

[54] **AZIRIDINE PHOTOREDUCTIVE IMAGING**
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[22] Filed: **Nov. 2, 1973**

[21] Appl. No.: **412,082**

[52] U.S. Cl. **96/48 R; 96/48 HD; 96/88;**
 96/89; 96/90 R; 96/90 PC

[51] Int. Cl. **G03c 5/24; G03c 1/52; G03c 1/72**

[58] Field of Search **96/89, 88, 90 R, 90 PC,**
 96/48 R, 48 HD, 49, 91 R

[56] **References Cited**

UNITED STATES PATENTS

3,609,165 9/1971 Heine et al. 96/90 PC

FOREIGN PATENTS OR APPLICATIONS

670,883 4/1952 United Kingdom 96/90 R

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[57] **ABSTRACT**

A reducible, image-forming compound is present in a radiation-sensitive layer in combination with a 1,3-diazabicyclo[3.1.0]hex-3-ene, a photochromic aziridine. Upon exposure to actinic radiation the aziridine is converted to a reducing agent precursor. Heating above ambient temperature converts the reducing agent precursor to a reducing agent. If desired, a mineral acid can be used to fix the radiation-sensitive layer.

25 Claims, No Drawings

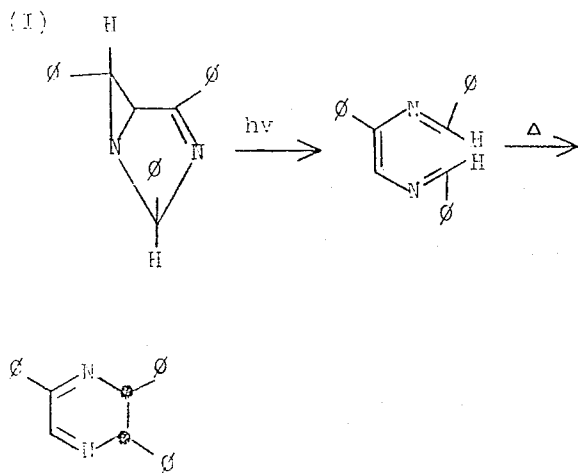
AZIRIDINE PHOTOREDUCTIVE IMAGING

This invention relates to a novel photographic element and to a process for its use in which a compound capable of changing its radiation-absorption characteristic upon reduction is employed in combination with a photoreductant for image recording. In a more specific aspect, this invention is directed to a photographic combination and process which utilizes imagewise exposure and heating to achieve image recording.

Image-recording elements employing compounds which are reducible and change their absorption of electromagnetic radiation upon reduction are known to the art. Compounds are known, for example, that are capable of reduction to form visible dyes. In patent applications Ser. Nos. 384,858; 384,859; 384,860 and 384,861; all filed Aug. 2, 1973, it is taught to reduce tetrazolium and triazolium salts to formazan and azoamine dyes, respectively, employing in the presence of labile hydrogen atoms a photoreductant which is capable of forming a reducing agent precursor upon exposure to actinic radiation. The reducing agent precursor is converted to a reducing agent by a base, such as ammonia. Instead of forming a dye image by reduction it is also known that a number of different categories of dyes, such as azo and amine triarylmethane dyes, can be bleached by reduction. Hence the formation of both positive and negative images using reducible compounds is known to the art.

It is taught by W. R. Schleigh in patent application Ser. No. 403,374, filed Oct. 4, 1973, now U.S. Pat. No. 3,881,930 titled 2H-Benzimidazole Photoreductive Imaging, to use 2H-benzimidazoles as photoreductants in combination with such reducible compounds. On exposure the 2H-benzimidazole is converted to a dihydrobenzimidazole reducing agent. Subsequent heating converts the unexposed 2H-benzimidazole to 1H-benzimidazole, which is not a photoreductant, thereby fixing the system.

Padwa et al. in the Journal of the American Chemical Society, Volume 92, at page 1778, have shown that 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene isomerizes on exposure to actinic radiation to the corresponding ene diimine, which on warming rearranges to the corresponding cis-2,3-dihydropyrazine. This is diagrammatically illustrated as follows:



It is an object of this invention to provide photographic elements and processes which are capable of forming latent images upon exposure to actinic radiation and which form visible images upon heating. In a specific form it is an object to provide photographic elements which can be fixed to avoid background printout, preferably by heating. It is an additional object of this invention to provide photographic elements which can be dry processed.

In one aspect this invention is directed to a photographic element comprised of an image-recording means which undergoes an electromagnetic radiation-absorption change upon reduction. A photoreductant is provided in intimate association with the image-recording means, and means are provided for supporting the image-recording means and the photoreductant. The photoreductant is chosen to be a 1,3-diazabicyclo[3.1.0]-hex-3-ene.

In another aspect this invention is directed to an image-recording process which comprises imagewise exposing to actinic radiation a photographic element incorporating an image-recording means which undergoes an electromagnetic radiation absorption change upon reduction and a 1,3-diazabicyclo[3.1.0]hex-3-ene photoreductant. Such exposure converts the photoreductant to a thermally activatable reducing agent precursor. The reducing agent precursor is thermally converted to a reducing agent, and a visible image is formed by selectively reducing the image-recording means within exposed portions of the photographic element.

In a specifically preferred embodiment of the invention, an image-recording compound capable of changing its electromagnetic radiation-absorption characteristic upon reduction, such as a salt reducible to a dye or a dye which is capable of being bleached by reduction, and a 1,3-diazabicyclo[3.1.0]hex-3-ene photoreductant are associated within a binder and coated onto a conventional photographic support to form a radiation-sensitive image-recording layer. The resulting photographic element is then exposed imagewise to actinic radiation—that is, in this instance, electromagnetic radiation of less than 700nm in wavelength and, preferably, below 500nm. Exposure causes the 1,3-diazabicyclo[3.1.0]hex-3-ene to be converted to the corresponding ene diimine reducing agent precursor. To convert the reducing agent precursor to a reducing agent and thereby convert the latent image which it represents into a visible image it is only necessary to heat the radiation-sensitive layer to a temperature somewhat above ambient—e.g., 70°C. For rapid conversion, heating in the range of from about 100° to 150°C is preferred.

If the imaged photographic element of this invention is re-exposed to actinic radiation at room temperature, there is little tendency for background printout to occur. This is partially attributable to the fact that the rate of conversion of the reducing agent precursor to the reducing agent is low at room temperature. Additionally, since the 1,3-bicyclo[3.1.0]hex-3-enes employed in the practice of this invention are photochromic, there is a spontaneous reversion of a portion of the reducing agent precursor to photoreductant with the passage of

time. Hence, the photographic elements of this invention do not require fixing.

In those applications where it is deemed desirable to insure against even minimal background printout the 1,3-bicyclo[3.1.0]hex-3-enes can be removed from unexposed areas by contact with a mineral acid, such as hydrochloric, sulfuric, nitric or phosphoric acid, as by swabbing or fuming. In a preferred approach to acid fixing a compound which releases a mineral acid upon heating, such as a salt of a higher alkylamine and hydrochloric acid (incorporating ten or more carbon atoms), can be associated with the radiation-sensitive layer. This can be conveniently accomplished by providing an acid-releasing coating adjacent the radiation-sensitive layer.

It is a specific advantage of this invention that photographic elements are provided incorporating image-forming compounds which are not degraded by the atmosphere. Whereas photographic elements employing oxidizable image-forming compounds tend to increase in background density or fade (depending on the specific choice of image-forming compound) due to atmospheric oxidation, the atmosphere is substantially free of reducing agents. Accordingly, there is no tendency of the image-forming compounds employed in the practice of this invention to be reduced upon storage. This then improves the stability of the areas not image-wise irradiated.

Whereas in classical photography a succession of developing, stopping, fixing and rinsing baths are typically used in the course of forming a stable photographic record, it is a significant feature of this invention that wet processing of the photographic element is not required. While it is recognized that the photographic elements of this invention could incorporate components requiring wet processing, if desired, in the preferred form the present invention employs only thermal processing after exposure. Since the single thermal processing step can be performed in commercially available equipment sold for this purpose and since no resort to comparatively cumbersome conventional processing techniques, such as processing baths, image area heating, volatilizing components and the like is required, it is apparent that the photographic elements of the present invention are advantageously simple and convenient to use.

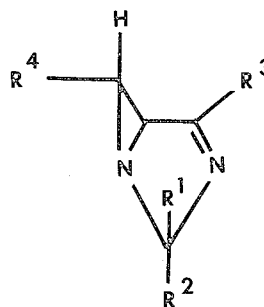
Photoreductants

This invention employs as a photoreductant a 1,3-diazabicyclo[3.1.0]hex-3-ene. As employed herein, the term "photoreductant" designates a material capable of molecular photolysis or photoinduced rearrangement to generate a reducing agent precursor. The term "reducing agent precursor" is employed to designate a material which can be thermally converted to a reducing agent. Applicants have recognized the utility of 1,3-diazabicyclo[3.1.0]hex-3-enes as photoreductants capable of forming successively reducing agent precursors and reducing agents upon exposure to actinic radiation and heat.

Since the photoresponse of 1,3-diazabicyclo[3.1.0]hex-3-enes is primarily a function of the ring structure, any known compound of this type can be used in the practice of this invention. 1,3-diazabicyclo[3.1.0]hex-3-enes are known having various combinations of substituents. Typical of the 1,3-

diazabicyclo[3.1.0]hex-3-enes useful in the practice of this invention are those defined by the formula (II)

(II)



wherein:

R¹ and R² are independently chosen from among such substituents as hydrogen, alkyl (including cycloalkyl), aralkyl, alkaryl and aryl substituents or together R¹ and R² constitute an alkylene substituent, preferably forming a 5- or 6-membered ring;

R³ is an aryl or electron withdrawing substituent, such as a cyano group, a carboxy group, a nitro group or a carbonyl-containing group; and

R⁴ is an aryl or alkaryl substituent.

In alternative 1,3-diazabicyclo[3.1.0]hex-3-enes according to this invention the nitrogen atom in ring position 1 (the nitrogen atom common to both rings) can be converted to form the corresponding quaternary salt or N-oxide. When the 1 position nitrogen atom is quaternized it can bear an alkyl or aralkyl substituent or hydrogen. The alkyl and aryl substituents and substituent moieties can be further substituted—e.g., mono- or di-substituted. Typical aryl and alkyl substituents contemplated include alkyl, benzyl, styryl, phenyl, biphenyl, naphthyl, alkoxy (e.g., methoxy, ethoxy, etc.), aryloxy (e.g., phenoxy), carboalkoxy (e.g., carbomethoxy, carboethoxy, etc.), carboaryloxy (e.g., carbophenoxy, carbonaphthoxy), acyloxy (e.g., acetoxy, benzoxy, etc.), acyl (e.g., acetyl, benzoyl, etc.), halogen (i.e., fluoride, chloride, bromide, iodide), cyano, azido, nitro, haloalkyl (e.g., trifluoromethyl, trifluoroethyl, etc.), amino (e.g., dimethylamino), amido (e.g., acetamido, benzamido, etc.), ammonium (e.g., trimethylammonium), azo (e.g., phenylazo), sulfonyl (e.g., methylsulfonyl, phenylsulfonyl), sulfoxy (e.g., methylsulfoxy), sulfonium (e.g., dimethyl sulfonium), silyl (e.g., trimethylsilyl) and thioether (e.g., methylthio) substituents. It is generally preferred that alkyl and alkylene substituents and substituent moieties having 20 or fewer carbon atoms, most preferably six or fewer carbon atoms, be employed. The aryl substituents and substituent moieties are preferably phenyl or naphthyl groups.

Exemplary 1,3-diazabicyclo[3.1.0]hex-3-ene photoreductants are set forth below in Table I.

TABLE I

Exemplary 1,3-Diazabicyclo[3.1.0]- hex-3-ene Photoreductants	
PR-1	4,6-diphenyl-1,3-diazabicyclo[3.1.0]- hex-3-ene
PR-2	4-phenyl-6-(4-nitrophenyl)-1,3-diazabi- cyclo[3.1.0]hex-3-ene
PR-3	2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]- hex-3-ene
PR-4	2,4-diphenyl-6-(4-nitrophenyl)-1,3-

TABLE I-Continued

	Exemplary 1,3-Diazabicyclo[3.1.0]- hex-3-ene Photoreductants
PR-5	diazabicyclo[3.1.0]hex-3-ene
PR-6	2,2-dicyclopropyl-4-phenyl-6-(4-nitro-phenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-7	2,6-diphenyl-4-cyano-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-8	2-(1-naphthyl)-4,6-di(4-chlorophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-9	2-methyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-10	2-n-propyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-11	2-iso-propyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-12	2,2-dimethyl-4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-13	2,2-dimethyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-14	2,2-dimethyl-4-(4-nitrophenyl)-6-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-15	2,2-dimethyl-4-phenyl-6-(4-chlorophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-16	2-methyl-2-ethyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-17	2-methyl-2-n-propyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-18	2-methyl-2-tert-butyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-19	2,4-diphenyl-2-methyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-20	2,2-diethyl-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-21	2,2-diethyl-4-phenyl-6-(3-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-22	2,2-di-n-hexyl-4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-23	spiro[cyclopentane-1,2'-[4'-phenyl-6'-(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene]]
PR-24	spiro[cyclohexane-1,2'-[4'-phenyl-6'-(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene]]
PR-25	spiro[cycloheptane-1,2'-[4'-phenyl-6'-(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene]]
PR-26	spiro[cyclooctane-1,2'-[4'-phenyl-6'-(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene]]
PR-27	spiro[1-methylcyclohexane-2,2'-[4'-phenyl-6'-(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene]]
PR-28	spiro[1-methylcyclohexane-4,2'-[4'-phenyl-6'-(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene]]
PR-29	2-(4-ethoxycarbonylphenyl)-4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-30	2,4-diphenyl-6-(benzoyloxyphenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-31	2,6-di(1-naphthyl)-4-nitro-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-32	2,6-di(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-33	2,4-diphenyl-6-(3-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-34	2,6-diphenyl-4-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-35	2-(4-tolyl)-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-36	2,6-di(4-tolyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-37	2,4,6-tri(2-aminophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-38	2-(4-diethylaminophenyl)-4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-39	2,4-diphenyl-6-(4-morpholinophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-40	2-benzyl-4-nitro-6-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-41	2,4-diphenyl-6-(4-ethylphenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-42	2,4-diphenyl-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene
PR-43	1-azonia-4,6-diphenyl-1-methyl-3-azabicyclo[3.1.0]hex-3-ene tetrafluoroborate
PR-44	1-azonia-4,6-diphenyl-1,2,2-trimethyl-3-azabicyclo[3.1.0]hex-3-ene hexafluorophosphate
PR-45	1-azonia-4-phenyl-6-(4-nitrophenyl)-1,2,2-trimethyl-3-azabicyclo[3.1.0]hex-3-ene

TABLE I-Continued

	Exemplary 1,3-Diazabicyclo[3.1.0]- hex-3-ene Photoreductants
PR-45	tetrafluoroborate
PR-46	1-azonia-4-nitro-2,6-diphenyl-3-azabicyclo[3.1.0]hex-3-ene chloride
PR-47	4,6-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene-1-oxide
PR-48	2,2-dimethyl-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene-1-oxide
PR-49	spiro{cyclopentane-1,2'-[4'-phenyl-6'-(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene-1-oxide]}
PR-50	spiro{1-methylcyclohexane-4,2'-[2',4',6'-triphenyl-1',3'-diazabicyclo[3.1.0]hex-3-ene-1-oxide]}
	spiro{1-cycloheptane-1,2'-[2',2'-dicyclopropyl-4',6'-di(4-nitrophenyl)-1',3'-diazabicyclo[3.1.0]hex-3-ene-1-oxide]}

Image-Recording Means

The invention can be practiced utilizing as an image-recording means any compound which is known to exhibit a change in its electromagnetic radiation-absorption characteristics upon reduction. For most applications it is preferred that a visibly detectable absorption change occur upon reduction. A variety of dyes are known which are bleached or converted to a colored form upon reduction. Such dyes have long been employed in silver-dye-bleach processes and can be employed in the practice of this invention. Exemplary dyes of this type include those set forth in Christensen U.S. Pat. No. 1,157,049. Other reducible dyes that have been used in silver-dye bleach processes and which can be employed in the practice of this invention include those disclosed by J. S. Friedman in *History of Color Photography*, Chapter 24, published 1944.

Preferred bleachable reducible dyes are aminotriarylmethane dyes and azo dyes, including such azo dyes as monoazo and disazo dyes, such as those having amino, pyrazolone, hydroxy, alkoxy and other substituents; disazo dyes having stilbene and triphenylmethane linkages and chelated azo dyes. Exemplary useful azo dyes are disclosed in U.S. Pat. Nos. 1,829,673; 1,985,344; 2,004,625; 2,028,279; 2,055,407; 2,074,259; 2,075,191; 2,080,041; 2,100,594; 2,166,049; 2,172,307; 2,183,395; 2,217,899; 2,231,685; 2,271,176; 2,281,149; 2,286,838; 2,294,892; 2,294,893; 2,331,755; 2,304,884; 2,350,736; 2,368,647; 2,418,624; 2,420,630; 2,420,631; 2,564,238; 2,612,448; 2,629,658; 2,681,856; 2,694,636; 2,899,305; 3,002,964; 3,157,508; and 3,167,537; which are incorporated by reference. Exemplary of aminotriarylmethane dyes useful in the practice of this invention are those disclosed in U.S. Pat. Nos. 3,042,515; 3,121,632 and 3,493,376. The aminotriarylmethane dyes are, of course, first oxidized to their colored form, so that they can be reduced in the practice of this invention. Other dyes which have found use in silver-dye-bleach processes and which are useful in the practice of this invention include xanthene dyes, triazine dyes, nitroso dye complexes, indigo dyes and phthalocyanine dyes. Exemplary dyes of these types are disclosed in U.S. Pat. Nos. 1,985,355; 2,080,041; 2,184,022 and 2,217,899, here incorporated by reference.

In contrast to bleaching radiation-struck areas of the photographic elements of this invention, it is also contemplated that reducible compounds can be chosen to

produce visibly detectable coloration in radiation-struck areas. For example, to form negative images it is generally desirable that the reducible compound be chosen to produce higher optical densities upon reduction. Exemplary of reducible compounds of this type are triazolium and tetrazolium salts capable of forming azoamine and formazan dye images, respectively, upon reduction.

Tetrazolium Salts

It is recognized that 1,3-diazabicyclo[3.1.0]hex-3-enes can be used as photoreductants with the tetrazolium salts disclosed in copending applications Ser. Nos. 384,858; 384,859 and 384,861, noted above. As is disclosed in these applications, any tetrazolium salt which on reduction forms a formazan dye of a detectibly different color can be employed. A wide variety of such tetrazolium salts are known to the art including bis-tetrazolium salts linked directly or through intervening divalent radicals in the 2 or 5 positions. As is well understood by those skilled in the art, tetrazolium salts require for preparation the presence of aromatic (e.g., phenyl, naphthyl, anthryl, pyridyl, oxazolyl, thiazolyl, quinolyl, benzoxazolyl, benzothiazolyl, etc.) substituents in the 2 and 3 positions of the tetrazole nucleus. For purposes of illustration exemplary suitable known tetrazolium salts are set forth in Tables II, IV and V.

It is recognized that some tetrazolium salts are yellow or can become yellow when exposed to light for an extended period in the imaging layer. To be useful in the practice of this invention it is required only that the tetrazolium salt incorporated into the image-forming layer undergo a detectible color change upon reduction to the corresponding dye. Since the formazan dyes are for the most part red and of significantly higher optical densities than their parent tetrazolium salts, they produce a sharp visible contrast with yellow, white or transparent background areas. Of course, white or fully transparent backgrounds present minimum optical densities (hence highest contrast), and for this reason it is generally preferred to choose tetrazolium salts that remain colorless until reduced to the corresponding dye. Additionally, aesthetic considerations dictate white or transparent backgrounds for many applications.

TABLE II

Exemplary Dye Forming Tetrazolium Salts	
T- 1	2,3,5-triphenyl-2H-tetrazolium chloride
T- 2	2-(2-methylphenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T- 3	2-(4-chlorophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T- 4	2,3-diphenyl-5-(4-chlorophenyl)-2H-tetrazolium tetrafluoroborate
T- 5	2-(4-iodophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T- 6	2-(4-chlorophenyl)-3-(2-chlorophenyl)-5-(2-pyridyl)-2H-tetrazolium iodide
T- 7	2,3-diphenyl-2H-tetrazolium sulfate
T- 8	2-(2-methoxyphenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T- 9	2,3-diphenyl-5-methyl-2H-tetrazolium chloride
T-10	2,3-diphenyl-5-dodecyl-2H-tetrazolium chloride
T-11	5-(3-iodophenyl)-2,3-diphenyl-2H-tetrazolium chloride
T-12	5-cyano-2,3-diphenyl-2H-tetrazolium chloride
T-13	5-acetyl-2,3-diphenyl-2H-tetrazolium chloride
T-14	2,5-diphenyl-3-(4-tolyl)-2H-tetrazolium

TABLE II-Continued

Exemplary Dye Forming Tetrazolium Salts	
5	T-15 bromide
	2,5-diphenyl-3-(4-diphenyl)-2H-tetrazolium chloride
	T-16 2,3-diphenyl-5-(2-chlorophenyl)-2H-tetrazolium iodide
	T-17 5-(3,4-dimethoxyphenyl)-3-(4-nitrophenyl)-2-phenyl-2H-tetrazolium iodide
	T-18 2,3-diphenyl-5-nitro-2H-tetrazolium chloride
10	T-19 2,3-diphenyl-5-(2-naphthyl)-2H-tetrazolium chloride
	T-20 ethylenebis[5-(2,2',3,3'-tetraphenyl-2H-tetrazolium chloride)]
	T-21 1,6-hexylenebis[5-(2,3-diphenyl-2H-tetrazolium chloride)]
15	T-22 4-phenylenebis[5-(2,3-diphenyl-2H-tetrazolium chloride)]
	T-23 4,4'-biphenylenebis[2-(5-methyl-3-phenyl-2H-tetrazolium chloride)]
	T-24 4,4'-phenylene sulfoxide-bis[2-(3,5-diphenyl-2H-tetrazolium chloride)]
	T-25 4,4'-biphenylenebis[2-(3-diphenyl-5-(3,4-methylenedioxyphenyl)-2H-tetrazolium chloride)]
20	T-26 2-phenyl-3-(4-nitrophenyl)-5-undecyl-2H-tetrazolium chloride
	T-27 2,3-diphenyl-5-carbethoxy-2H-tetrazolium chloride
	T-28 5-carbohexoxy-2,3-diphenyl-2H-tetrazolium chloride
25	T-29 5-acetyl-2-phenyl-3-(4-chlorophenyl)-2H-tetrazolium tetrafluoroborate
	T-30 2,3-diphenyl-5-(1-naphthyl)-2H-tetrazolium bromide
	T-31 2-(2,4,6-trichlorophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
30	T-32 2-(3,4-dichlorophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
	T-33 2,3-diphenyl-5-(3-nitrophenyl)-2H-tetrazolium tetrafluoroborate
	T-34 2-(3-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
	T-35 2,3-diphenyl-5-(4-nitrophenyl)-2H-tetrazolium tetrafluoroborate
35	

For many applications it is preferred to use tetrazolium salts which produce formazan dyes exhibiting high image densities and having a low susceptibility to fading. A preferred class of such tetrazolium salts are those having substituents on the tetrazole nucleus which are, collectively, predominantly electronegative (i.e., electron withdrawing). Particularly stable tetrazolium salts are those having tetrazole nucleus substituents the algebraic sum of whose Hammett sigma values is collectively greater than 0.78 and, preferably, greater than 1.00. If one or more of the substituent rings is in turn substituted at only one ring position adjacent to the ring-to-nucleus bonding position—i.e., the ring position (or positions) ortho to the bonding position, the algebraic sum of the sigma values for all tetrazole nucleus substituents need only be greater than 0.40 and, preferably, 0.50 in order to achieve the advantages of significantly improved image densities and dye stabilities. When two such ortho position electronegative substituents are present in a single substituent ring, however, they are essentially subtractive in effect. For example, two like ortho substituents on a 2,3, or 5 position phenyl ring of a tetrazolium salt are substantially self-cancelling in effect. A comparable tetrazolium salt having only one ortho substituent and having summed Hammett sigma values for all substituents of 0.40 or greater exhibits marked stability. If a 2,3-diphenyl or 2,3,5-triphenyl-2H-tetrazolium salt has no ortho substituents (or cancelling ortho substituents), but has meta and/or para substituents so that the summed sigma values for the phenyl rings are greater than 0.78,

then the salt exhibits a marked improvement in its stability.

In certain applications it can be advantageous to produce formazan dye images that fade at an accelerated rate. For example, it may be desirable to form a slide in which the image or a portion thereof disappears while being viewed or after a prescribed period of projection. By incorporating a predominance of electron donating (electropositive) substituents in the tetrazolium salts used in the practice of this invention the fading characteristics of the resulting formazan dyes can be augmented.

The tetrazolium salts used in the preferred practice of this invention can be comprised of any desired combination of 2, 3 and, optionally, 5 position aromatic or aromatic-like heterocyclic rings such as phenyl, naphthyl, anthryl, quinolinyl pyridyl, azolyl, and the like. Typical azolyl rings include oxazolyl, thiazolyl, benzoxazolyl, benzothiazolyl and the like. These rings can in turn carry substituents. Exemplary of specifically contemplated ring substituents are lower alkyl (i.e., 1 to 6 carbon atoms), lower alkenyl (i.e., 2 to 6 carbon atoms), lower alkynyl (i.e., 2 to 6 carbon atoms), benzyl, styryl, phenyl, biphenyl, naphthyl, alkoxy (e.g., methoxy, ethoxy, etc.), aryloxy (e.g., phenoxy), carboalkoxy (e.g., carbomethoxy, carboethoxy, etc.), carboaryloxy (e.g., carbophenoxy, carbonaphthoxy), acyloxy (e.g., acetoxy, benzoxy, etc.), acyl (e.g., acetyl, benzoyl, etc.), halogen (i.e., fluoride, chloride, bromide, iodide), cyano, azido, nitro, haloalkyl (e.g., trifluoromethyl, trifluoroethyl, etc.), amino (e.g., dimethylamino), amido (e.g., acetamido, benzamido), ammonium (e.g., trimethylammonium), azo (e.g., phenylazo), sulfonyl (e.g., methylsulfonyl, phenylsulfonyl), sulfoxy (e.g., methylsulfoxy), sulfonium (e.g., dimethyl sulfonium), silyl (e.g., trimethylsilyl) and thioether (e.g., methylthio) substituents.

Hammett sigma values for the substituents of the tetrazole nucleus can be determined by reference to the published literature or can be determined directly using known determination procedures. Exemplary meta and para sigma values and procedures for their determination are set forth by H. VanBekkum, P. E. Verkade and B. M. Wepster in *Rec. Trav. Chim.*, volume 78, page 815, published 1959; by P. R. Wells in *Chem. Revs.*, volume 63, page 171, published 1963, by H. H. Jaffe, *Chem. Revs.*, volume 53, page 191, published 1953; by M. J. S. Dewar and P. J. Grisdale in *J. Amer. Chem. Soc.*, volume 84, page 3548, published 1962; and by Barlin and Perrin in *Quart. Revs.*, volume 20, page 75 et seq., published 1966.

In accordance with established practice, electron withdrawing (electronegative) substituents are assigned positive sigma values while electron donating (electropositive) substituents are assigned negative sigma values. Each tetrazole nucleus substituent is assigned a Hammett sigma value which is the algebraic sum of its unsubstituted sigma value and the sigma value of its own substituents, if any. For example, unsubstituted phenyl tetrazole nucleus substituents have neutral sigma values, while the sigma values of substituted phenyl tetrazole nucleus substituents can be determined algebraically simply by determining from the literature the known Hammett sigma values for each substituent and obtaining the algebraic sum thereof. Other tetrazole nucleus substituents, particularly heterocyclic tetrazole nucleus substituents, can exhibit

sigma values even when unsubstituted. For example, a 2-pyridyl substituent exhibits a sigma value of 0.56; a 3-pyridyl substituent exhibits a sigma value of 0.73; a 4-pyridyl substituent exhibits a sigma value of 0.83; a 2-thiazolyl substituent exhibits a sigma value of approximately 0.5; a 2-oxazolyl substituent exhibits a sigma value of 0.75. It is then apparent that a tetrazolium salt including an unsubstituted 4-pyridyl or 2-pyridyl substituent constitutes a preferred, stabilized dye producing tetrazolium salt, provided the remaining tetrazole nucleus substituents are on balance neutral or electro-negative in their sigma values.

Sigma values for a given substituent are noted to vary as a function of ring position and resonance induced by conjugation. For example, a given substituent to a phenyl ring can exhibit one sigma value in the meta position and another when in the para position. A few substituents, such as nitro, dimethylamino and cyano substituents, for example, produce a conjugated system as para position substituents to 2 and 3 position phenyl rings and accordingly are assigned differing sigma values depending on the ring to which they are appended. For the purpose of assigning sigma values in accordance with the teachings of this invention the sigma value for an ortho substituent is considered to be identical to the non-conjugated para position sigma value for that substituent. Certain illustrative Hammett sigma values for ring substituents of triphenyltetrazolium salts are set forth in Table III.

TABLE III

Substituent	Exemplary Hammett Sigma Values For Triphenyltetrazolium Salt Substituents	
	meta	Ortho/para
-N(CH ₃) ₂	+0.05	+0.12 ^a
-t-C ₄ H ₉	-0.07	-0.14
-C ₂ H ₅	-0.07	-0.12
-CH ₃	-0.07	-0.13
-OCH ₃	+0.08	-0.17
-Si(CH ₃) ₃	-0.05	+0.01
-H	≡0.0	≡0.0
-C ₆ H ₅	+0.06	0.0
-F	+0.34	+0.08
-Cl	+0.37	+0.25
-Br	+0.39	+0.27
-I	+0.35	+0.30
-CN	+0.62	+0.65 ^b
-NO ₂	+0.71	+0.78 ^c
-C(O)CH ₃	+0.38	+0.50
-SO ₂ CH ₃	+0.68	+0.68
-N(CH ₃) ₃ ⁺	+0.86	+0.80
-CO ₂ CH ₃	+0.32	+0.39
-CHO	+0.38	+1.00
-SCH ₃	+0.22	+0.22
-S(CH ₃) ₂ ⁺	+1.0	+1.2
-CF ₃	+0.47	+0.53

^a-0.60 for 2 and 3 position phenyl rings as para substituent

^b+0.75 for 2 and 3 position phenyl rings as para substituent

^c+0.93 for 2 and 3 position phenyl rings as para substituent

Exemplary preferred tetrazolium salts having predominately electronegative tetrazole nucleus substituents are set forth in Table III. These tetrazolium salts in all instances incorporate tetrazole nucleus substituents the summed sigma values of which are equal to or greater than those required to impart enhanced stability to the corresponding formazan dye—i.e., greater than 0.78 or, in the case of tetrazolium salts having a substituent ring which is in turn singly substituted at a carbon atom adjacent the bonding carbon atom, greater than 0.40.

TABLE IV

Exemplary Preferred Tetrazolium Salts for forming Dyes of Enhanced Stability	
Tetrazolium Salt	
T-36	2-(4-methylthiophenyl)-3-(3,5-dichlorophenyl)-5-(3-nitrophenyl)-2H-tetrazolium hexafluorophosphate
T-37	2-(4-cyanophenyl)-3-(3-benzamidophenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium perchlorate
T-38	2-(2-naphthyl)-3-(3-nitro-5-chlorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium sulfate
T-39	2-(4-bromo-1-naphthyl)-3-(4-cyanophenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium chloride
T-40	2-(3-pyridyl)-3-phenyl-5-(4-chlorophenyl)-2H-tetrazolium bromide
T-41	2-(2,4-dichlorophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-42	2-(2,4,5-trichlorophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-43	2-(2,4,5-trichlorophenyl)-3-(4-phenylsulfonyl phenyl)-5-phenyl-2H-tetrazolium chloride
T-44	2-(2,3,4,5-tetrachlorophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium iodide
T-45	2-(2-trifluoromethyl-5-chlorophenyl)-3-(4-cyanophenyl)-5-phenyl-2H-tetrazolium bromide
T-46	2-(4-pyridyl)-3-(2-trifluoromethylphenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-47	2-(2-chloro-5-trifluoromethylphenyl)-3-(3,4-dichlorophenyl)-5-phenyl-2H-tetrazolium hexafluorophosphate
T-48	2-(2-chloro-5-nitrophenyl)-3-(4-acetyl phenyl)-5-(3-nitrophenyl)-2H-tetrazolium chloride
T-49	2-(2-chloro-4-cyanophenyl)-3-(4-benzoylphenyl)-5-(3-chlorophenyl)-2H-tetrazolium perchlorate
T-50	2-(2-nitro-4-chlorophenyl)-3-(4-phenylazophenyl)-5-(4-chlorophenyl)-2H-tetrazolium chloride
T-51	2-[4-(4-nitrophenyl)thiophenyl]-3-(2-chloro-5-trifluoromethylphenyl)-5-(3-nitrophenyl)-2H-tetrazolium bromide
T-52	2-(4-phenylsulfonylphenyl)-3-(2-chloro-5-trifluoromethyl phenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium bromide
T-53	2-(4-benzylphenyl)-3-(2,4-dichlorophenyl)-5-(4-nitrophenyl)-2H-tetrazolium sulfate
T-54	2-(4-phenylsulfonylphenyl)-3-(2-chloro-4-cyanophenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium chloride
T-55	2-(2-methoxy-4-nitrophenyl)-3-(4-cyanophenyl)-5-phenyl-2H-tetrazolium chloride
T-56	2-(3-propionylphenyl)-3-(2,4-dichlorophenyl)-5-(3-nitrophenyl)-2H-tetrazolium chloride
T-57	2-(2-biphenyl)-3-(3,4-dichlorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium chloride
T-58	2-(4-nitrophenyl)-3-(3-pyridyl)-5-phenyl-2H-tetrazolium perchlorate
T-59	2-(2-chloro-4-cyanophenyl)-3-(2-chloro-5-trifluoromethylphenyl)-5-(3-chlorophenyl)-2H-tetrazolium tetrafluoroborate
T-60	2-(4-pyridyl)-3-(2,3,4,5-tetrafluorophenyl)-5-phenyl-2H-tetrazolium hexafluorophosphate
T-61	2-(2-benzoylphenyl)-3-(2,4-dichlorophenyl)-5-(3-nitrophenyl)-2H-tetrazolium hexafluorophosphate
T-62	2-(1-nitro-2-naphthyl)-3-(2-methyl-4-nitrophenyl)-5-(4-chlorophenyl)-2H-tetrazolium chloride
T-63	2-(3-phenylformamidophenyl)-3-(2-nitro-4-chlorophenyl)-5-(3-chlorophenyl)-2H-tetrazolium tetrafluoroborate
T-64	2-(anthraquinone-2-yl)-3-(2-nitro-4-chlorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium tetrafluoroborate
T-65	2-(2,5-dichlorophenyl)-3-phenyl-5-(4-nitrophenyl)-2H-tetrazolium tetrafluoroborate

TABLE IV-Continued

Exemplary Preferred Tetrazolium Salts for forming Dyes of Enhanced Stability	
Tetrazolium Salt	
T-66	2-(2,4-dibromophenyl)-3-(4-nitrophenyl)-5-methyl-2H-tetrazolium chloride
T-67	2-(2,5-dichlorophenyl)-3-(2-methoxy-4-nitrophenyl)-5-(4-methoxyphenyl)-2H-tetrazolium chloride
10 T-68	2-(2,4,5-trichlorophenyl)-3-(3-nitrophenyl)-5-ethyl-2H-tetrazolium bromide
T-69	2-(4-trifluoromethylphenyl)-3-(4-cyanophenyl)-5-n-propyl-2H-tetrazolium bromide
T-70	2-(2-phenoxy-4-chlorophenyl)-3-(4-nitrophenyl)-5-n-hexyl-2H-tetrazolium tetrafluoroborate
15 T-71	2-(2-bromophenyl)-3-(2-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-72	2,3-di(4-nitrophenyl)-5-methyl-2H-tetrazolium hexafluorophosphate
T-73	2-(4-bromophenyl)-3-(4-nitrophenyl)-5-tert-butyl-2H-tetrazolium tetrafluoroborate
20 T-74	2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride
T-75	2-(2-nitro-1-naphthyl)-3-(4-cyanophenyl)-5-methyl-2H-tetrazolium tetrafluoroborate
T-76	2-(2-nitro-4-chloro-1-naphthyl)-3-(4-trifluoromethylphenyl)-5-methyl-2H-tetrazolium perchlorate
25 T-77	2-(2-bromo-4-cyano-1-naphthyl)-3-(4-nitrophenyl)-5-n-propyl-2H-tetrazolium chloride
T-78	2-(1-bromo-4-nitro-2-naphthyl)-3-(3,4-dichlorophenyl)-5-ethyl-2H-tetrazolium hexafluorophosphate
T-79	2-(3,6,7-trichloro-1-naphthyl)-3-(4-nitrophenyl)-5-n-hexyl-2H-tetrazolium hexafluorophosphate
30 T-80	2-(5-nitro-2-naphthyl)-3-(2,4,5-trichlorophenyl)-5-isobutyl-2H-tetrazolium hexafluorophosphate
T-81	2-(5,8-dichloro-1-naphthyl)-3-(4-nitrophenyl)-5-methyl-2H-tetrazolium sulfate
35 T-82	2-(3,5-dibromo-2-naphthyl)-3-(4-chlorophenyl)-5-propyl-2H-tetrazolium iodide
T-83	2,3-di(2-chlorophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-84	2-(2-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
40 T-85	2-(2-chloro-4-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-86	2-(2-chlorophenyl)-3-phenyl-5-(3-nitrophenyl)-2H-tetrazolium tetrafluoroborate
T-87	2-(2,4-dinitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-88	2,3,5-tri(4-nitrophenyl)-2H-tetrazolium chloride
45 T-89	2-(2-methyl-4-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-90	2-(4-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-91	2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-92	2-(4-nitrophenyl)-3-phenyl-5-(4-chlorophenyl)-2H-tetrazolium tetrafluoroborate
50 T-93	2,3-di(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-94	2,5-di(4-nitrophenyl)-3-phenyl-2H-tetrazolium tetrafluoroborate
T-95	2,3-di(4-nitrophenyl)-5-(4-methoxyphenyl)-2H-tetrazolium tetrafluoroborate
55 T-96	2-(3-chlorophenyl)-3-(4-cyanophenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium iodide
T-97	2-(4-phenylsulfonyl phenyl)-3-(3,5-dichlorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium chloride
T-98	2-(4-diphenyl)-3-(3,5-dinitrophenyl)-5-(4-trimethylammonium phenyl)-2H-tetrazolium dichloride
60 T-99	2-(4-acetylphenyl)-3-(3-trifluoromethyl-4-chlorophenyl)-5-(4-nitrophenyl)-2H-tetrazolium bromide

65 Any anion known to be useful in formazan dye forming tetrazolium salts can be used in the practice of this invention. Preferred anions are those set forth in Tables II and IV. Any one of these anions can be incorporated

in place of any other anion in any of the tetrazolium salts set forth in Tables II and IV. Non-basic, non-nucleophilic anions are preferred, such as tetrafluoroborate and hexafluorophosphate, for example. Such anions provide the resulting tetrazolium salt with enhanced protection against anion induced reduction, and for this reason their use is preferred.

It has been recognized prior to this invention that the color of the formazan dye can be influenced by the incorporation of various metal salts in combination with the tetrazolium salt. Jaeken et al, British Pat. No. 670,883, published April 30, 1952, of salts of metals such as iron, nickel, cobalt, copper, zinc, cadmium, chromium, titanium, molybdenum or tungsten, for this purpose. It is recognized that such metal salts can be used also in the practice of this invention for the purpose of chelating the formazan dye produced on exposure, thereby stabilizing the dye against subsequent fading. All formazan dyes are capable of forming at least bidentate chelates. While distinct stabilization is observed for bidentate and tridentate formazan dye chelates, the use of tetrazolium salts that form tridentate chelates gives greater stabilization and is preferred. Exemplary of tetrazolium salts capable of forming tridentate formazan dye chelates are those having one or more N-heterocyclic aromatic rings in the 2 or 3 position, such as 2-pyridyl and 2-azolyl (e.g. 2-thiazolyl, 2-benzothiazolyl, 2-oxazolyl, 2-benzoxazolyl, etc.) ring structures, for example. Certain exemplary preferred tetrazolium salts for forming highly stable tridentate formazan dye chelates are set forth in Table V.

TABLE V

Exemplary Preferred Tetrazolium Salts for Forming Tridentate Formazan Dye Chelates	
T-100	2-(2-pyridyl)-3-(2,6-dimethylphenyl)-5-phenyl-2H-tetrazolium hexafluorophosphate
T-101	2-(2-pyridyl)-3-phenyl-5-n-hexyl-2H-tetrazolium tetrafluoroborate
T-102	2-(2-pyridyl)-3,5-diphenyl-2H-tetrazolium bromide
T-103	2-(benzothiazol-2-yl)-3,5-diphenyl-2H-tetrazolium bromide
T-104	2-(2-pyridyl)-3-(4-chlorophenyl)-5-phenyl-2H-tetrazolium nitrate
T-105	2,2'-di(thiazol-2-yl)-3,3'-diphenyl-5,5'-diphenylene-di(2H-tetrazolium iodide)
T-106	2,3-di(benzothiazol-2-yl)-5-dodecyl-2H-tetrazolium chloride
T-107	2-phenyl-3-(benzothiazol-2-yl)-5-(3-chlorophenyl)-2H-tetrazolium chloride
T-108	2,3-di(benzothiazol-2-yl)-5-cyano-2H-tetrazolium chloride
T-109	2-phenyl-3-(benzothiazol-2-yl)-5-propyl-2H-tetrazolium iodide
T-110	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide
T-111	2-(2-pyridyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-112	2-(2-quinolyl)-3-phenyl-5-(3-nitrophenyl)-2H-tetrazolium tetrafluoroborate
T-113	2-(2-pyridyl)-3-(2-tolyl)-5-(4-cyanophenyl)-2H-tetrazolium hexafluorophosphate
T-114	1,5-naphthalene-bis[3-[2-(2-pyridyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium tetrafluoroborate]]
T-115	2-(2-pyridyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium nitrate
T-116	2-(benzothiazol-2-yl)-3,5-di(4-chlorophenyl)-2H-tetrazolium chloride
T-117	2-(benzothiazol-2-yl)-3-(3-nitrophenyl)-5-(4-iodophenyl)-2H-tetrazolium tetrafluoroborate
T-118	2-(benzothiazol-2-yl)-3-(2-fluorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium tetrafluoroborate
T-119	2-(4,5-dimethylthiazol-2-yl)-3-(3-trifluoromethylphenyl)-5-(4-bromophenyl)-

TABLE V-Continued

Exemplary Preferred Tetrazolium Salts for Forming Tridentate Formazan Dye Chelates	
T-120	2H-tetrazolium tetrafluoroborate 2-(benzoxazol-2-yl)-3-(4-chlorophenyl)-5-phenyl-2H-tetrazolium chloride

In addition to greater stabilities, another advantage of chelated formazan dyes is that they are generally more absorptive in the red spectrum than the corresponding unchelated formazan dyes. Thus, whereas formazan dyes generally tend toward red images, chelated formazan dyes are considerably bluer, producing more neutral images.

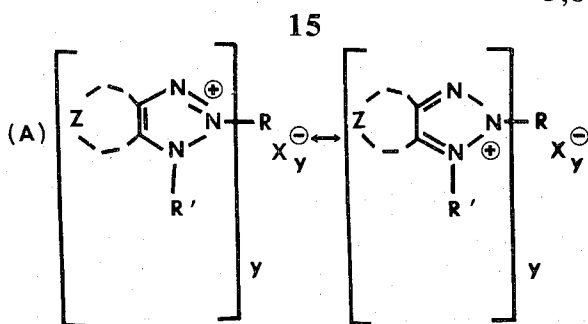
From the foregoing it is apparent that the formazan dye images produced according to this invention can, if desired, be stabilized either by adding electronegative substituents to the tetrazole nucleus or by incorporating metal salts in combination with the tetrazolium salts. If desired, these two stabilization techniques can be used in combination. For example, the tetrazolium salts T-104 and T-112 through T-120 are sufficiently electronegative in their tetrazole nucleus substituents to constitute preferred tetrazolium salts in terms of stability, even without chelation. These tetrazolium salts can be used to produce formazan dyes of even greater stability by forming tridentate chelates.

Triazolium Salts

It is further recognized that 1,3-diazabicyclo[3.1.0]hex-3-enes can be used as photoreductants with the triazolium salts disclosed in copending application Ser. No. 384,860, noted above. As disclosed in that application, any triazolium salt which undergoes a detectible color change upon reduction to the corresponding dye can be employed. Since the azo-amine dyes exhibit higher optical densities than their parent triazolium salts, they produce a sharp visible contrast with background areas. It is a distinct advantage of this invention that triazolium salts are readily available in colorless form and tend to remain colorless in background areas during storage of the photographic elements. Also of importance is that the azo-amine dyes produced by the triazolium salts of this invention can be chosen to provide any one of a wide variety of colors, and, most importantly, images of neutral hue can be formed by the azo-amine dyes. Hence, it is possible for the photographic elements of this invention to provide readily neutral hue images on transparent or white backgrounds, as is most desirable for many recording applications. Finally, the azo-amine dye images produced are generally more stable than comparable formazan dye images.

The triazolium salts preferred for the practice of this invention are those having an aromatic ring fused with the triazole nucleus. Such triazolium salts produce azo-amine dyes of increased density as compared to triazolium salts lacking a fused aromatic ring. Further, these latter triazolium salts typically produce azo-amine dyes of a yellow hue, whereas triazolium salts containing an aromatic ring fused with the triazole nucleus are typically either shifted toward the red portion of the spectrum or more neutral in hue.

The triazolium salts which are most preferred for use in the practice of this invention are those which exist in the tautomeric forms indicated below:



wherein Z is comprised of the atoms necessary to complete a fused, aromatic ring structure; y is 1 or 2; R is an aromatic or aromatic-like heterocyclic group; R' is an aromatic substituent, an aromatic-like heterocyclic substituent or an alkyl group having from 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms and X is an anion.

As employed herein the term "aromatic-like heterocyclic substituent" is defined as a substituent group including a 5 or 6 member ring structure having conjugated unsaturation and containing in addition to carbon atoms in the ring structure at least one atom selected from the group consisting of nitrogen, oxygen and sulfur. Exemplary of such aromatic-like heterocyclic substituents are pyridyl, oxazolyl, thiazolyl, quinolyl, benzoxazolyl, benzothiazolyl and similar substituents.

In a specific preferred form of the invention Z is chosen to form a benzotriazole, naphtho[1,2-d]triazole or naphtho[2,3-d]triazole nucleus. Generally triazolium salts containing naphthotriazole nuclei are preferred over those containing benzotriazole nuclei. When y is 2, R is preferably an arylene group—e.g., a phenylene, bisphenylene, naphthylene, anthrylene, etc. When y is 1, R is preferably an aryl group. R' is preferably an aryl or aromatic-like heterocyclic group.

It is recognized that R, R' and Z can include a variety of ring substituents. Exemplary of specifically contemplated ring substituents are lower alkyl (i.e., 1 to 6 carbon atoms), lower alkenyl (i.e., 2 to 6 carbon atoms), lower alkynyl (i.e., 2 to 6 carbon atoms), benzyl, styryl, phenyl, biphenyl, naphthyl, alkoxy (e.g., methoxy, ethoxy, etc.), aryloxy (e.g., phenoxy), carboalkoxy (e.g., carbomethoxy, carboethoxy, etc.), carboaryloxy (e.g., carbophenoxy, carbonaphthoxy), acyloxy (e.g., acetoxy, benzoxy, etc.), acyl (e.g., acetyl, benzoyl, etc.), halogen (i.e., fluoride, chloride, bromide, iodide), cyano, azido, nitro, haloalkyl (e.g., trifluoromethyl, trifluoroethyl, etc.), amino (e.g., dimethylamino), amido (e.g., acetamido, benzamido), ammonium (e.g., trimethylammonium), azo (e.g., phenylazo), sulfonyl (e.g., methylsulfonyl, phenylsulfonyl), sulfoxy (e.g., methylsulfoxy), sulfonium (e.g., dimethyl sulfonium), silyl (e.g., trimethylsilane) and thioether (e.g., methylthio) substituents. While these and other substituents

can be chosen to advantage to influence image densities, ease of reduction, dye color and stability, etc., the capability of a triazolium salt to be reduced to an azoamine dye is in general controlled by the triazole nucleus configuration rather than the substituents chosen. To enhance the stability of the azoamine dyes produced it is preferred to incorporate within the triazolium salts of this invention predominantly electro-negative substituents.

Any anion known to be useful in azoamine dye forming triazolium salts can be used in the practice of this invention. Preferred anions are those set forth in Table VI. Any one of these anions can be incorporated in place of any other anion in any of the triazolium salts set forth in Table VI. Non-basic non-nucleophilic anions are preferred, such as tetrafluoroborate and hexafluorophosphate, for example. Such anions provide the resulting triazolium salt with enhanced protection against anion induced reduction, and for this reason their use is preferred.

As with formazan dyes, it is recognized that the color of the azoamine dyes can be influenced by the incorporation of various metal salts in combination with the triazolium salt. Salts of metals such as iron, nickel, cobalt, copper, zinc, cadmium, chromium, titanium molybdenum or tungsten are useful for this purpose. It is also recognized that such metal salts can be used in the practice of this invention for the purpose of chelating the azoamine dye produced on exposure to thereby further stabilize the dye against subsequent fading. All azoamine dyes are capable of forming at least bidentate chelates. While distinct stabilization can be achieved with bidentate and tridentate chelates, the use of triazolium salts that form tridentate chelates gives greater stabilization and is preferred. Exemplary of triazolium salts capable of forming tridentate azoamine dye chelates are those having one or more N-heterocyclic aromatic rings in the 1 or 2 position, such as 2-pyridyl and 2-azolyl (e.g., 2-thiazolyl, 2-benzothiazolyl), 2-oxazolyl, 2-benzoxazolyl, etc.) ring structures, for example.

Exemplary preferred triazolium salts useful in the practice of this invention are set forth below in Table VI:

TABLE VI

Exemplary Preferred Triazolium Salts for Forming Azo-Amine Dyes	
T-121	1-methyl-2-phenyl-2H-1,2,3-triazolium tetrafluoroborate
T-122	1-phenyl-2-(2-anilino-4-nitrophenyl)-2H-1,2,3-triazolium fluorosulfonate
T-123	1-(n-propyl)-2-phenyl-2H-1,2,3-triazolium chloride
T-124	1-neopentyl-2-phenyl-2H-1,2,3-triazolium iodide
T-125	1-(2,4-dinitrophenyl)-2-phenyl-2H-1,2,3-triazolium fluorosulfonate
T-126	1-methyl-2-phenyl-5(or 6)-nitro-2H-benzo-1,2,3-triazolium hexafluorophosphate
T-127	1-(n-butyl)-2-phenyl-6-nitro-2H-benzo-1,2,3-triazolium iodide
T-128	2,3-diphenyl-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate
T-129	2-phenyl-3-(n-hexyl)-2H-naphtho[1,2-d]-1,2,3-triazolium iodide
T-130	2-phenyl-3-(pyrid-2-yl)-2H-naphtho[1,2-d]-1,2,3-triazolium perchlorate
T-131	2-(3-chlorophenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium perchlorate
T-132	2-(2-trifluoromethylphenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate

TABLE VI-Continued

Exemplary Preferred Triazolium Salts for Forming Azo-Amine Dyes	
T-133	2-(4-carbomethoxyphenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate
T-134	di[2-(2,3,4,5-tetrachlorophenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium] tetrachlorozincate
T-135	2-(4-fluoro-4-biphenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium chloride
T-136	2-(4-cyano-1-naphthyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium bromide
T-137	2-(4-nitrophenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate
T-138	2-(2,4-dinitrophenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate
T-139	2-(1-nitro-2-naphthyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate
T-140	2-[2-(9,10-anthraquinolyl)]-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium bromide
T-141	2-(4-Methoxyphenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate
T-142	2,3-diphenyl-2H-(5-phenoxy-naphtho[1,2-d])-1,2,3-triazolium nitrate
T-143	2-phenyl-3-(4-thiomethylphenyl)-2H-naphtho[1,2-d]-1,2,3-triazolium chloride
T-144	2-phenyl-3-(2-fluorophenyl)-2H-(7,8-dimethylnaphtho[1,2-d])-1,2,3-triazolium hexafluorophosphate
T-145	2,2'-(p-phenylene)-bis(3-phenyl)-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate
T-146	2,2'-(2-methyl-1,4-phenylene)-bis(3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate)
T-147	2,2'-(p-phenylene)-bis(3-benzothiazol-2-yl-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate)
T-148	2,2'-(2-chloro-1,4-phenylene)-bis(3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate)
T-149	2,2'-(4,4'-biphenylene)-bis(3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate)
T-150	2,2'-(3,3'-dimethoxy-4,4'-biphenylene)-bis(3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate)
T-151	2,2'-(1,5-naphthylene)-bis(3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium hexafluorophosphate)
T-152	2,2'-[1,5-(9,10-anthraquinolyl)]-bis(3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate)
T-153	2-(4-methoxyphenyl)-3-phenyl-2H-naphtho[1,2-d]-1,2,3-triazolium bromide
T-154	2,3-di(4-methoxyphenyl)-5-nitro-2H-naphtho[1,2-d]-1,2,3-triazolium bromide
T-155	2,3-di(4-chlorophenyl)-5-methoxy-2H-naphtho[1,2-d]-1,2,3-triazolium perchlorate
T-156	2-(3-trifluoromethylphenyl)-6,9-dibromo-2H-naphtho[1,2-d]-1,2,3-triazolium tetrafluoroborate

Procedures for preparing triazolium salts useful in the practice of this invention are known in the art. Exemplary of known preparative techniques are those disclosed by Krollpfeiffer, Mulhausen and Wolf, *Annalen*, 508, 39, (1933); Begtrup and Poulsen, *Acta Chem. Scand.* 25, 2096 (1971); and Charrier and Beretta, *Gazzetta Chimica Italiana*, 53, 773 (1923) as well as the French patent noted above.

To form a radiation-sensitive composition useful in the present invention it is merely necessary to bring together the photoreductant and the image-recording compound. The radiation-sensitive composition can then be brought into a spatially fixed relationship, as by coating the composition onto a support to form a photographic element according to the present invention. For maximum efficiency of performance it is preferred that the components of the radiation-sensitive

composition, particularly, the photoreductant and the image-recording compound, be intimately associated. This can be readily achieved, for example, by dissolving the reactants in a solvent system.

5 The solvent system can be a common solvent or a combination of miscible solvents which together bring all of the reactants into solution. Typical preferred solvents which can be used alone or in combination are lower alkanols, such as methanol, ethanol, isopropanol, 10 t-butanol and the like; ketones, such as methylethyl ketone, acetone and the like; water; liquid hydrocarbons; chlorinated hydrocarbons, such as chloroform, ethylene chloride, carbon tetrachloride and the like; ethers, such as diethyl ether, tetrahydrofuran, and the like; acetonitrile; dimethyl sulfoxide and dimethyl formamide.

For ease of coating and for the purposes of imparting strength and resilience to the radiation-sensitive layer it is generally preferred to disperse the radiation-sensitive reactants in a resinous polymer matrix or 20 binder. A wide variety of polymers can be used as binders. In order to be useful it is only necessary that the binders be chemically compatible with the radiation-sensitive reactants. In addition to performing their function as a binder the polymers can also serve as hydrogen sources. For example, certain of the polymers set forth below can be used both as binders and as hydrogen sources.

It is preferred to employ linear film-forming polymers such as, for example, cellulose compounds, such as 30 ethyl cellulose, butyl cellulose, cellulose acetate, cellulose triacetate, cellulose butyrate, cellulose acetate butyrate and the like; vinyl polymers, such as poly(vinyl acetate), poly(vinylidene chloride), a poly(vinyl acetal) such as poly(vinyl butyral), poly(vinyl chloride-co-vinyl acetate), polystyrene, and polymers of alkyl acrylates and methacrylates including copolymers incorporating acrylic or methacrylic acid; and polyesters, such as poly(ethylene glycol-co-isophthalic acid-co-terephthalic acid), poly(p-cyclohexane dicarboxylic acid-co-isophthalic acid-co-cyclohexylenebismethanol), poly(p-cyclohexanedicarboxylic acid-co-2,2,4,4-tetramethylcyclobutane-1,3-diol) and the like. The condensation product of epichlorohydrin and bisphenol is also a preferred useful binder. Generally any binder known to have utility in photographic elements and, particularly, diazo photographic elements can be used in the practice of this invention. These binders are well known to those skilled in the art so that no useful purpose would be served by including an extensive catalogue of representative binders in this specification. Any of the vehicles disclosed in *Product Licensing Index* Vol. 92, December 1971, publication 9232, at 55 page 108, can be used as binders in the photographic elements of this invention.

While the proportions of the reactants forming the radiation-sensitive layer of a photographic element can be varied widely, it is generally preferred for most efficient utilization of the reactants that they be present in roughly stoichiometric concentrations—that is, equal molar concentrations. One or more of the reactants can, of course, be present in excess. Where a metal is added for the purpose of chelating the formazan dye, it is preferably incorporated in a proportion of from 0.1 to 10 moles per mole of triazolium salt. The binder can account for up to 99% by weight of the radiation-sensitive layer, but is typically employed in proportions

of from 50 to 90% by weight of the radiation-sensitive layer. It is, of course, recognized that the binder can be omitted entirely from the radiation-sensitive layer. The surface or areal densities of the reactants can vary as a function of the formazan dyes formed and the image densities desired. It is generally preferred to incorporate the tetrazolium salt in a concentration of at least 1×10^{-6} moles per square decimeter and, most preferably, in a concentration of from 1×10^{-5} to 4×10^{-5} moles per square decimeter. The areal densities of the remaining reactants are, of course, proportionate. Typically the radiation-sensitive layer can vary widely in thickness depending on the characteristics desired for the photographic element—e.g. image density, flexibility, transparency, etc. For most photographic applications coating thicknesses in the range of from 2 to 20 microns are preferred.

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. Preferred photographic supports for most applications are paper or film supports. The support can incorporate one or more subbing layers for the purpose of altering its surface properties. Typically subbing layers are employed to enhance the adherency of the radiation-sensitive coating to the support. Suitable exemplary supports are disclosed in *Product Licensing Index* Vol. 92, December 1971, publication 9232, at page 108.

The radiation-sensitive layer can be formed on the support using any conventional coating technique. Typically the reactants, the binder (if employed) and any other desired addenda are dissolved in a solvent system and coated onto the support 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* publication cited above, at page 109. Coating aids can be incorporated into the coating composition to facilitate coating as disclosed on page 108 of the *Product Licensing Index* publication. It is also possible to incorporate antistatic layers and/or matting agents as disclosed on this page of the *Product Licensing Index* publication.

It is a distinct advantage of this invention that the photographic elements can be processed in a dry state using commercially available exposure and processing equipment. Exposure to actinic radiation in the ultraviolet or visible portions of the spectrum can be readily achieved using mercury arc lamps, carbon arc lamps, photoflood lamps, lasers and the like.

The invention is further illustrated by the following examples.

EXAMPLE 1

A. β -phenyl- β -methoxyaminopropiophenone

This compound is prepared according to the procedure of A. H. Blatt, *J. Am. Chem. Soc.* 61, 3494 (1939).

A solution of benzalacetophenone (10.4gm., 0.05 mole) and methoxyamine hydrochloride (4.18gm., 0.05 mole) in ethyl alcohol (25ml.) was treated with N,N-diisopropylethylamine (6.46gm., 0.05 mole). The resulting solution was treated in a water bath at 60°C for 4 hours. On cooling, a colorless solid crystallized. The solid was collected, washed with a small volume of

ethyl alcohol, and air-dried to yield a colorless crystalline solid, 5.23gm., 41%; m.p. 50°–52°C. (Reported m.p. 54°–55°C).

B. Trans-2-phenyl-3-benzoylaziridine

This compound is also prepared according to the procedure of A. H. Blatt given above.

A solution of β -phenyl- β -methoxyaminopropiophenone (5.10gm., 0.02 mole) in methanol (20ml.) containing sodium methoxide (prepared by adding 0.92gm. sodium metal to 20ml. methanol) was heated in a water bath at 60°C for 10 minutes. A solid began to crystallize almost immediately. The mixture was cooled and the solid was collected, washed with methanol, and then air-dried to yield a colorless solid, 3.37gm., 76%, m.p. 99°–102°C. (Reported m.p. 100°–101°C).

C. 2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene (PR-3)

This compound is prepared according to the procedure of H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, *J. Org. Chem.* 32, 2708 (1967).

A solution of trans-2-3-benzoylaziridine (2.0gm., 9mmole) in absolute ethyl alcohol (40ml.) containing benzaldehyde (6ml.) and ammonium bromide (0.2gm.) was saturated with ammonia and allowed to stand 4 days at room temperature. Crystals began to separate after a few hours. The colorless solid that had separated was collected, washed with ethyl alcohol and air-dried to yield colorless crystals, 1.30gm., 49%, m.p. 128°–30°C (mixture of two isomers). (Reported m.p. 153°–154°C for one isomer; see A. Padwa, et al., *J. Am. Chem. Soc.* 92, 1778 (1970)).

D. Radiation-Sensitive Element

PR-3 (0.30gm., 1mmole) and 2,3,5-triphenyl-2H-tetrazolium chloride (T-1) (0.66gm., 2mmoles) were dissolved in 1 ml. of an equivolume mixture of methanol and chloroform and then brought to a volume of 15 ml. with a solution of 10% by weight cellulose acetate butyrate in dichloroethane. The resulting mixture was coated on a poly(ethylene terephthalate) film support to produce a wet coating thickness of 150 microns. After drying the film coating was imagewise exposed with an exposure unit employing a 40 cm wide belt transport spaced 1.3 cm beneath a dry cathode, high pressure mercury vapor lamp rich in ultraviolet, rated at approximately 30 watts per cm, commercially available under the tradename Ozalid, at a speed of 150 cm per minute. The resulting exposed strip was heated at 150°C for 30 seconds to give a stable, reddish-orange printout in areas exposed to actinic radiation. No significant background printout was observed upon handling the image element in room light.

EXAMPLE 2

The procedure of Example 1 was repeated, except that the imaged radiation-sensitive element was given a uniform re-exposure to actinic radiation under conditions similar to those of the original, imagewise exposure. Some background printout was noted.

EXAMPLE 3

The procedure of Example 1 was repeated, except that the imaged radiation-sensitive element was swabbed over the coating with concentrated hydro-

chloric acid. The imaged element was then given a uniform re-exposure to actinic radiation under conditions similar to those of the original, imagewise exposure. No background printout was observed.

EXAMPLES 4 through 10

The procedure of Example 1 was repeated, except that photoreductants PR-3, PR-12, PR-31 and PR-4 were employed in combination with tetrazolium salts T-1 and T-74. Similar results were obtained.

Based on known comparative reactivities of other tetrazolium and triazolium salts, as is amply shown in copending applications Ser. Nos. 384,858; 384,859; 384,860 and 384,861, previously noted, other tetrazolium and triazolium salts are capable of similarly producing images when substituted for T-1 or T-74. Similarly, based on the knowledge of the art with respect to reductive imaging, as in silver-dye bleach systems, it is apparent that azo, aminotriphenylmethane, xanthene, triazine, nitroso, indigo and phthalocyanine dye images can be bleached by substituting these dyes for T-1 or T-74.

The invention has been described with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In a photographic element comprising an image-recording means for registering an imagewise change in absorption of electromagnetic radiation, when reduced by an activated photoreductant, said means being selected from the group consisting of aminotriarylmethane dyes, azo dyes, xanthene dyes, triazine dyes, nitroso dye complexes, indigo dyes, phthalocyanine dyes, triazolium salts and tetrazolium salts,

a photoreductant in intimate association with said image-recording means, and

means for supporting said image-recording means and said photoreductant,

the improvement comprising employing as said photoreductant, a 1,3-diazabicyclo[3.1.0]hex-3-ene.

2. In a photographic element according to claim 1, the further improvement in which a binder is employed to hold said photoreductant and said image-recording means in intimate association and in fixed spatial relationship.

3. In a photographic element according to claim 2 the further improvement in which said polymer binder is a cellulosic compound.

4. In a photographic element according to claim 3 the further improvement in which said polymer binder is cellulose acetate butyrate.

5. In a photographic element according to claim 1, the further improvement in which said image-recording means is a triaryl-2H-tetrazolium salt.

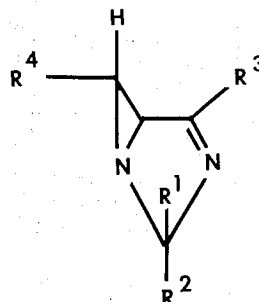
6. In a photographic element according to claim 1 the further improvement in which from 0.1 to 10 moles of said image-recording means are present per mole of photoreductant.

7. In a photographic element according to claim 6 the further improvement in which said image-recording means and said photoreductant are present in substantially equal molar proportions.

8. In a photographic element according to claim 1 the further improvement in which said photographic element incorporates a binder in said image-recording layer in a concentration of up to about 99% by weight.

9. In a photographic element according to claim 8 the further improvement in which said photographic element incorporates a binder in said image-recording layer in a concentration of from 50 to 90% by weight.

10. In a photographic element according to claim 1 the further improvement in which said photoreductant defined by formula



wherein:

R¹ and R² are independently chosen from the class consisting of alkyl, aralkyl, alkaryl and aryl substituents or in conjunction constitute an alkylene substituent;

R³ is an aryl or electron withdrawing substituent; and R⁴ is an aryl or alkaryl substituent.

11. In a photographic element according to claim 10 the further improvement in which R³ is a phenyl substituent.

12. In a photographic element according to claim 10 the further improvement in which at least one of said aryl substituents is in turn substituted with at least one alkyl, nitro, halogen, alkoxycarbonyl, aryloxy carbonyl or amino substituent.

13. In a photographic element according to claim 10 the further improvement in which R³ and R⁴ are phenyl substituents.

14. In a photographic element according to claim 13 the further improvement in which said photographic element is a 2,4,6-triphenyl-diazabicyclo[3.1.0]hex-3-ene.

15. In a photographic element according to claim 14 the further improvement in which at least one of said 2-, 4- and 6-position phenyl rings is nitro-substituted.

16. In a photographic element according to claim 10, the further improvement in which R¹ and R² are alkyl substituents.

17. In a photographic element according to claim 16 the further improvement in which R³ and R⁴ are aryl substituents.

18. In a photographic element according to claim 10 the further improvement in which said alkyl and alkylene substituents and substituent moieties each have 20 or fewer carbon atoms.

19. In a photographic element according to claim 10 the further improvement in which said alkyl and alkylene substituents and substituent moieties each have 6 or fewer carbon atoms.

20. In a photographic element according to claim 10 the further improvement in which said aryl substituents are phenyl or naphthyl substituents.

21. A process of image-recording which comprises imagewise exposing to actinic radiation a photographic element incorporating an image-recording means for registering an absorption change when

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reduced by an activated photoreductant, said means being selected from the group consisting of aminotriarylmethane dyes, azo dyes, xanthene dyes, triazine dyes, nitroso dye complexes, indigo dyes, phthalocyanine dyes, triazolium salts and tetrazolium salts; and a 1,3-diazabicyclo[3.1.0]hex-3-ene photoreductant; to convert the photoreductant to a thermally activatable reducing agent precursor; heating the reducing agent precursor to a temperature sufficient to convert it to a reducing agent, and forming a visible image by selectively reducing the image-recording means within exposed portions of the photographic element.

22. An image-recording process according to claim 21 in which said photographic element is heated to a temperature in the range of from 70° to 150°C.

23. An image-recording process according to claim 21 in which said photographic element is imagewise exposed to light.

24. An image-recording process according to claim 23 in which said radiation-sensitive layer is imagewise exposed to ultraviolet light.

25. An image-recording process according to claim 21 in which said photographic element is fixed after exposure and heating by use of a mineral acid.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,894,874

DATED : July 15, 1975

INVENTOR(S) : Schleigh et al

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

Line [75] of the title page , "C. Deselms" should read --C. DeSelms--.

Column 21, line 33, "xanthane" should read --xanthene--.

Signed and Sealed this

thirteenth Day of April 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks