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Schleigh

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[54] **2H-BENZIMIDAZOLE PHOTOREDUCTIVE IMAGING**

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[56] **References Cited**

UNITED STATES PATENTS

3,278,366	10/1966	Schiele	96/88
3,390,996	7/1968	MacLachlan	96/48 R

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[57] **ABSTRACT**

A reducible, image-forming compound is present in a radiation-sensitive layer in combination with a 2H-benzimidazole. Upon exposure the 2H-benzimidazole is converted to a dihydrobenzimidazole reducing agent in radiation-struck areas of the layer. Subsequent heating of the layer fixes the 2H-benzimidazole remaining in non-irradiated areas by converting it to a 1H-benzimidazole. Heating can also have the effect of accelerating reduction of the image-forming compound.

26 Claims, No Drawings

2H-BENZIMIDAZOLE PHOTOREDUCTIVE IMAGING

This invention relates to a photographic element which requires only heat processing and which exhibits low, stable background densities and to a process for recording images therewith. In a specific aspect, this invention is directed 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 for image recording.

It is well known in the photographic arts to record images by incorporating within a radiation-sensitive layer of a photographic element a dye precursor of low optical density capable of conversion to a visible dye. In order to avoid dye printout in background areas after exposure it is conventional practice to inactivate and/or wash out the dye precursor. Where the dye is formed by oxidation of its precursor there is frequently a problem with background printout attributable to atmospheric oxidation of the dye precursor remaining in the background areas. The loss of contrast is, of course, further accelerated if the dye itself also tends to fade.

Photographic systems utilizing imidazoles as oxidants for leuco dyes are known to the art. In MacLachlan U.S. Pat. No. 3,383,212, Cescon U.S. Pat. No. 3,390,994 and MacLachlan U.S. Pat. No. 3,390,996, for example, photographic systems are disclosed which convert leuco dyes to visibly colored forms by oxidation upon exposure. A variety of suitable oxidants is disclosed, including biimidazoles, such as hexaarylbiimidazoles. These systems also require other compounds forming a redox couple to be present.

Image-recording elements employing compounds which are reducible to change their absorption of electromagnetic radiation 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 azo-amine dyes, respectively, employing in the presence of labile hydrogen atoms a photo-reductant 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 amino 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 an object of this invention to provide an image-recording element and a process for its use capable of direct image printout using reducible image-recording compounds. It is a more specific object to provide such an element and process that uses only heat alone for fixing. It is a further object to provide such an element and a process for its use which after exposure can enhance printout and fix unexposed areas in a single heating step. It is an additional object to provide a direct printout, dry processed photographic element that is capable of producing photographs having low density, stable backgrounds.

In one aspect this invention is directed to a photographic element having a support and coated thereon at least one radiation-sensitive image-recording layer.

The image-recording layer is comprised of an image-recording means which undergoes a radiation-absorption change upon reduction and, as a photoreductant in intimate association with said image-recording means capable of forming a reducing agent in the presence of labile hydrogen atoms, a 2H-benzimidazole.

In another aspect this invention is directed to an image-recording process which comprises converting a 2H-benzimidazole within a selected areal portion of a radiation-sensitive layer of a photographic element to a dihydobenzimidazole by imagewise exposing the 2H-benzimidazole to actinic radiation in the presence of labile hydrogen atoms. An image-recording means capable of changing its radiation-absorption characteristic upon reduction is reduced with the dihydrobenzimidazole generated within the selected areal portions of the layer. The layer is heated to convert residual 2H-benzimidazole not exposed to actinic radiation to 1H-benzimidazole.

In a specifically preferred embodiment of the invention an image-recording compound capable of changing its 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 2H-benzimidazole photoreductant are associated within a binder in the presence of a source of labile hydrogen atoms 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. Actinic radiation in this case is radiation in the ultraviolet and/or visible spectrum—that is, electromagnetic radiation or less than 700nm in wavelength and, preferably, below 500nm. Exposure causes the 2H-benzimidazole to be converted to the corresponding dihydrobenzimidazole. The dihydrobenzimidazole reduces the image-forming compound so that the exposure is recorded. To allow the element to be re-exposed to actinic radiation, as in viewing, without printout of previously non-irradiated areas, the radiation-sensitive layer is heated to a temperature in the range from about 100° to 150°C to convert the remaining 2H-benzimidazole to 1H-benzimidazole, which is neither a photoreductant nor a reducing agent for the image-recording compound.

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 of 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 imagewise irradiated, both before and after fixing.

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 to

fix 2H-benzimidazole and thereby permit re-exposure to actinic radiation. Of course, if reexposure to actinic radiation is not contemplated, even heat processing can be avoided. 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 2H-benzimidazole. As employed herein, the term "photoreductant" designates a material capable of molecular photolysis or photo-induced rearrangement to generate a reducing agent. Applicant has recognized that 2H-benzimidazoles are capable, upon exposure to actinic radiation in the presence of labile hydrogen atoms, of forming dihydrobenzimidazoles, which are reducing agents.

Although it is contemplated that the 2H-benzimidazoles useful in the practice of this invention can include those having electron withdrawing substituents, such as halogen atoms, cyano groups, carboxy groups, nitro groups, carbonyl containing groups and the like, it is preferred to employ 2H-benzimidazoles which incorporate one or more electron donating substituents, since electron donating substituents increase the ease with which the dihydrobenzimidazoles produced from 2H-benzimidazoles on exposure are oxidized. Illustrative of electron donating substituents are hydroxy groups; alkoxy groups; primary, secondary and tertiary amino groups—e.g., amino, alkylamino, dialkylamino, arylamino, diarylamino, aralkylamino, diarlkylamino, morpholino, piperidino, and the like; alkylazo; alkenyl; styryl; and the like. It is generally preferred that the alkyl substituents and substituent moieties have 20 or fewer carbon atoms, most preferably six or fewer carbon atoms. The aryl substituents and substituent moieties are preferably phenyl groups.

Exemplary 2H-benzimidazole photoreductants are set forth below in Table I.

TABLE I

Exemplary 2H-Benzimidazole Photoreductants

PR-1	2,2-dimethyl-2H-benzimidazole
PR-2	2,2-diethyl-2H-benzimidazole
PR-3	2,2-di-n-hexyl-2H-benzimidazole
PR-4	spiro(2H-benzimidazole-2,1'-cyclohexane)
PR-5	dispiro(2H-benzimidazole-2,1'-cyclohexane-4',2''-2H-benzimidazole)
PR-6	2,2-dibenzyl-2H-benzimidazole
PR-7	2,2-diphenyl-2H-benzimidazole
PR-8	2,2-dimethyl-4-n-butyl-2H-benzimidazole
PR-9	2,2-diphenyl-5-n-hexyl-2H-benzimidazole
PR-10	2'-methylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-11	3'-methylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-12	4'-methylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-13	2',6'-dimethylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-14	5-methylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-15	5,6-dimethylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-16	5,5''-dimethyldispiro(2H-benzimidazole-2,1'-cyclohexane-4',2''-2H-benzimidazole)
PR-17	5,6,5'',6''-tetramethyldispiro(2H-benzimidazole-2,1'-cyclohexane-4',2''-2H-benzimidazole)
PR-18	4-bromo-2,2-dimethyl-2H-benzimidazole
PR-19	5-iodo-2,2-dimethyl-2H-benzimidazole
PR-20	5-chlorospiro(2H-benzimidazole-2,1'cyclohexane)
PR-21	4-fluorospiro(2H-benzimidazole-2,1'-cyclohexane)
PR-22	2,2-diethyl-4-trichloromethyl-2H-benzimidazole
PR-23	2,2-diphenyl-4-trifluoromethyl-2H-benzimidazole
PR-24	2',3',4',5',6'-pentachlorospiro(2H-benzimidazole-2,1'-cyclohexane)
PR-25	5-trifluoromethylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-26	2,2-dibenzyl-4-methoxy-2H-benzimidazole
PR-27	2,2-diethyl-4-isopropoxy-2H-benzimidazole
PR-28	2,2-diethyl-5-ethoxy-2H-benzimidazole
PR-29	5-methoxyspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-30	4-ethoxyspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-31	5-isopropoxyspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-32	2'-methoxyspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-33	3'-neopentoxyspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-34	4,4'-dimethoxydispiro(2H-benzimidazole-2,1'-cyclohexane-4',2''-2H-benzimidazole)
PR-35	5,5''-diisopropoxy-2'-methoxydispiro(2H-benzimidazole-2,1'-cyclohexane-4',2''-2H-benzimidazole)
PR-36	2,2-dimethyl-4-amino-2H-benzimidazole
PR-37	2,2-dimethyl-4-(N,N-dimethylamino)-2H-benzimidazole
PR-38	2,2-dimethyl-5-(N-phenylamino)-2H-benzimidazole
PR-39	2,2-dimethyl-5-(N-tolylamino)2H-benzimidazole
PR-40	4-(N,N-diphenylamino)spiro(2H-benzimidazole-2,1'-cyclohexane)
PR-41	4-(N-phenylamino)spiro(2H-benzimidazole-2,1'-cyclohexane)
PR-42	2'-morpholinospiro(2H-benzimidazole-2,1'-cyclohexane)
PR-43	2,2-diphenyl-4-piperidino-2H-benzimidazole
PR-44	2,2-diphenyl-5-methylazo-2H-benzimidazole
PR-45	2'-methylazospiro(2H-benzimidazole-2,1'-cyclohexane)
PR-46	2,2-dimethyl-5-styryl-2H-benzimidazole
PR-47	2,2-dimethyl-4-vinyl-2H-benzimidazole
PR-48	5-vinylspiro(2H-benzimidazole-2,1'-cyclohexane)
PR-49	2,2-diphenyl-5-nitro-2H-benzimidazole
PR-50	5-carbomethoxyspiro(2H-benzimidazole-2,1'-cyclohexane)

IMAGE-RECORDING MEANS

The invention can be practiced utilizing as an image-recording means any compound which is known to exhibit a change of radiation absorption characteristic upon reduction. For most applications it is preferred that a visibly detectible 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 as well as those disclosed in the MacLachlan and Cescon patents previously referred to. 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 detectible 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 compopunds 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 2H-benzimidazoles 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, etc.) or aromatic-like (e.g., pyridyl, oxazolyl, thiazolyl, quinolinyl, benzoxazolyl, benzothiazolyl, etc.) substituents in the 2 and 3 positions of the tetrazole nucleus. For purposes of illustration exemplary suitable known tetrzolium 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), are 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 bromide
T-15	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
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)]
T-22	4-phenylenbis[5-(2,3-diphenyl-2H-tetrazolium chloride)]
T-23	4,4'-biphenylylenebis[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'-biphenylylenebis[2-(3-diphenyl-5-(3,4-methylenedioxyphenyl-2H-tetrazolium chloride)]
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
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
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

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 alegbraic 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., one to six carbon atoms), lower alkenyl (i.e., two to six carbon atoms), lower alkynyl (i.e., two to six 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 nuleus 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 electronegative 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

Exemplary Hammett Sigma Values For Triphenyltetrazolium Salt Substituents

Substituent	meta	Ortho/para
$-N(CH_3)_2$	+0.05	+0.12[a]
$-t-C_4H_9$	−0.07	−0.14
$-C_2H_5$	−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
$-C_6H_5$	+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
$-SO_2CH_3$	+0.68	+0.68
$-N(CH_3)_3^+$	+0.86	+0.80
$-CO_2CH_3$	+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]+0.95 for 2 and 3 position phenyl rings as para substituent

Exemlary preferred tetrazolium salts having predominately electronegative tetrazole nucleus substituents are sete forth in Table IV. 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-chloro-phenyl)-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-chloro-phenyl)-2H-tetrazolium bromide
T-41	2-(2,4-dichlorophenyl)-3-(4-nitro-phenyl)-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-trifluoromethyl-phenyl)-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-benzoyl-phenyl)-5-(3-chlorophenyl)-2H-tetrazolium perchlorate
T-50	2-(2-nitro-4-chlorophenyl)-3-(4-phenyl-azophenyl)-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-trifluoromethylphenyl)-5-(3,4-dichloro-phenyl)-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-cyano-phenyl)-5-phenyl-2H-tetrazolium chloride
T-56	2-(3-propionylphenyl)-3-(2,4-dichloro-phenyl)-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 hexaflurophosphate
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
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
T-68	2-(2,4,5-trichlorophenyl)-3-(3-nitro-phenyl)-5-ethyl-2H-tetrazolium bromide
T-69	2-(4-trifluoromethylphenyl)-3-(4-cyano-phenyl)-5-n-propyl-2H-tetrazolium bromide
T-70	2-(2-phenoxy-4-chlorophenyl)-3-(4-nitrophenyl)-5-n-hexyl-2H-tetrazolium tetrafluoroborate
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
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
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
T-80	2-(5-nitro-2-naphthyl)-3-(2,4,5-

TABLE IV-Continued

	Exemplary Preferred Tetrazolium Salts for forming Dyes of Enhanced Stability Tetrazolium Salt
	trichlorophenyl)-5-isobutyl-2H-tetrazolium hexafluorophosphate
T-81	2-(5,8-dichloro-1-naphthyl)-3-(4-nitrophenyl)-5-methyl-2H-tetrazolium sulfate
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
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
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
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
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
T-99	2-(4-acetylphenyl)-3-(3-trifluoromethyl-4-chlorophenyl)-5-(4-nitrophenyl)-2H-tetrazolium bromide

Any anoin 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 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 Apr. 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-chlorphenyl)-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-tetrazoliuim bromide
T-111	2-(2-pyridyl)3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-112	2-(2-quinolinyl)-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)-2H-tetrazolium tetrafluoroborate
T-120	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.

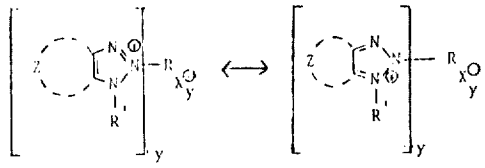
From the foregoing it is apparent that the formazan dye images produced according to this invention can, if desired, be stabilized either by adding electronegative substituents to the tetrazole nucleus or by incorporating metal salts in combination with the tetrazolium salts. If desired, these two stabilization 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 2H-benzimidazoles 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 azoamine 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:

(A) 

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, quinolinyl, 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 and 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., one to six carbon atoms), lower alkenyl (i.e., two to six carbon atoms), lower alkynyl (i.e., two to six 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. 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 azo-amine dye is in general controlled by the triazole nucleus configuration rather than the substituents chosen. To enhance the stability of the azo-amine dyes produced it is preferred to incorporate within the triazolium salts of this invention predominantly electronegative substituents.

Any anion known to the useful in azo-amine 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 azo-amine 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 azo-amine dye produced on exposure to thereby further stabilize the dye against subsequent fading. All azo-amine 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 azo-amine 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
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-phenoxynaphtho[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 hexaflurophosphate
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.

HYDROGEN SOURCE

Any conventional source of labile hydrogen atoms that is not otherwise reactive with the remaining components or their reaction products contained within the photographic element can be utilized. Generally preferred for use are organic compounds having a hydrogen atom attached to a carbon atom to which a substituent is also attached which greatly weakens the carbon to hydrogen bond, thereby rendering the hydrogen atom labile. Preferred hydrogen source compounds are those which have a hydrogen atom bonded to a carbon atom to which is also bonded the oxygen atom of an oxy substituent and/or the trivalent nitrogen atom of an amine substituent. As employed herein the term "amine substituent" is inclusive of amide and imine substituents. Exemplary preferred substituents which produce marked lability in a hydrogen atom associated with a common carbon atom are oxy substituents, such as hydroxy, alkoxy, aryloxy, alkaryloxy and aralkoxy substituents and amino substituents, such as alkylarylamino, diarylamino, amido, N,N-bis(1-cyanoalkyl)amino, N-aryl-N-(1-cyanoalkyl)amino, N-alkyl-N-(1-cyanoalkyl)amino, N,N-bis(1-carbalkoxyalkyl)amino, N-aryl-N-(1-carbalkoxyalkyl)amino, N-alkyl-N-(1-carbalkoxyalkyl)amino, N-N-bis-(1-nitroalkyl)amino, N-alkyl-N-(1-nitroalkyl)amino, N-aryl-N-(1-nitroalkyl)amino, N,N-bis(1-acylalkyl)amino, N-alkyl-N-(1-acylalkyl)amino, N-aryl-N-(1-acylalkyl)amino, and the like. The aryl substituents and substituent moieties are preferably phenyl or phenylene while the aliphatic hydrocarbon substituents and substituent moieties preferably incorporate 20 or fewer carbon atoms and, most preferably, six or fewer carbon atoms. Exemplary of compounds which can be used in the practice of this invention for the purpsoe of providing a ready source of labile hydrogen atoms are those set forth in Table VII. If desired, the source of labile hydrogen atoms can be incorporated directly in the 2H-benzimidazole through the proper choice of substituent groups.

TABLE VII

	Exemplary Hydrogen Source Compounds
HS-1	poly(ethylene glycol)
HS-2	phenyl-1,2-ethanediol

TABLE VII-Continued

Exemplary Hydrogen Source Compounds	
HS-3	nitrilotriacetonitrile
HS-4	triethylnitrilotriacetate
HS-5	poly(ethylene glycol)
HS-6	poly(vinyl butyral)
HS-7	poly(vinyl acetal)
HS-8	1,4-benzenedimethanol
HS-9	methyl cellulose
HS-10	cellulose acetate butyrate
HS-11	2,2-bis-(hydroxymethyl)propionic acid
HS-12	1,3-bis-(hydroxymethyl)-urea
HS-13	4-nitrobenzyl alcohol
HS-14	4-methoxybenzyl alcohol
HS-15	2,4-dimethoxybenzyl alcohol
HS-16	3,4-dichlorophenylglycol
HS-17	N-(hydroxymethyl)-benzamide
HS-18	N-(hydroxymethyl)-phthalimide
HS-19	5-(hydroxymethyl)-uracil hemihydrate
HS-20	nitrilotriacetic acid
HS-21	2,2',2''-triethylnitrilotripropionate
HS-22	2,2',2''-nitrilotriacetophenone
HS-23	poly(vinyl acetate)
HS-24	poly(vinyl alcohol)
HS-25	ethyl cellulose
HS-26	carboxymethyl cellulose
HS-27	poly(vinyl formal)

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 in the presence of labile hydrogen atoms. The radiation-sensitive composition can then be brought into a spacially 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, the image-recording compound and the external hydrogen source, if any, be intimately associated. This can be readily achieved, for example, by dissolving the reactants in a solvent system.

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, t-butanol and the like; ketones, such as methylethyl ketone, acetone and the like; 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 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 to supplement or replace other hydrogen sources as described above. For example, any of the polymers set forth in Table VII 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 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 and 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 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. For example, where the external hydrogen source is also used as a binder, it is typically present in much greater concentration than is essential merely for donation of labile hydrogen atoms. It is generally preferred to incorporate from 0.1 to 10 moles of the tetrazolium salt per mole of the photoreductant. External hydrogen sources supplied solely to perform this function are typically conveniently incorporated in concentrations of from 0.5 to 10 moles per mole of photoreductant. 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 tetrazolium salt. The binder can account for up to 99 percent by weight of the radiation-sensitive layer, but is typically employed in proportions of form 50 to 90 percent 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 microns 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* pbulication 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.

In most instances the photographic elements of this invention will provide a useable record directly on exposure to actinic radiation and heating to a temperature sufficient to convert a 2H-benzimidazole to the corresponding 1H-benzimidazole, which is not a reducing agent. Temperatures in the range of from about 100° to 150°C are generally preferred for heat fixing. Where the element will not again be exposed to actinic radiation in use or where it is desired to retain in the element the capability of additional image recording, the step of thermally fixing the element can be omitted. In some instances reduction of the image-recording compound may require heat for completion. In this instance thermal fixing simultaneously drives the reaction of the image-recording means and the dihydrobenzimidazole to completion. It is contemplated that, if desired, the image-recording compound can be introduced into the photographic element after imagewise exposure, as by incorporating the image-recording compound in a separate medium, such as a processing solution, which is brought into contact with the radiation-sensitive layer after exposure thereof. However, this approach is not generally preferred, since it introduces added processing. In still another variation is is contemplated that photographic elements according to this invention can be imagewise fixed followed by uniform exposure to actinic radiation. In this instance the image-recording compound can be present initially or added later in processing. Still other variations will readily occur to those skilled in the art.

This invention is further illustrated by the following examples of preferred embodiments.

EXAMPLE 1

Spiro[cyclohexane-1′, 2-(2,3-dihydrobenzimidazole)] was prepared according to the procedure of R. Garner, G. V. Garner, and H. Suschitzky, *J. Chem. Soc.* (C), 825 (1970). A mixture of o-phenylenediamine (10.80 g, 0.1 mole) and cyclohexanone (9.82 g, 0.1 mole) in tetrahydrothiophene-1,1-dioxide (30 ml) was heated 90 minutes on a steam bath. The hot mixture was poured into water. The solid that separated was collected, and washed first with water, then with a small volume of ethyl alcohol, and finally with ligroin (b.p. 35°–55°C). The washed material was air-dried to yield a yellow solid, 10.52 g, m.p. 135°C dec. Recrystallization from ethyl alcohol gave yellow needles, 5.10 g, 27 percent, m.p. 144°C dec. (Reported m.p. 138°C).

A mixture of spiro[cyclohexane-1′, 2-(2,3-dihydrobenzimidazole)] (5.0 g, 0.027 mole) and MnO_2 (15 g; Winthrop Laboratories, activated grade) in benzene (100 ml) was stirred at room temperature for 30 minutes, then heated on a steam bath for 15 minutes. The solution was filtered and the filtrate concentrated to yield a pale yellow oil which slowly crystallized. The material was dissolved in a small volume of ligroin (b.p. 63°–75°C) and allowed to stand at 0°C for 12 hours. The crystals that separated were removed, washed with a few milliliters of ligroin (b.p. 63°–75°C), and air-dried to yield spiro(2H-benzimidazole-2,1′-cyclohexane) (PR-4) as colorless crystals (2.66 grams; melting point 61° to 65°C). The ligroin from which the crystals were originally seprated was allowed to stand again under similar conditions and additional crystals were separated (1.56 grams; melting point 61° to 65°C) for a total yield of 4.22 grams or 85 percent.

A portion of the spiro(2H-benzimidazole-2,1′-cyclohexane) (PR-4) produced (0.19 gram or 1 millimole), 2,3,5-triphenyl-2H-tetrazolium chloride (T-1) (0.66 gram or 2 millimoles), and 1-phenyl-1,2-ethanediol (HS-2) (0.3 gram or 2.2 millimoles) was dissolved in methanol (1 ml) and then brought to a volume of 15 ml with a solution of 10 percent cellulose acetate butyrate (HS-10) in dichloroethane. The resulting mixture was coated on poly(ethylene terephthalate) film support to produce a wet coating thickness of 150 microns. After drying the film 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 rated at approximately 30 watts per cm, commercially available under the tradename Ozalid, at a speed of 76 cm per minute. The resulting exposed strip was heated at 150°C for 1.5 minutes to give a stable, reddish-orange printout in areas exposed to actinic radiation. The printout recorded the image employed on exposure. There was no tendency observed after fixing for printout to occur in areas not exposed to actinic radiation during imagewise exposure, even though the element was handled in room light.

EXAMPLES 2 THROUGH 12

Employing procedures similar to those described in Example 1, similar images were obtained employing as photo-reductants PR-5, PR-10, PR-11, PR-12, PR-14, PR-15, PR-20, PR-25, PR-29, PR-31 and PR-50.

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.

I claim:

1. In a photographic element having a support and coated thereon at least one radiation-sensitive image-recording layer comprised of a source of labile hydrogen atoms, an image-recordng means for registering an absorption change upon reduction by a 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, tetrazolium salts, and triazolium salts; and a photoreductant in intimate association with said image-recording means, said photoreductant being capable of forming a reducing agent in the presence of said hydrogen atoms; the improvement in which said photoreductant is a 2H-benzimidazole.

2. In a photographic element according to claim 1 the further improvement in which said hydrogen atoms are supplied by a compound external to said photoreductant.

3. In a photographic element according to claim 2 the further improvement in which said external hydrogen source compound incorporates a labile hydrogen atom attached to a carbon atom which is also bonded to the oxygen atom of an oxy substituent or the nitrogen atom of an amine substituent.

4. In a photographic element according to claim 2 the further improvement in which said external hydrogen source compound is a polymer capable of functioning as a binder for said image recording layer.

5. In a photographic element according to claim 4 the further improvement in which said polymer binder is a cellulosic compound.

6. In a photographic element according to claim 5 the further improvement in which said polymer binder is cellulose acetate butyrate.

7. In a photographic element according to claim 2 the further improvement in which said hydrogen source means is phenyl-1,2-ethanediol.

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

9. In a photographic element according to claim 1 the further improvement in which said 2H-benzimidazole incorporates an electron donating substituent.

10. In a photographic element according to claim 9 the further improvement in which said 2H-benzimidazole incorporates an alkoxy group as an electron donating substituent.

11. In a photographic element according to claim 10 the further improvement in which said alkoxy group contains 6 or fewer carbon atoms.

12. In a photographic element according to claim 1 the further improvement in which said 2H-benzimidazole incorporates a trihalomethyl group.

13. In a photographic element according to claim 1 te further improvement in which said 2H-benzimidazole incorporates a carboalkoxy group.

14. In a photographic element according to claim 13 the further improvement in which said carboalkoxy group incorporates six or fewer carbon atoms in said alkyl moiety.

15. In a photographic element according to claim 1 the further improvement in which said 2H-benzimidazole is a spiro(2H-benzimidazole-1',2-cyclohexane).

16. In a photographic element according to claim 1 the further improvement in which said 2H benzimidazole is a dispiro(2H-benzimidazole-2,1'-cyclohexane-40',2''-2H-benzimidazole).

17. 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.

18. In a photographic element according to claim 2 the further improvement in which said hydrogen source means is present in a concentration of at least 0.5 moles per mole of said photoreductant.

19. 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 percent by weight.

20. In a photographic element according to claim 19 the further improvement in which said photographic element incorporates a binder in said image-recording layer in a concentration of from 50 to 90 percent by weight.

21. In a photographic element according to claim 17 the further improvement in which said image-recording means and said photoreductant are present in substantially equal molar proportions.

22. An image-recording process comprising

converting a 2H-benzimidazole within a selected areal portion of a radiation-sensitive layer of a photographic element to a dihydrobenzimidazole by imagewise exposing the 2H-benzimidazole to actinic radiation in the presence of labile hydrogen atoms,

reducing an image-recording compound capable of changing its radiation-absorption characteristic upon reduction with the dihydrobenzimidazole generated within the selected areal portions of the layer, said compound being selected from the group consisting of aminotriarylmethane dyes, azo dyes, xanthene dyes, triazine dyes, nitroso dye complexes, indigo dyes, phthalocyanine dyes, tetrazolium salts, and triazolium salts; and

heating the layer to convert residual 2H-benzimidazole not exposed to actinic radiation to 1H-benzimidazole.

23. An image-recording process according to claim 22 in which said radiation-sensitive layer is heated to a temperature in the range of from 100° to 150°C.

24. An image-recording process according to claim 22 in which said radiation-sensitive layer is imagewise exposed to light.

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

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

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