incorporated by reference. Still others which can be used include 2-isopropoxy-3-chloro-1,4-naphthoquinone and 2-isopropoxy-1,4-anthraquinone.

As noted above, photoreductants do not require the use of an amplifier, but such a use gives improved results.

It will be appreciated from the foregoing that, unlike the other reducing agent precursors or other destabilizer materials described heretofore, the quinone photoreductants rely upon a light exposure between about 300 nm and about 700 nm to form the reducing agent which reduces the cobalt(III) complex. It is to be noted that thermal irradiation is not needed, after the light exposure, to cause the redox reaction to take place. However, an additional thermal exposure can be used to drive the reaction to completion. Furthermore, heat is desirable to insure the formation of dye B described above. The activity of some of the above described destabilizers, particularly those that respond to thermal radiation, can be enhanced by the addition of a dodecanamide.

Photoinhibitor

Photoinhibitors which are sensitive to radiation longer than 300 nm are selected because the plastic film supports for the imaging elements and the optical glass in the exposing system absorb radiation shorter than 300 nm. However, photoinhibitors which are sensitive only to radiation shorter than 300 nm are useful in conjunction with spectral sensitizers. Such UV-sensitive photoinhibitors include carbon tetrabromide, 2-tribromomethyl sulfonylbenzothiazole, 2-bromo-2-tosylacetamide, 2,2-dibromo-2-phenyl-sulfonylacetamide, β-tribromoethanol and 2-bromo-2-nitro-1,3-trimethylene glycol dibenzoate. Useful spectral sensitizers include rhodamine, carbocyanine and cyanine dyes, Eosin and Erythrosin, triphenylmethane dyes, thiazine dyes, anthroquinonoid dyes and styryl dyes. Specific examples of such sensitizers are disclosed in Yamada et al U.S. Patent No. 3,503,745.

Preferred embodiments are those in which the photoinhibitor comprises a composition free of accompanying spectral sensitizers. Highly useful examples of such photoinhibitors are photolytic acid generators, although it is not known whether all photolytic acid generators will function as photoinhibitors. O-nitrobenzaldehyde is a known photolytic acid generator which is not useful because it complexes with cobalt, and is therefore incompatible in the composition of the invention. Therefore, only those photolytic acid generators are useful which are capable of inhibiting the release of amines without interfering with the desired reaction in some other way.

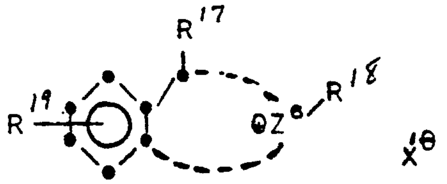
Any photoinhibitor having the desired property of inhibiting the release of amines in response to an exposure, can be utilized. Where the mixture of image precursor composition and photoinhibitor is intended to be used as a dry coating composition, it is preferable that the photoinhibitor be capable of being coated without extensive volatilization. Where a photoinhibitor is to be used with a photoreductant, each of the two photoresponsive compounds are selected so that their wavelengths of maximum absorption do not overlap appreciably.

Examples of useful photoinhibitor compounds are photolytic acid generators having an inherent sensitivity to radiation of a wavelength longer than about 300 nm., including the following materials as well as equivalents thereof:

(a) heterocyclic compounds containing at least one trihalogenated methyl group, preferably those with a chromophore substituent, such chromophores being any unsaturated substituent which imparts color to the compound, for example, those disclosed in U.S. Patent No. 3,987,037;

(b) o-nitroacetanilides;

(c) anthranilium salts such as those having the structure:



wherein:

R^{17} represents a hydrogen atom, a phenyl group or an alkyl group containing from 1 to about 4 carbon atoms, such as methyl, ethyl, isopropyl and the like;

R^{18} represents an alkyl group containing from 1 to about 4 carbon atoms, such as methyl, ethyl, isopropyl and the like, or a 1-adamantyl group;

R^{19} represents a hydrogen or a halogen atom such as chloride, bromide or the like;

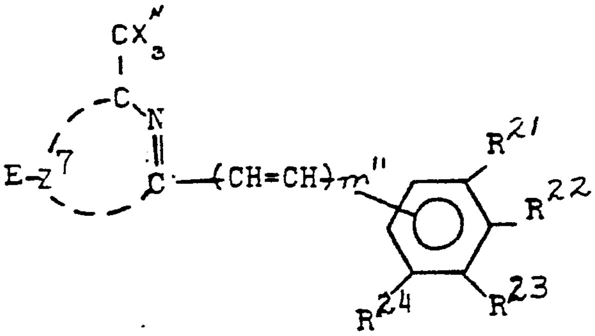
Z^6 represents a $=\underset{|}{\overset{\oplus}{N}}-O-$, $=\underset{|}{\overset{\oplus}{N}}-S-$, or $=\underset{|}{\overset{\oplus}{N}}-\underset{R^{20}}{\underset{|}{N}}-$ group, and

R^{20} represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms; and

$X^{\ominus}$ is a suitable anion. Useful examples include N-methyl-3-phenyl-2,1-benzisoxazolium perchlorate and N-methyl-3-phenyl-2,1-benzisoxazolium fluorosulfonate; and

(d) other halogenated organic compounds such as idoform and the like.

Highly preferred class (a) photoinhibitors are those having the formula:



wherein:

E represents a hydrogen atom, a methyl or trihalomethyl group;

R^{21} represents a hydrogen atom or an alkoxy group having from 1 to 5 carbon atoms, such as methoxy, ethoxy and the like;

R^{22} represents a hydrogen or a halogen atom such as chloride, fluoride and the like, a nitro group or an alkyl, dialkylamino, or alkoxy group containing from 1 to 5 carbon atoms in the alkyl portion such as methyl, ethyl, isopropyl and the like;

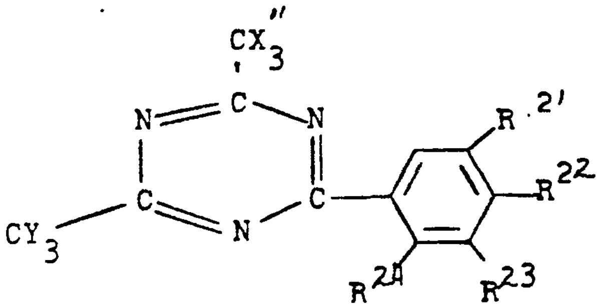
R^{23} represents a hydrogen atom or an alkoxy group having from 1 to 5 carbon atoms, or together with R^{24} comprises the non-metallic atoms necessary to complete an aromatic ring;

R^{24} represents a hydrogen atom or together with R^{23} comprises the non-metallic atoms necessary to complete an aromatic ring;

Z^7 represents the non-metallic atoms necessary to complete one or more substituted or unsubstituted heterocyclic rings containing from 6 to 10 atoms, such as S-triazine, quinoline, quinoxaline, pyrazine, pyrimidine, and the like.

m" is 0, 1 or 2; and

X" represents a halogen atom such as chloride, bromide, and the like. Particularly useful examples include S-triazines having the formula:

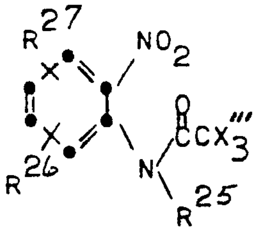


wherein:

X", R^{21}, R^{22}, R^{23}, and R^{24} are as defined above, and

Y is the same or different from X" and is selected from the group consisting of halogen and hydrogen, at least one of X" and Y being halogen.

Class (b) photoinhibitors are highly preferred which have the formula:



wherein:

R^{25} represents an alkyl group having from 1 to 3 carbon atoms, an aralkyl group having from 7 to 8 carbon atoms, such as benzyl, phenethyl and the like, or when taken together with R^{26}, the atoms necessary to complete a fused heterocyclic ring such as indole and the like;

R^{26} represents a halogen atom such as chlorine, bromine and the like, or together with R^{25} it forms a fused heterocyclic ring;

R^{27} represents a hydrogen atom or an alkoxy group having from 1 to 3 carbon atoms, such as methoxy, ethoxy and the like; and

X''' represents a halogen atom such as a chlorine, bromine or flourine atom.

The following Table I is a partial listing of useful photoinhibitors of the invention:

TABLE I -- Photoinhibitors

PI 1 - iodoform
PI 2 - 2,4-bis(trichloromethyl)-6-(p-anisyl)-s-triazine
PI 3 - 2,4-bis(trichloromethyl)-6-(4-methoxystyryl)-s-triazine
PI 4 - 2,4-bis(trichloromethyl)-6-[4-dimethylaminophenyl)-1,3-butadienyl]-s-triazine
PI 5 - 2-tribromomethylquinoline
PI 6 - 2-tribromomethylquinoxaline
PI 7 - 2-tribromomethyl-4-oxo-4H-1-benzopyran
PI 8 - N-methyl-o-nitrotrifluoroacetanilide
PI 9 - N-benzyl-o-nitrotrifluoroacetanilide
PI 10 - N-benzyl-2-nitro-5-methoxy-trifluoroacetanilide
PI 11 - 2,4-bis(trichloromethyl)-6-(1-naphthyl)-s-triazine
PI 12 - 2,4-bis(trichloromethyl)-6-(4-methoxy-1-naphthyl)-s-triazine
PI 13 - 6-bromo-8-nitro-N-trifluoroacetyl-benzo [b] piperidine
PI 14 - N-methyl-3-diazo-4-quinolonium-p-toluenesulfonate
PI 15 - 2,4-bis(trichloromethyl)-6-[p-dimethylamino)-styryl]-s-triazine
PI 16 - N-methyl-3-phenyl-2,1-benzisoxazolium perchlorate
PI 17 - N-methyl-3-phenyl-2,1-benzisoxazolium fluorosulfonate

PI 18 - carbon tetrabromide
PI 19 - β-tribromoethanol
PI 20 - hexabromoethane
PI 21 - ethyl tribromoacetate
PI 22 - tribromoacetamide
PI 23 - tribromomethylbenzene
PI 24 - pentabromoethane
PI 25 - α,α,α-tribromoacetophenone
PI 26 - 3-nitro-α,α,α-tribromoacetophenone
PI 27 - 2,3-bis(tribromomethyl) quinoxaline.

Elements

In the simplest form of the invention an imaging element comprises a support coated with a single layer containing an image precursor composition and a photoinhibitor as described above. Alternatively, the image precursor composition and the photoinhibitor can be divided into a plurality of integral layers. Alternatively the outermost layer can be coated on a separate support and disposed in reactable association subsequently, such as after exposure of the photoinhibitor composition. For example, the image-forming material can be included either as an integral portion of the element of the invention, or it can be subsequently associated therewith as a separate image-recording layer. In those embodiments wherein the image-forming material is an integral part of the element, it can either be admixed with the image precursor (cobalt(III) complex) preferably as a dye-forming material, or it can be in a separate, adjacent layer. In those embodiments wherein it is admixed with the cobalt(III) complex, it is highly preferred that the image-forming material is also an amplifier, such as phthalaldehyde which also functions as a reducing agent precursor.

Yet another alternative is to imbibe the photoinhibitor into the image precursor composition, such as by spraying or otherwise applying a solution of the photoinhibitor to the element already containing the precursor composition.

Preferably the image precursor composition and photoinhibitor are contained in a layer or layers coated onto a support. Any conventional photographic support can be used in the practice of this invention. Typical supports include transparent supports, such as film supports and glass supports, as well as opaque supports, such as metal and photographic paper supports. The support can be either rigid or flexible. The most common photographic supports for most applications are paper and transparent film supports. Suitable exemplary supports are disclosed in Product Licensing Index, Volume 92, December 1971, Publication No. 9232, at page 108, and Research Disclosure, Volume 134, June 1975, Publication No. 13455, published by Industrial Opportunities Limited, Homewell, Havant Hampshire PO91EF, United Kingdom. The support can incorporate one or more subbing layers for the purpose of altering its surface properties so as to enhance the adhesion of the radiation-sensitive coating to the support.

A binder can be included in the radiation-sensitive composition layer. Any binder compatible with cobalt(III) complexes can be used, for example, the binders listed in the aforesaid Publication No. 12617 of Research Disclosure, expecially paragraph I(D), the details of which are expressly incorporated herein by reference. Typical of such binders are acetates, cellulose compounds, vinyl polymers, polyacrylates and polyesters. In those embodiments relying upon phthalaldehyde as the dye-forming material and/or as an amplifier, it is preferred that the binder be selected which will maximize the minimum neutral densities produced during exposure and development. Highly preferred examples of such binders include certain polysulfonamides, for example, poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide) and poly(ethylene-co-hexamethylene-1-methyl-2,4-benzenedisulfonamide), and poly(methacrylonitrile).

The coating solvent selected will, of course, depend upon the makeup of the composition, including the binder if any. Typical preferred solvents which can be used alone or in combination are lower alkanols, such as methanol, ethanol, isopropanol, t-butanol and the like; ketones, such as methylethyl ketone, acetone and the like; water; ethers, such as tetrahydrofuran, and the like; acetonitrile; dimethyl sulfoxide, dimethylformamide and chlorinated hydrocarbon solvents which are not effective as acid generators, because they volatize out of the coating.

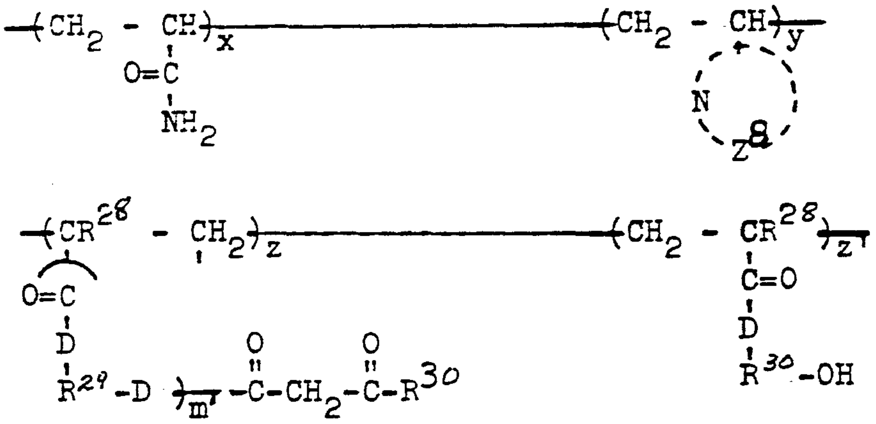
The proportions of the non-binder reactants forming the composition to be coated on the imaging element can vary widely, depending upon which materials are being used.

A useful range of coating coverage of cobalt(III) complex is between about 5 and about 50 mg/dm^2.

Since a cobalt(III) complex is always present, the molar amounts of other components are expressed per mole of complex. Thus, if destabilizer materials are incorporated in the composition in addition to cobalt(III) complex, they can vary widely such as from 0.004 moles of ferrocene to 5 moles of other destabilizers per mole of complex. For example, 5-n-butylbarbituric acid can be present in an amount of between about 0.005 moles and about 5 moles per mole of the complex. The photoinhibitor can be present in an amount from 0.005 to 2.5 moles per mole of cobalt(III) complex. For example, 2,4-bis (trichloromethyl)-6-(p-anisyl)-s-trizaine can be present in those amounts.

Typically, the energy sensitive composition is coated onto the support in a solution by such means as whirler coating, brushing, doctor-blade coating, hopper coating and the like. Thereafter, the solvent is evaporated. Other exemplary coating procedures are set forth in the Product Licensing Index, Volume 92, December 1971, Publication No. 9232, at page 109, published by Industrial Opportunities Limited, Homewell, Havant Hampshire PO91EF, United Kingdom. Addenda such as coating aids and plasticizers can be incorporated into the coating composition.

In certain instances, an overcoat for the radiation-sensitive layer of the element can provide improved handling characteristics, and can help to retain otherwise volatile components. Useful examples include crosslinked gelatin overcoats crosslinked with a crosslinking agent such as hexamethoxy methyl melamine, and polymers having the recurring units:



wherein:

R^{28} represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms;

R^{29} represents an alkylene group having from 1 to 3 carbon atoms;

R^{30} represents an alkyl group having from 1 to 3 carbon atoms;

m' is 1 or 0;

Z^8 represents from 3 to 8 non-metallic atoms necessary to complete one or more saturated or unsaturated heterocyclic ring;

D represents -NH- or -O-; and

x, y, z and z' represent weight percents of the recurring units of the polymer and

$25 \leq x \leq 90$

$10 \leq y \leq 75$

$0 \leq z \leq 10$

$0 \leq z' \leq 10$.

The preferred form of the overcoat is a dual coating first of gelatin crosslinked as noted, and as a final coat, a layer of cellulose acetate having an acetyl content of 19 weight percent and an ash content of 0.04 weight percent.

Further details of the imaging element, and the process of use, can be understood by reference to the drawings. In Fig. 1A, element 10 comprises a support 12 and a layer 14 containing, in admixture, an energy-activatable image precursor composition designated by wavy lines, a photoinhibitor, and an image-forming material such as a dye-forming material. The element is exposed through an image 18 to radiation which activates the photoinhibitor, preferably light, designated by arrows 16. The radiation activates the photoinhibitor in portions 20 and 22 of Fig. 1B to inhibit the image precursor composition, as indicated by the absence of wavy lines, but not in the unexposed portion 24.

Imaging elements containing light-activatable photoreductants are usable even though they also contain light-activatable photoinhibitors because the photoinhibitors are generally activated more rapidly than the photoreductants. Generally the photoinhibitors are activated by shorter wavelength radiation than the photoreductants. Therefore it may be desirable to interpose an optional filter 25, shown in phanton in Fig. 1A, which transmits shorter wavelength radiation 16 that activates the photoinhibitor but does not transmit longer wavelength radiation that activates the photoreductant. For example, if the photoinhibitor is iodoform and the image precursor composition includes a quinone photoreductant, a "Wratten 18A" filter, manufactured by Eastman Kodak Company, can be used. 'Wratten' is a trade mark

Thereafter, as shown in Fig. 1B, the entire element 10 is given a uniform exposure to thermal radiation or light which activates the image precursor composition as indicated by arrows 26. If the image precursor composition contains a photoreductant, the uniform exposure is to light and it is necessary to prevent the photoinhibitor in portion 24 from responding. A preferred method for accomplishing this is the interposition of a suitable filter 28, shown in phanton in Fig. 1B. Such a filter is selected to cut off the light wavelengths which are necessary for the photo-activation of the photoinhibitor, and to transmit the wavelengths, usually longer, useful in activating the photoreductant. For example, if the photoinhibitor is iodoform and the image precursor composition includes a quinone photoreductant, a "Wratten 2A" filter can be used.

The effect of the uniform exposure of the image precursor composition is to generate a dye in portion 24, Fig. 1C, and none in the inhibited portions 20 and 22, thus rendering element 10 positive-working. The dye is schematically shown by the superimposed straight lines.

For example, the presently preferred embodiment features phthalaldehyde as an amplifier and dye-forming material incorporated in layer 14, along with an s-triazine photoinhibitor such as 2,4-bis(trichloromethyl)-6-(p-anisyl)-s-triazine, hexa-ammine cobalt(III) trifluoroacetate complex and either 5-butylbarbituric acid or diphenylhydantoin destabilizer material. Imagewise exposure to light activates the photoinhibitor. A subsequent overall thermal exposure, such as at 150°C for the barbituric acid and 130°C for the hydantoin, causes reduction of the complex, release of ammonia, formation of the adduct of phthalaldehyde further reduction of remaining cobalt (III) complex, release of more ammonia, and amplified dye formation.

Alternatively, the image-forming material of the image precursor composition, which can be, for example, phthalaldehyde as noted above, can be disposed in an adjacent layer 30, shown in phanton in Figs. 1B and 1C. As shown, layer 30 can be positioned as an overlay in contact with element 10 after the imagewise exposure as shown in Fig. 1A, or. alternatively, it can be overcoated onto layer 14 as an integral portion of element 10. In either case the uniform exposure which activates the image precursor composition, arrows 26, will develop the release of NH_3 ligands in portion 24 only. The NH_3 ligands will migrate to portion 32 of the layer 30 as shown by arrows 34, where either a dye is formed or a pre-incorporated dye is bleached or altered in color. Thereafter, layer 30 can be removed from or retained on, element 10.

In Fig. 2A, the same element as in Fig. 1A is given a different treatment to render it negative-working. Specifically, the same identical element, regardless of the image precursor composition used, is rendered negative-working merely by changing the exposure sequence. That is, the process step effectuated by imagewise exposure is now an exposure capable of activating the image precursor composition rather than the photoinhibitor. Parts similar to those previously described bear the same reference numerals to which the distinguishing suffixes "a" are added. For purposes of comparing this negative-working mode to the positive-working mode previously discussed, it is again assumed that the image-forming material of the image precursor composition is a dye-forming material. Thus, element 10a comprises the same coating 14a on support 12a as described before. However, imagewise exposure (arrows 16a) through image 18a must not activate the photoinhibitor. If exposure 16a is thermal, only the image precursor composition is activated. In such instance, image 18a is selected so as not to significantly reradiate in the "dark" areas. If however, exposure 16a is broadband light radiation, it preferably passes through a suitable filter 28a, shown in phantom, selected to prevent transmission of radiation sufficient to activate the photoinhibitor, but to allow transmission of radiation sufficient to activate the image precursor composition. As noted before, a "Wratten 2A" filter is effective if the photoinhibitor is iodoform and the image precursor composition contains a quinone photoreductant destabilizer. In the case where a photoreductant destabilizer material is used, an optional subsequent thermal exposure can be included.. Dye imagewise develops in areas 20a and 22a, Fig. 2B.

The element is then given overall exposure, arrows 26a of Fig. 2B, to radiation which activates the photoinhibitor to prevent background printup. As in the case of the imagewise exposure step of Fig. 1A, it may be desirable in some instances to interpose a suitable filter 25a, shown in phantom, to insure that the exposure 26a does not activate the image precursor composition.

As in the case of the process shown in Figs. 1B and 1C, the negative image can be formed instead in an adjacent layer, not shown, by transfer of ligands thereto from layer 14a.

If the photoinhibitor includes a compound having a response only to radiation of wavelengths shorter than about 300 nm. and a spectral sensitizer, as described above, it is contemplated that the composition and/or element of the invention is one in which the photoinhibitor and the image precursor composition each occupy two separate but adjacent layers 40 and 50, element 10b of Fig. 3. In this manner, the spectral sensitizer will sensitize only the photoinhibitor and not also the cobalt(III) complex or the destabilizer material, so that photoinitiation of the inhibitor will not also act to activate the image precursor composition. If the photoinhibitor does not inherently produce a volatile acid capable of being readily transferred to the layer containing the image precursor composition, for the inhibition step, the photoinhibitor layer can optionally include sodium trifluoroacetate, to produce in the presence of the nonvolatile acid generated by the photoinhibitor, trifluoroacetic acid which is sufficiently volatile.

Examples

Examples 1-3 - Use of Organo-Metallic Destabilizer

Stock solution A was prepared by dissolving 265 mg of the cobalt complex, hexaamminecobalt(III) trifluoroacetate, 535 mg of phthalaldehyde as amplifier and image-former and 30 mg of 2,4-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine as photoinhibitor in 2 g of acetone. To this solution was added 10 g of a 20% solution of the binder poly(ethylene-co-hexamethylene-1-methyl-2,4-benzenedisulfonamide) in 1:1 acetone/methylethylketone.

Solution B was prepared by dissolving 4 mg of the destabilizer ferrocene (dicyclopentadienyl iron) in 6 g of acetone. Solution C was prepared by dissolving 4 mg of the destabilizer 1,1-dimethylferrocene in 6 g of acetone. Solution D was prepared by dissolving 10 mg of the destabilizer N,N-dimethylaniline chromium tricarbonyl in 6 g of acetone.

To 1.0 g of stock solution A was added 0.1g of solution B to form the coating solution for Example 1. This solution was then coated with a 100-micron doctor blade on a subbed poly(ethylene terephthalate) support, dried, and overcoated with a 5% aqueous solution of poly(acrylamido-co-N-vinyl-2-pyrrolidinone-co-2-acetoacetoxyethylmethacrylate using a 50-micron doctor blade, and dried. After drying, the film was exposed through a silver negative for about 8 seconds to the light from a 400 watt medium pressure mercury arc lamp in an IBM Microcopier IID exposing apparatus and dye-developed by heating, face up, for five seconds on a heated block at 160°C. A high density, positive image resulted. Similar results were obtained when solutions C and D were substituted for solution B to make the coating solutions for Examples 2 and 3.

Example 4 - 4-Phenyl Catechol as A Destabilizer Material Without Phthalaldehyde

20 mg of $[Co(NH_3)_6](CF_3CO_2)_3$, 7 mg of the destabilizer, 4-phenyl catechol and 16 mg of iodoform as the photoinhibitor were dissolved in 700 mg of acetone. 1.4 g of a 15 percent solution of cellulose acetate butyrate, as binder, in acetone were added and the resulting solution was coated with a 100 micron doctor blade on a subbed poly(ethylene terephthalate) support. This film was exposed for 8 seconds through a 0.3 log E silver step tablet in a copying apparatus containing a 400-watt medium pressure mercury arc

lamp (commercially available as a Micro Master Diazo T.M. Copier). The exposed film was placed in face-to-face contact with a diazo-coupler recording element as an image forming layer (commercially available from Eastman Kodak Company under the trade name Kodak Diazo Type M) and the sandwich was passed twice through a set of rollers heated to 140°C at a speed of 12.7 cm per minute. A positive bluish image of the step tablet was produced with minimum densities of 0.07 and maximum densities of 0.5, when read using red light.

Examples 5-6 - Use of Sulfonamidophenyls and Naphthols as Destabilizer Materials

The following composition was prepared:

Acetone (solvent)	81.5	g
Poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide (binder)	11.1	g
N,N-bis(2-hydroxyethyl)dodecanamide (destabilizer enhancer)	0.748	g
$[Co(NH_3)_6](CF_3CO_2)_3$	1.73	g
2-4-bis(trichloromethyl)-6-(p-methoxystyryl)-s-triazine (photoinhibitor)	0.0196	g
2,4-bis(trichloromethyl)-6-(p-anisyl)-s-triazine (photoinhibitor)	0.288	g
Phthalaldehyde (amplifier and image-former)	3.46	g
"SF-1066" Surfactant, a dimethyl polyoxyalkylene ether copolymer supplied by General Electric Company (coating aid)	0.92	g

To identical 4.0 g portions of the above solution were added respective 12.0 mg portions of the following sulfonamidophenol destabilizers:

Example 5

4-phenylsulfonamido-2,6-dichlorophenol

Example 6

4-phenylsulfonamido-2-methyl-1-naphthol

The resulting solutions were then coated with a 150-micron doctor blade on subbed poly(ethylene terephthalate) support, dried and then overcoated with a 4.7% aqueous solution of poly(acrylamido-Co-N-vinyl-2 pyrrolidinone-Co-2-acetoacetoxy methacrylate copolymer (50:45:5 by weight) containing 0.05% Surfactant 10G, a nonylphenoxyglycerol coating aid, with a 50-micron doctor blade.

Samples of the dried coatings were then exposed for about two seconds through a 0.15 log E step tablet in an IBM Microcopier IID exposing apparatus. Processing for a 7.3 second contact time at 150-155°C in a Canon Kal-Developer Model 360 VC resulted in positive images for each coating.

Further coating samples were similarly exposed and dye-developed for ten seconds, face up, on a hot block. The neutral D-max obtained as a function of process temperature follows:

Example	Temperature	D-min	D-max
5	145°C	0.03	0.04
5	150°C	0.03	0.08
5	155°C	0.04	0.15
5	160°C	0.04	0.60
5	165°C	0.04	0.72
5	170°C	0.08	2.10
6	145°C	0.08	2.79
6	150°C	0.08	3.14
6	155°C	0.08	3.19
6	160°C	0.23	3.21
6	165°C	0.31	3.28
6	170°C	0.66	3.37

Example 7 - Other Naphthol Destabilizer Materials

A solution was prepared by dissolving 200 mg of $[Co(NH_3)_6](CF_3CO_2)_3$, 400 mg of the amplifier and image-former phthalaldehyde, and 200 mg of

2,4-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine as photoinhibitor in 2 g of acetone. To this solution were added 8 g of a 20% solution of the binder poly(ethylene-co-hexamethylene-1-methyl-2,4-benzenedisulfonamide) in acetone.

In 2 g of this solution was dissolved 1 mg of the destabilizer, 4-methoxynaphthol. This solution was coated with a 100 micron doctor blade on subbed poly(ethylene terephthalate)support, dried, and then overcoated with a 5% aqueous solution of the overcoat polymer of Example 1 using a 50 micron doctor blade. After drying, the film was exposed and dye-developed in the manner described in Example 1, to give a neutral positive image with a D-max of 2.7 and a D-min of 0.08.

<u>Example 8</u> - <u>A Pyrazolidone as a Destabilizer Material</u>

The following composition was prepared:

Acetone (solvent)	15.87	g
Poly(ethylene-co-1,4-cyclohexylenedimethyl-1-methyl-2,4-benzenedisulfonamide) (binder)	77.6	g
N,N-bis(2-hydroxyethyl)dodecanamide (destabilizer enhancer)	0.65	g
$[Co(NH_3)_6](CF_3 \cdot CO_2)_3$	1.73	g
2,4-bis(trichloromethyl-6-(p-methoxystyryl)-s-triazine (photoinbibitor)	0.017	g
2,4-bis(trichloromethyl)-6-(p-anisyl)-s-triazine (photoinhibitor)	0.25	g
Phthalaldehyde (amplifier and image-former)	3.01	g
GE SF-1066 Surfactant (coating aid)	0.80	g

To a 3.8 g portion of this composition was added 6.5 mg of 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone.

The resulting solution was then coated with a 150-micron doctor blade on a subbed poly(ethylene terephthalate) support, and dried. The coating was overcoated with a 5% aqueous solution of the overcoat polymer of Example 1 containing 0.05% Surfactant 10G with a 50-micron doctor blade.

A sample of the dried coating was then exposed for about 16 seconds through a 0.15 log E step tablet to the light from a medium pressure mercury arc lamp in an IBM Microcopier IID exposing apparatus and heat processed for a 5.5-second contact time at 150°C in a Canon Kal-Developer, Model 360 VC. A positive image with neutral D-max of about 2.73 and a brownish D-min of 0.21 was obtained.

Example 9 - Another Pyrazolidone Destabilizer

A solution was prepared by dissolving 200 mg of $[Co(NH_3)_6](CF_3 \cdot CO_2)_3$, 400 mg of phthalaldehyde (amplifier and image-former), and 200 mg of the photoinhibitor 2,4-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine in 2 g cf acetone. To this solution were added 8 g of a 20% solution of the binder poly(ethylene-co-hexamethylene-1-methyl-2,4-benzenedisulfonamide) in acetone.

In 2 g of the above solution was dissolved 1 mg of 4,4-dimethyl-1-phenyl-3-pyrazolidone. This solution was coated with a 4-mil doctor blade on subbed poly(ethylene terephthalate) support, dried, and then overcoated with a 5% aqueous solution of the overcoat polymer of Example 1 using a 50-micron doctor blade. After drying again, the film was exposed through a silver negative for about 8 seconds in an IBM microcopier IID exposing apparatus and heat-processed, face up, for five seconds on a 160°C hot block to give a neutral positive image with a D-max of 3.0 and a D-min of 0.05.

Example 10 - Acids as Destabilizer Materials

An image precursor composition solution was prepared for Example 10 comprising 400 mg of $[Co(NH_3)_6] (CF_3 \cdot CO_2)_3$, 800 mg of phthalaldehyde as amplifier and image-former, 200 mg of N,N-bis(2-hydroxyethyl) dodecanamide as destabilizer enhancer, and 40 mg of 2,4-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine as photoinhibitor in 20 gms of 20% poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide (binder) in acetone.

To two grams of this solution was added 4 mg of phthalamic acid, and the solution was then coated on subbed poly(ethylene terephthalate) with a 100-micron coating knife. A 50-micron overcoat of the overcoat polymer of Example 1 (5% in water) was then applied after drying. The resulting film was exposed for 8 seconds in an IBM Microcopier IID exposing device through a 0.3 log E step tablet and heated for 5 seconds, face up, on a 160°C hot block. A positive neutral image with a D-max/D-min ratio of 2.0/0.06 was produced.

Example 11

Example 10 was repeated except that 4 mg of the destabilizer, 2-carboxycyclohexylamide was used in place of the phthalamic acid. A positive image was produced having D-max/D-min ratio of 2.1/0.06.

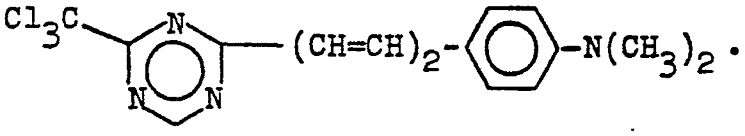
Example 12 - A Urea as a Destabilizer Material

A solution of an image precursor composition was prepared by dissolving 266 mg of $[Co(NH_3)_6](CF_3 \cdot CO_2)_3$ and 534 mg phthalaldehyde as amplifier and image-former in 2 g of acetone and adding to this 10 g of a 20% solution of the binder, poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide) in acetone.

In 2 g of this solution, were dissolved 8 mg of iodoform as photoinhibitor and 5 mg of 1-(2-hydroxyphenyl)urea as destabilizer. This solution was coated with a 100-micron doctor blade and overcoated with a 5% aqueous solution of the overcoat polymer of Example 1 using a 50-micron doctor blade. The film was dried and exposed through a silver negative for 8 seconds on a Microcopier IID and dye-developed by heating, face up, for 5 seconds on a 160°C hot block to produce a neutral positive image with a maximum density of 2.8.

Example 13

Example 12 was repeated except that the photoinhibitor iodoform was replaced with 1 mg of



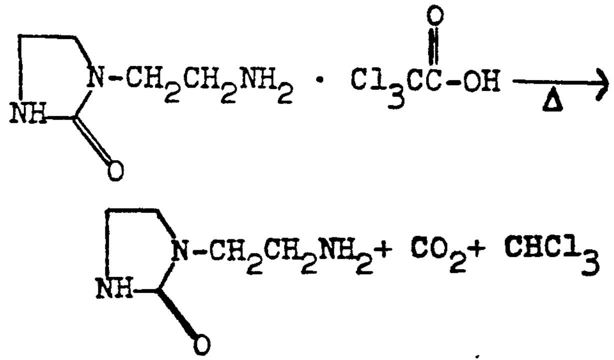
The film was exposed through a silver negative for 7 seconds to a 650-watt incandescent light source (commercially available under the trade name Nashua 120 Multi-Spectrum Copier). When dye-developed by the process described in Example 10, a neutral positive image with a maximum density of 2.3 was produced.

Example 14 - Salts as Destabilizer Materials

In 3.8 g of a 13.6% solution of the binder, poly(ethylene-*co*-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide) in acetone were dissolved 66.4 mg of $[Co(NH_3)_6]$ $(CF_3 \cdot CO_2)_3$, 120 mg of the image-former o-phthalaldehyde; 9.9 mg of the photoinhibitor, 2,4-bis(trichloromethyl)-6-(p-anisyl)-s-Triazine; 26 mg of N,N-bis(2-hydroxyethyl) dodecanamide as destabilizer enhancer; and 12 mg of SF-1066 surfactant (from General Electric). To this solution was added 9.6 mg of 1-β-aminoethyl)-2-imidazolidione trichloroacetate as destabilizer and the resulting solution was coated with a 150-micron doctor blade on subbed poly(ethylene terephthalate) support. This coating was then overcoated with a 4.5% solution of the overcoat polymer of Example 1 in water with 0.06% 10G surfactant coating aid using a 50-micron doctor blade.

The dried coating was exposed for 2 seconds through a 0.15 log E step tablet using a Micro Master Diazo T.M. Copier and dye-developed by heating, face up, in a 150°C Canon Kal-Developer, Model 360 VC for 5.5 seconds. A brownish positive image having a D-max of 0.98 and a D-min of 0.17 to blue light was obtained.

It is believed that the destabilizer underwent the following thermal decomposition to generate an amine:



Examples 15 - 16

In Example 15, Example 14 was repeated except that the destabilizer material comprised 2-amino-2-thiazoline trichloroacetate. Example 16 was a repetition of Example 14 except the destabilizer material was anilinium trichloroacetate. Both of these produced a satisfactory positive image.

Example 17 - Use of a Morpholine Precursor Destabilizer Material

In 78 g of acetone were dissolved 15.9 g of the binder, poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide); 650 mg of N,N-bis(2-hydroxyethyl) dodecanamide as destabilizer enhancer; 1.66 g of $[Co(NH_3)_6]$ $(CF_3\cdot CO_2)_3$; 17 mg of 2,4-bis (trichloromethyl)-6-(p-methoxystyryl)-s-triazine as photoinhibitor; 250 mg of the photoinhibitor, 2,4-bis(trichloromethyl)-6-(p-anisyl)-s-triazine; 3.0 g of o-phthalaldehyde as amplifier and image-former; and 800 mg of SF-1066 surfactant (General Electric). To 3.8 g of this solution were added 3.2 mg of the destabilizer, 3,3-bis(morphilino)oxindole. The resulting solution was coated with a 150-micron doctor blade on subbed poly(ethylene terephthalate) support, dried, and subsequently overcoated with a 4.5% solution of the overcoat polymer of Example 1 in water with 0.05% 10G surfactant coating aid using a 50-micron doctor blade.

The dried coating was exposed for 8 seconds through a 0.15 log E silver step tablet using the Micro Master Diazo T.M. Copier and dye developed by heating, face up, on a 150°C hot block. A neutral positive image having a D-max of 2.56 and D-min of 0.06 was obtained.

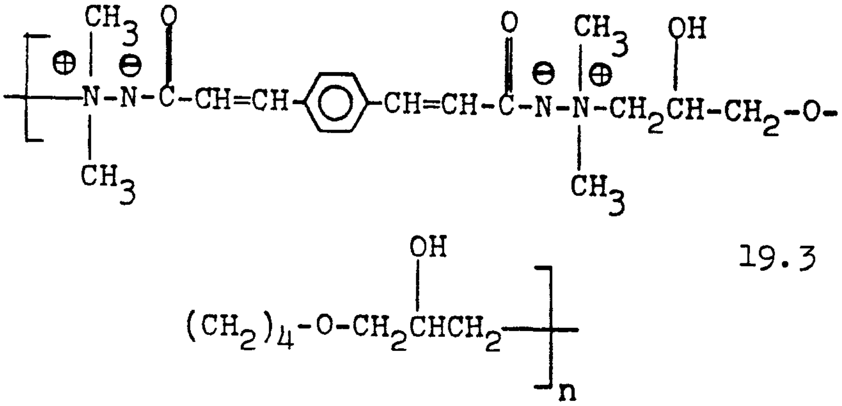
Examples 18-27 - Aminimides as Destabilizer Materials

A solution of an image precursor composition was prepared as follows:

12.9	g	Poly(ethylene-*co*-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide (binder)
81.6	g	Acetone (solvent)
0.30	g	General Electric SF-1066 Surfactant
0.65	g	Recrystallized N,N-bis(2-hydroxyethyl)-dodecanamide (destabilizer enhancer)
3.01	g	o-phthalaldehyde (amplifier and image-former)
0.25	g	2,4-bis(trichloromethyl)-6-p-anisyl-s-triazine (photoinhibitor)
0.017	g	2,4-bis(trichloromethyl)-6-[p-methoxystyryl]-s-triazine (photoinhibitor)
1.66	g	$[Co(NH_3)_6](CF_3 \cdot CO_2)_3$

To 10.0 g samples of the preceding solution were added the aminimides of Table III. A separate control was prepared using the destabilizer, 5,5-diphenylhydantoin in place of the aminimide.

TABLE III - Aminimides

Example	Aminimide	Amount (mg)
Control	None (5,5-diphenylhydantoin)	20.8
18	(trimethylamine)cinnamimide	16.8
19	bis(diemthyl-2-hydroxypropyl-amine) adipimide	14.3
20		19.3
21	(Dimethyl-2-hydroxypropylamine) palmitimide	29.3
22	(Dimethyl-2-hydroxypropylamine) laurimide	24.8
23	(Dimethyl-2-hydroxypropylamine) myristimide	27.0
24	bis(trimethylamine)sebacimide	13.0
25	Poly[(N,N-dimethyl-2-hydroxy-propylamine)methacrylimide)]	15.3
26	Poly[(trimethylamine)methacrylimide)]	11.8
27	bis(trimethylamine)azelaimide	13.8

After mixing the resulting solutions, handcoatings were made utilizing a 150-micron wet laydown upon a transparent, subbed, poly(ethylene terephthalate(support). The coatings were appropriately dried and then overcoated with a 50-micron wet laydown of 4.5% aqueous solution of the overcoat polymer of Example 1 containing 0.6% 10G surfactant and dried. Coating samples were sensitometrically exposed in an IBM Microcopier IID exposing unit and dye-developed by heating, face up, for 5 to 10 seconds in a 150°C Canon Kalfile processor. All samples and the control developed black dye in the non-image areas and remained clear in the exposed areas, and thus were positive-working. Example 18 was 1.2 log E slower and 0.3 higher in neutral D-max than the control which exhibited a D-max of 2.6.

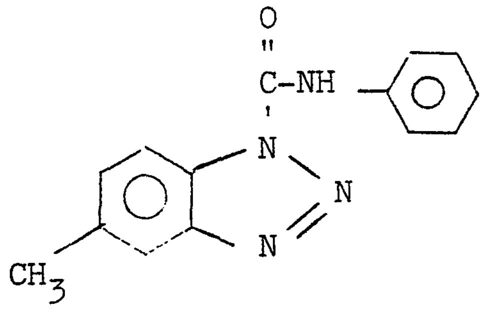
It was further found that Example 18 gave a substantial improvement over the control in processing, or development, latitude.

Examples 28-31 - Use of Triazole Destabilizer Materials

In 81.5 g of acetone were dissolved 11.1 g of poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide) (binder), 748 mg of N,N-bis(2-hydroxyethyl)dodecanamide (destabilizer enhancer), 1.73 g of $[Co(NH_3)_6](CF_3\cdot CO_2)_3$, 19.6 mg of 2,4-bis(trichloromethyl)-6-(p-methoxystyryl)-s-triazine (photoinhibitor), 288 mg of 2,4-bis(trichloromethyl)-6-(p-anisyl)-s-triazine (photoinhibitor), 3.46 g of o-phthalaldehyde (image-former) and 920 mg of SF-1066 surfactant (obtained from General Electric).

Example 28

To 4.0 g of this solution were added 9.5 mg of the destabilizer 5-methyl-1(2)-N-(anilinocarbonyl) benzotriazole, having the formula:



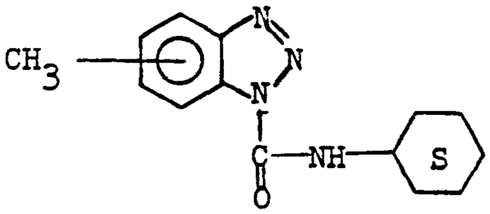
the anilinocarbonyl group being a thermally releasable blocking group.

The resulting solution was coated with a 150-micron doctor blade on a subbed poly(ethylene terephthalate) support, dried and then overcoated with a 4.7% solution of the overcoat polymer of Example 1 in water containing 0.05% 10G surfactant coating aid, using a 50-micron doctor blade.

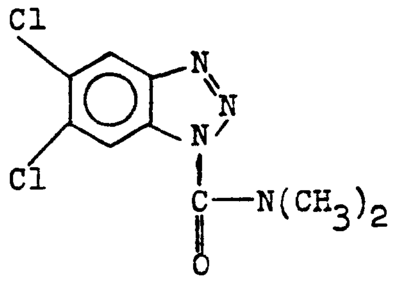
The dried coating was then exposed for 2 seconds through a 0.15 log E silver step tablet using a Micro Master Diazo T.M. Copier and dye-developed by heating, face up, on a 160°C hot block. A brownish, positive image having a D-max of 1.30 and D-min of 0.58 to blue light was obtained.

Examples 29-31 were the same as Example 28, with approximately the same results, except that the destabilizer materials were:

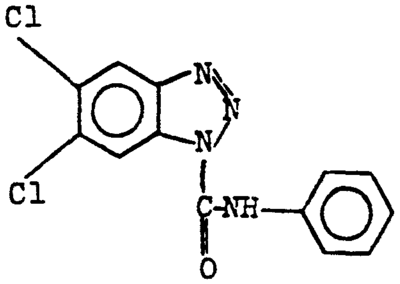
Example 29



Example 30



Example 31



Example 32 - Thiolate Precursor Destabilizer Material

8.2 mg of 2-methyl-2-[2-pyridyl]-5-chlorobenzothiazoline (destabilizer); 24.7 mg of N,N-bis-(2-hydroxyethyl)-dodecanamide (destabilizer enhancer); 63.1 mg of $[Co(NH_3)_6](CF_3.CO_2)_3$; 0.7 mg of

2,4-bis(trichloromethyl)-6-[p-methoxystyryl]-s-triazine (photoinhibitor); 9.5 mg of 2,4-bis(tri-chloromethyl)-6-[p-anisyl]-s-triazine (photoinhibitor); 114.4 mg of phthalaldehyde (image-former); and 30.4 mg of SF-1066 surfactant were added to 3.6 g of 17% poly(ethylene-*co*-1,4-cyclohexylene-dimethylene-1-methyl-2,4-benzenedisulfonamide) (binder) in acetone. This solution was coated with a 150-micron doctor blade on subbed poly(ethylene terephthalate) support and dried. This image precursor composition layer was then overcoated with a 5% solution of poly(acryl-amide-co-N-vinyl-2-pyrollidone-co-2-acetoacetoxy-ethylmethacrylate) in water with 0.05% surfactant 10G coating aid using a 50-micron doctor blade and dried. A sample of the film coating was exposed through a silver negative for 8 seconds on an IBM Microcopier IID device and dye-developed by heating in a 155°C Canon Kal-developer, model 360 VC for 5.5 seconds. A black, positive image with a neutral D-min of 0.12 and a D-max of 3.2 was produced.

Examples 33 - 35

Example 32 was repeated except that the destabilizer material was, respectively, 2-methyl-2-carboxamidothiazolidine, 2-methyl-2-[2-pyridyl]benzo-thiazoline, and 2-methyl-2-[4-nitrophenyl]benzothia-zoline. When tested at equivalent chemical levels and similar exposure and processing conditions, these materials also yielded satisfactory results.

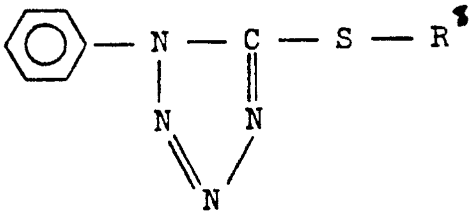
Example 36 - Use of a Blocked Mercaptotetrazole as a Destabilizer Material

0.037 moles of 1-phenyl-[3-(4-toluene-sulfonyl)propionyloxy]-5 mercaptotetrazole(See Table IV), 29.9 mg of N,N-bis(2-hydroxyethyl) dodecanamide as destabilizer enhancer, 69.0 mg of $[\mathrm{Co(NH_3)_6}]\ \mathrm{CF_3 \cdot CO_2)_3}$, 0.8 mg of the photoinhibitor 2,4-bis(trichloro-methyl)-6-[p-methoxystyryl]-s-triazine, 11.5 mg of the photoinhibitor 2,4-bis(trichloromethyl)-6-[p-anisyl]-s-triazine, 138.5 mg of phthalaldehyde as amplifier and dye-former, and 36.8 mg of SF-1066 surfactant were added to 3.7 g of 12% poly(ethylene-*co*-1,4-cyclohexylene-dimethylene-1-methyl-2,4-benzenedisulfonamide)(binder) in acetone. This solution was coated with a 150-micron doctor blade on a subbed poly(ethylene terephthalate) support and dried. This basecoat was then overcoated with a 4.7% solution of the overcoat polymer of Example 1 in water with a 0.05% surfactant 10G coating aid using a 50-micron doctor blade and dried. A sample of the film coating was exposed through a silver negative for 2 seconds on an IBM Microcopier IID device and dye-developed by heating on a 170°C hot block for 10 seconds, support side down. A positive image was produced with a D-min of 0.19 and a D-max of 0.90.

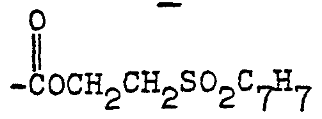
Examples 37 - 41

Example 36 was repeated except that equivalent amounts of the blocked mercaptotetrazoles listed in Table IV were substituted for that of Example 36. When similarly exposed and processed, the elements of Examples 37-41 produced comparable results.

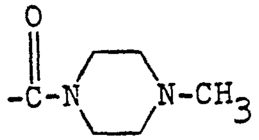
TABLE IV - Mercaptotetrazoles



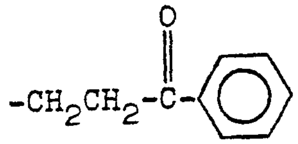
<u>Example 36</u> $\underline{R}^{9}$


$-\overset{O}{\overset{\|}{C}}OCH_2CH_2SO_2C_7H_7$

<u>Example 37</u>

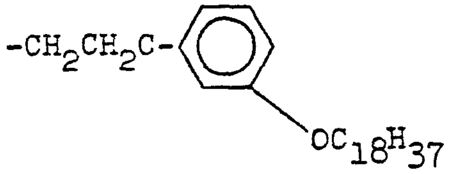


<u>Example 38</u>

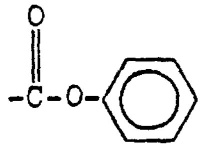


<u>Example 39</u> $-CH_2CH_2CN$

<u>Example 40</u>



<u>Example 41</u>



<u>Example 42</u> - <u>Use of a Cyclic Imide as the Destabilizer Material</u>

In 2 g of a 20% solution of poly(ethylene-<u>co</u>-1,4-cyclohexylene-dimethylene-1-methyl-2,4-benzenedisulfonamide) (binder) in 95:5 acetone:H_2O were dissolved 40 mg of $[Co(NH_3)_6](CF_3\cdot CO_2)_3$, 48 mg o-phthalaldehyde (amplifier and image-former), 5 mg of succinimide as destabilizer, and 30 mg of iodoform as photoinhibitor. This solution was coated with a 100-micron doctor blade on a subbed poly(ethylene terephthalate) support. This film was exposed through a silver negative for 0.5 seconds on an IBM microcopier IID device and dye-developed by heating for 10 seconds face-up on a 145°C hot block. A black positive image with a neutral density D-max of 1.4 and a D-min of 0.04 was formed.

Example 43

In 10 gms of a 20% solution of the binder, poly(ethylene-co-1,4-cyclohexylene-dimethylene-1-methyl-2,4-benzenedisulfonamide) in acetone were dissolved 200 mg of $[Co(NH_3)_6]$ $(CF_3 \cdot CO_2)_3$, 400 mg phthalaldehyde (image-former), 25 mg 5,5-diphenylhydantoin (destabilizer) and 20 mg 2,6-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine (photoinhibitor). This solution was coated as in Example 42 and aged for one week to allow sensitometry to stabilize. A sample was exposed through a silver negative for four seconds in the IBM Micropier IID device. Ten seconds dye-development by heating on a 140°C hot block produced a black positive image with a D-max of 2.05 and a D-min of 0.05.

Example 44 - Use of a Barbiturate as a Destabilizer Material

A stock solution was prepared by adding 798 mg of $[Co(NH_3)_6]$ $(CF_3 \cdot CO_2)_3$, 1.6 g of phthalaldehyde image-former, and 60 mg of 2,4-bis(trichloromethyl)-6-p-anisyl-s-triazine photoinhibitor to 30 g of 20% solution of poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide) in acetone.

In 1 g of acetone were dissolved 3 mg of 5-n-butylbarbituric acid. 0.1 g of this solution was then added to 1.0 g of the stock solution, coated, overcoated, exposed, and processed as in Example 7 to give a positive image with a D-max of 3.0 and a D-min of 0.1.

Example 45 - Use of a Quinone Photoreductant as a Destabilizer Material

75 mg of $[Co(NH_3)_6]$ $(CF_3 \cdot CO_2)_3$ and 60 mg of 2-(N-ethyl-N-benzylamino)-3-chloro-1,4-naphthoquinone, a photoreductant, were dissolved in 1.7 g of 2-methoxyethanol. To this solution, 3.4 g of a 15

percent solution of cellulose acetate butyrate in acetone was added to form a stock solution.

A quantity of 40 mg of iodoform was dissolved in 1 g of chloroform. To this solution, a quantity of 2 g of the above stock solution was added. The resulting solution was coated with a 100-micron doctor blade on a subbed poly(ethylene terephthalate) support.

A sample of this film was exposed for 2 minutes through a silver test object on a U.V. exposing device, available commercially as a Canon Kalfile Printer 340VC. This exposure imagewise generated inhibitor. The film was then given an overall 30-second exposure to tungsten light using a Hashua 120 Multi-Spectrum Copier to photogenerate reductant. The exposed film was placed in face-to-face contact with a diazo recording element (commercially available under the trade name Kodak Diazo Type M) and the sandwich was passed twice at 76.2 cm per minute through a set of rollers heated to a temperature of 100°C. A positive image was developed with a maximum density of 1.0 and a minimum density of 0.07 measured in red light. (The heating step was used to increase the dye-development reaction initiated by the overall exposure.)

Examples 46-47 - Using a Quinone Photoreductant to be Either Positive- or Negative-Working

In 1 g of dioxane were dissolved 120 mg of iodoform (photoinhibitor) and 25 mg of the destabilizer 2-dibenzylamino-3-chloro-1,4-naphthoquinone. To this solution was added a second solution consisting of 120 mg of $[Co(NH_3)_6](CF_3 \cdot CO_2)_3$ and 166 mg phthalaldehyde (image-former) in a 20% solution of the binder poly(ethylene-co-1,4-cyclohexylenedimethylene-1-methyl-2,4-benzenedisulfonamide) in 95:5 by volume acetone:H_2O. This solution was coated with a 100-micron doctor blade on subbed poly(ethylene terephthalate) support and overcoated with a 10% solution of (copolyester 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan bisphenol A) in toluene.

A dried coating was exposed to visible light for 0.5 seconds on an IBM Microcopier IID device through a silver negative and a Wratten 2A filter which removes ultraviolet radiation. Upon heating for 15 seconds face-up on a 140°C hot block, a dense black negative image was formed.

Example 47 comprised a repetition of Example 46, except that the element was exposed for 6 seconds on an IBM Microcopier IID through a silver negative and a Wratten 34 filter which passes ultraviolet radiation, followed by a 0.5 seconds dye-development exposure through a Wratten 2A filter. Fifteen seconds of heating face-up on a 140°C hot block developed a dense positive image.

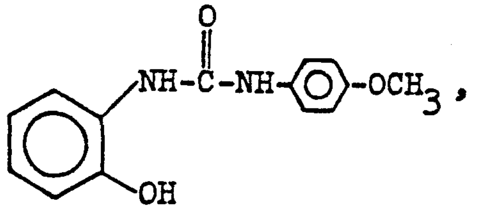
<u>Comparative Examples</u> (C.E.)

<u>C.E.No. 1</u>

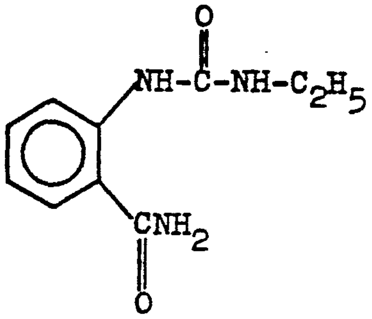
Example 13 was repeated except that anilinium methenebisulfonyl acetate was tested as a potential destabilizer material. This was found to be incompatible inasmuch as it caused precipitation of the cobalt(III) complex.

<u>C.E. Nos. 2 and 3</u>

Example 11 was repeated except that the urea of Example 11 was replaced by, respectively,



or



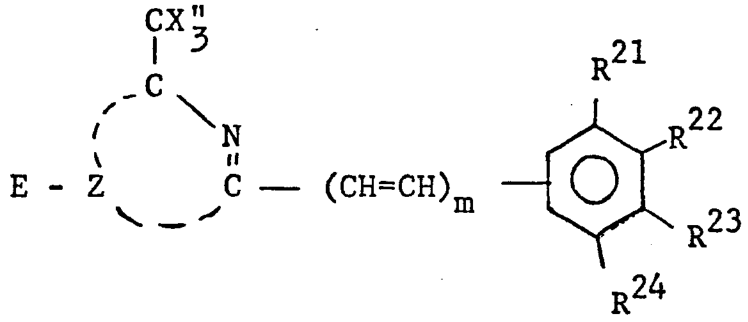
No image discrimination was found in either example, demonstrating that these compounds are not acceptable destabilizer materials.

CLAIMS

1. A negative-working or positive-working imaging element containing, in one or more operatively associated layers, an energy-activatable image precursor composition comprising at least one cobalt III complex having releasable ligands and an image-forming material which generates an image in response to the release of the ligands, characterized in that, the imaging element contains, in chemical association with the image precursor composition, a photoinhibitor which inhibits the release of ligands from the cobalt III complex or inhibits the effect of released ligands on the image-forming material upon exposure to activating radiation.

2. An imaging element as claimed in Claim 1, characterized in that the photoinhibitor is a heterocyclic compound having at least one trihalomethyl substituent group.

3. An imaging element as claimed in Claim 2, characterized in that the photoinhibitor is a heterocyclic compound having the formula:



in which,

E represents a hydrogen atom, a methyl or trihalomethyl group;

R^{21} represents a hydrogen atom or an alkoxy group having up to 5 carbon atoms;

R^{22} represents a hydrogen atom, a halogen atom, a nitro group or an alkyl, dialkylamino or alkoxy group having up to 5 carbon atoms in the alkyl portion;

R^{23} represents a hydrogen atom or an alkoxy group having up to 5 carbon atoms, or together with R^{24}, the non-metallic atoms necessary to complete an aromatic ring;

R^{24} represents a hydrogen atom, or together with R^{23}, the non-metallic atoms necessary to complete an aromatic ring;

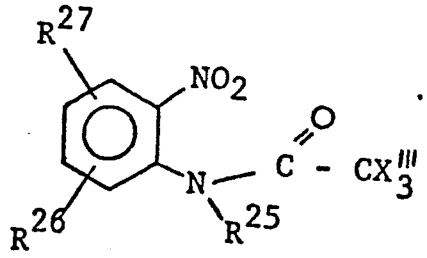
Z^7 represents the non-metallic atoms necessary to complete one or more heterocyclic rings containing from 6 to 10 atoms;

m' is 0, 1 or 2; and

X" represents a halogen atom.

4. An imaging element as claimed in Claim 2, characterized in that the photoinhibitor is 2,4-bis(trichloromethyl)-6-(p-anisyl)-s-triazine; 2,4-bis(trichloromethyl) 6-(4-methoxystyryl)-s-triazine; 2,4-bis(trichloromethyl)-6-[4-(4-dimethylaminophenyl)-1,3-butadienyl]-s-triazine; 2-tribromomethylquinoline, 2-tribromomethylquinoxaline; 2-tribromomethyl-4-oxo-4H-1-benzopyran; 2,4-bis(trichloromethyl)-6-(1-naphthyl)-s-triazine; 2,4-bis(trichloromethyl)-6-(4-methoxy-1-naphthyl)-s-triazine; tribromomethylbenzene; or 2,3-bis(tribromomethyl)quinoxaline.

5. An imaging element as claimed in Claim 1, characterized in that the photoinhibitor is an o-nitroacetanilide, having the formula:



in which,

R^{25} represents an alkyl group having up to 3 carbon atoms, an aralkyl group having 7 or 8 carbon atoms, or when taken together with R^{26}, the atoms necessary to complete a fused heterocyclic ring,

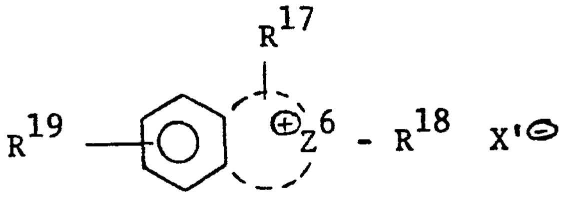
R^{26} represents a halogen atom, or when taken together with R^{25}, the atoms necessary to complete a fused heterocyclic ring;

R^{27} represents a hydrogen atom or an alkoxy group having up to 3 carbon atoms; and

X"' represents a halogen atom.

6. An imaging element as claimed in Claim 5, characterized in that the photoinhibitor is N-methyl-o-nitrotrifluoroacetanilide; N-benzyl-o-nitrotrifluoroacetanilide; N-benzyl-2-nitro-5-methoxy-trifluoroacetanilide; or 6-bromo-8-nitro-N-trifluoroacetylbenzo [b] piperidine.

7. An imaging element as claimed in Claim 1, characterized in that the photoinhibitor is an anthranilium salt having the formula:



in which,

R^{17} represents a hydrogen atom, a phenyl group or an alkyl group having up to 4 carbon atoms;

R^{18} represents an alkyl group having up to 4 carbon atoms, or an adamantyl group;

R^{19} represents a hydrogen or a halogen atom;

Z^6 represents a $=\underset{|}{N}-\overset{\ominus}{O}-$, $=\underset{|}{\overset{\oplus}{N}}-S-$, or a $=\underset{|}{\overset{\oplus}{N}}-\underset{R^{20}}{N}-$ group, and;

R^{20} represents a hydrogen atom or an alkyl group having up to 5 carbon atoms; and

X' represents an anion.

8. An imaging element according to Claim 5, characterized in that said photoinhibitor is N-methyl-3-diazo-4-quinolinium-p-toluenesulphonate; N-methyl-3-phenyl-2,1-benzisoxazolium perchlorate or N-methyl-3-phenyl-2,1-benzisoxazolium fluoroborate.

9. An imaging element as claimed in Claim 1, characterized in that the photoinhibitor is one of the halogenated organic compounds iodoform, carbon tetrabromide, β-tribromoethanol, hexabromoethane, ethyl tribromoacetate, tribromoacetamide, tribromomethyl benzene, pentrabromoethane, α,α,α-tribromoacetophenone or 3-nitro-α,α,α-tribromoacetophenone.

10. An imaging element as claimed in any of the preceding claims, characterized in that the cobalt III complex is unstable at a temperature greater than 100°C.

11. An imaging element as claimed in any of the claims 1 to 9, characterized in that the cobalt III complex is thermally stable up to a temperature of at least 130°C and there is present in the image precursor composition a destabilizer compound.

12. An imaging element as claimed in any of the preceding claims, characterized in that the image precursor composition contains an amplifier as herein defined.

13. An imaging element as claimed in claim 12, characterized in that the amplifier is phthalaldehyde.

14. An imaging element as claimed in any of the preceding claims, characterized in that the photoinhibitor is activated by wavelengths longer than 300nm.

15. The method of forming an image comprising imagewise exposing an imaging element as claimed in any of the preceding claims 1 to 14 to activating radiation to release the inhibitor imagewise and

thereafter supplying uniformly sufficient energy to activate the image precursor composition.

16. The method as claimed in claim 15 characterized in that the image precursor composition is activated by uniform heating.

FIG. 1a

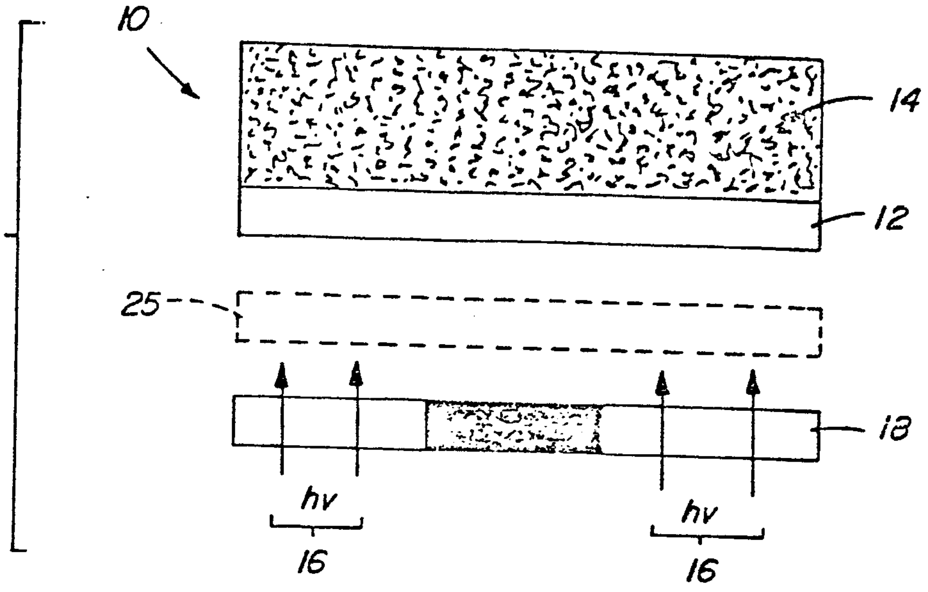


FIG. 1b

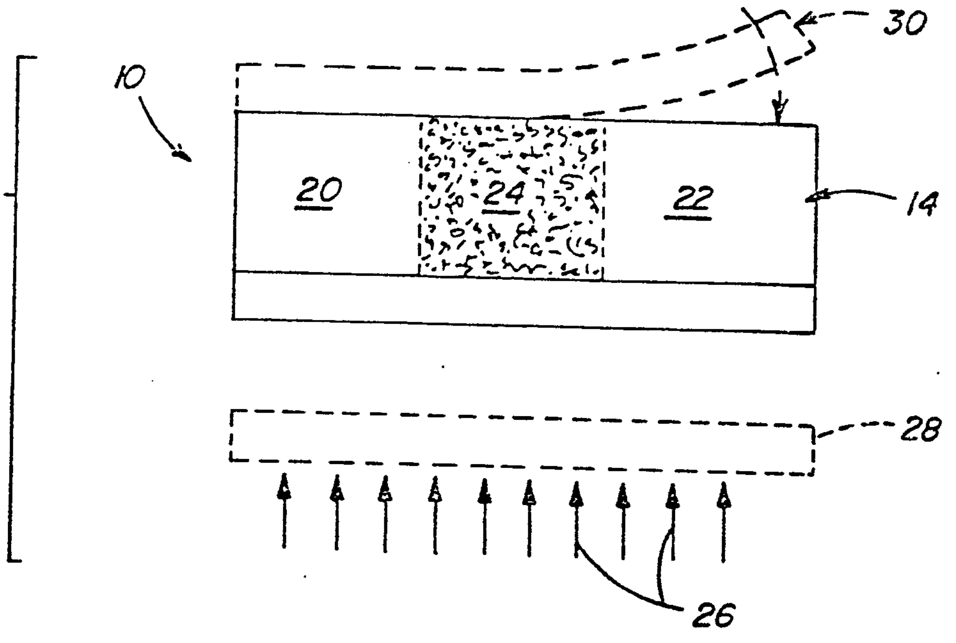
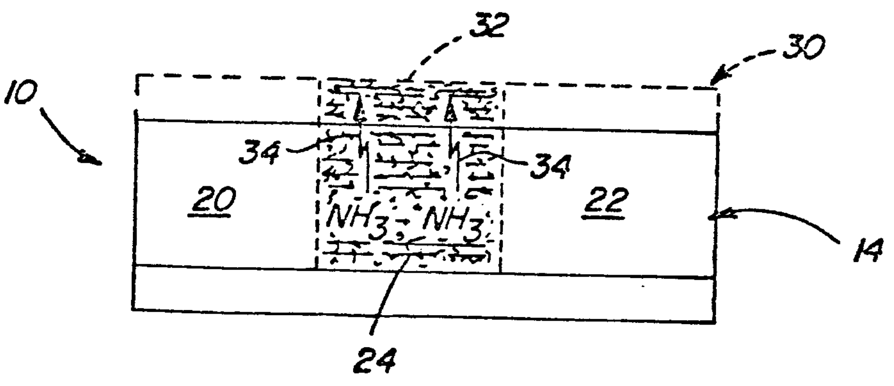


FIG. 1c



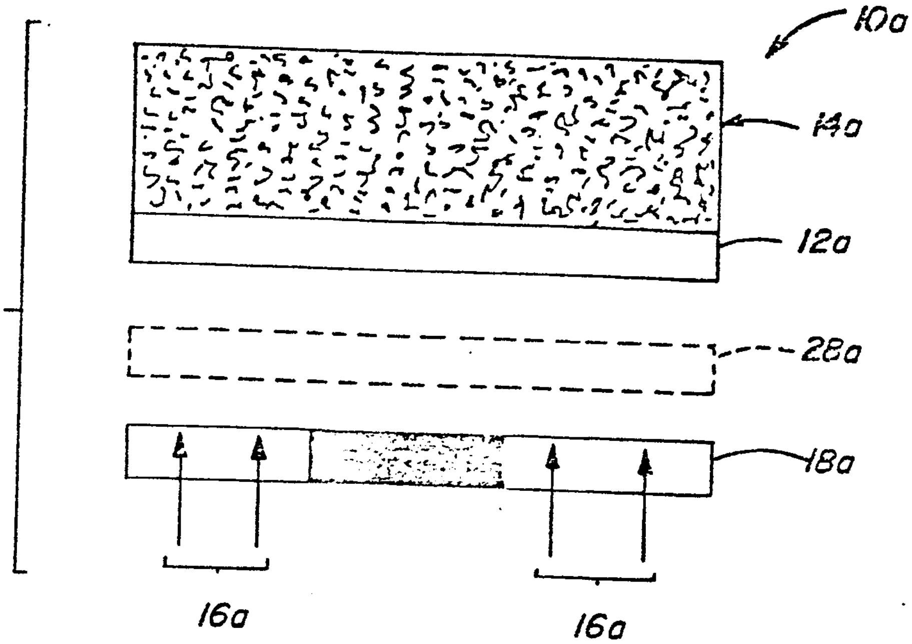


FIG. 2a

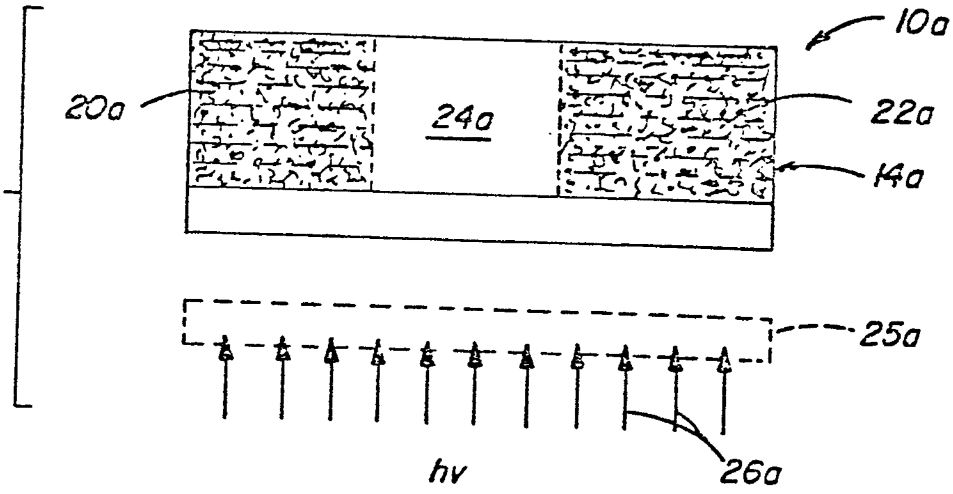


FIG. 2b

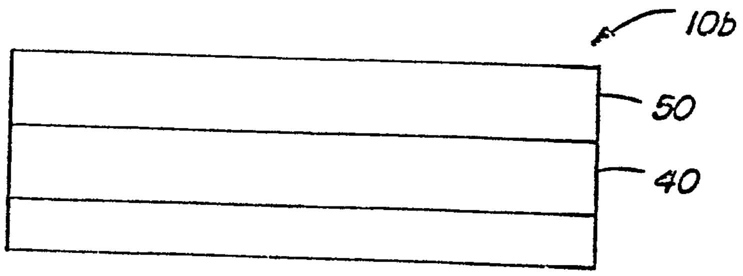


FIG. 3

0003263

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 78 30 0914

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	FR - A - 2 267 571 (EASTMAN KODAK) * Page 2, line 7 to page 3, line 6; page 17, line 40 to page 18, line 19; example 178, page 47; claims 1-3, 11-14 * --	1,9-16
D	US - A - 3 987 037 (J.A. BONHAM et al.) * Abstract; claims * -----	2-4

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

G 03 C 1/72
5/00
5/56
C 07 F 15/06

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

G 03 C 1/72
5/00
5/56

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
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E: conflicting application
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L: citation for other reasons

&: member of the same patent family, corresponding document

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

Place of search	Date of completion of the search	Examiner
The Hague	28-03-1979	PHILOSOPH

EPO Form 1503.1 06.78