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[54] **PHOTOGRAPHIC ELEMENTS AND PROCESSES FOR PRODUCING FORMAZAN DYE IMAGES OF ENHANCED STABILITY**

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[58] **Field of Search** ..... 96/48 R, 90 R, 49, 75, 96/76 R, 91 R, 88, 1.5

[56] **References Cited**

UNITED STATES PATENTS

3,278,366	10/1966	Schiele	96/1.5
3,642,478	2/1972	Brault et al.	96/48

FOREIGN PATENTS OR APPLICATIONS

670,883	4/1972	United Kingdom	96/48
908,299	10/1962	United Kingdom	96/48

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[57] **ABSTRACT**

An electronegatively substituted tetrazolium salt capable of reduction to a formazan dye of enhanced stability is present in a radiation-sensitive layer in combination with a photoreductant capable of producing in the presence of labile hydrogen atoms a reducing agent precursor in radiation-struck areas of the layer. An image is produced in the layer by bringing the layer into contact with a base after imagewise exposure to actinic radiation.

70 Claims, No Drawings

PHOTOGRAPHIC ELEMENTS AND PROCESSES FOR PRODUCING FORMAZAN DYE IMAGES OF ENHANCED STABILITY

This invention relates to an improved photographic element which exhibits low, stable background densities without fixing and to a process for recording images therewith. In a specific aspect, this invention is directed to an improved photographic element and to a process for its use in which a visible formazan dye of enhanced stability is selectively produced from a formazan dye precursor in image areas, while the background areas remain stable and of low optical density in the presence of actinic radiation and without removal or alteration of the formazan dye precursor.

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.

The reduction of a tetrazolium salt to form a formazan dye image is generally well known in the art. For example, in Brault et al U.S. Pat. No. 3,642,478, issued Feb. 15, 1972; Brault et al U.S. Pat. No. 3,655,382, issued Apr. 11, 1972 and Bissonette et al U.S. Pat. No. 3,671,244, issued June 20, 1972, there are disclosed processes for utilizing a zero valent metal image to reduce a tetrazolium salt and produce a formazan dye image.

A system that does not require the presence of a metal image is disclosed by Jaeken et al in British Patent No. 670,883, published Apr. 30, 1952. Jaeken et al incorporates into a photographic element a tetrazolium salt and a reducing agent precursor which on exposure to light produce a formazan dye image. After exposure the photographic element is washed in up to three successive aqueous baths intended to fix the image by removal of the unreduced tetrazolium salt remaining in the background areas, enhance the image density and remove the remaining reducing agent precursor and the reaction products which, if left in place, would stain the background of the photographic element. Reducing agent precursors such as ferric salts, vanadic compounds, tungstic compounds and uranium salts are employed. Baths containing organic hydroxy acids or their ammonium salts are used to remove the brown oxides produced by ferric salts. Aqueous ammonia solutions are optionally used for image enhancement while water or dilute acid fixing baths are used to remove residual tetrazolium salts.

As improvements on the teachings of Jaeken et al, Telefunken British Patent No. 1,016,822, published Jan 12, 1966, and Schiele U.S. Pat. No. 3,278,366, issued Oct. 11, 1966, teach the reduction of a tetrazolium salt to a formazan dye in response to radiation of 200 nm or less. In contrast to the system of Jaeken et al in which the reducing agent precursor is acted on by radiation to produce a reducing agent, Telefunken and Schiele activate the tetrazolium salt by radiation to cause it to react with the available reducing agent. For very high-energy radiation below 200 nm, no separate reducing agent is required to convert the tetrazolium salt to a formazan dye. The exposed photographic elements of Schiele and Telefunken can be viewed without fixing since they are insensitive to radiation within the visible spectrum. Of course, re-exposure to actinic radiation would result in background printout.

It is an object of this invention to provide photographic elements that are responsive to radiation within the ultraviolet and visible spectrum, that do not require the incorporation of metals or metal salts, that can be processed in a dry state, that do not require fixing prior to re-exposure, that exhibit low, stable background densities, that exhibit enhanced speed and that produce formazan dye images of enhanced stability.

It is another object to provide a process for using such photographic elements which requires only image exposure followed by a single processing step, which can be performed in a dry state.

In one aspect this invention is directed to a photographic element having a support and at least one radiation-sensitive image recording layer thereon comprised of a tetrazolium salt capable of reduction to a formazan dye and a photoreductant. This invention is specifically directed to the improvement in which the tetrazolium salt includes dye stabilizing tetrazole nucleus substituents which are collectively, predominantly electronegative so that the algebraic sum of the Hammett sigma values of the tetrazole nucleus substituents are in excess of 0.78.

Alternatively, when the tetrazole nucleus is provided with a ring substituent bonded to the tetrazole nucleus at a first ring position and including a single substituent, which is ortho to the first ring position, the algebraic sum of the Hammett sigma values of the tetrazole nucleus substituents need be only in excess of 0.40.

In another aspect this invention relates to a process which comprises converting a photoreductant within a selected areal portion of a radiation-sensitive layer of photographic element to a reducing agent precursor by imagewise exposing the photoreductant to actinic radiation in the presence of labile hydrogen atoms. The precursor is activated with a base to form a reducing agent, and, to produce a formazan dye of enhanced stability, a tetrazolium salt is reduced. The tetrazolium salt includes dye stabilizing tetrazole nucleus substituents which are, collectively, predominantly electronegative. The sum of the Hammett sigma values of the tetrazole nucleus substituents are (a) in excess of 0.78 or (b) in excess of 0.40 when the tetrazole nucleus is provided with a ring substituent bonded to the tetrazole nucleus at a first ring position and including a single substituent ortho to the first ring position.

In a specifically preferred embodiment of the invention an electronegatively substituted tetrazolium salt capable of reduction to form a stabilized formazan dye and a 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 of less than 700 nm in wavelength and, preferably, below 500 nm. Exposure causes the photoreductant to form a latent image in the radiation-struck areas of the image recording

layer. In latent image formation the photoreductant is converted to a reducing agent precursor which, in turn, can be readily converted to a reducing agent in the presence of a base.

While Applicant does not wish to be bound by any particular theory as to how the photoreductant forms the latent image, it is believed that one or more of the labile hydrogen atoms present in the image recording layer chemically bond to the photoreductant at a radiation-sensitive site within the photoreductant molecule. As formed, the reducing agent precursor generated by the radiation-struck photoreductant is incapable of directly reducing the tetrazolium salt to produce a formazan dye. However, when the expopsed radiation-sensitive layer is treated with a base, preferably gaseous ammonia, the reducing agent precursor is converted to an active reducing agent which reacts with the tetrazolium salt to form a formazan dye.

It is a specific advantage that the exposed image-bearing photograhic elements of this invention can be re-exposed to actinic radiation without fixing. The reason for this is that, while the remaining photoreductant will form a second latent image in the background areas when the photographic element is re-exposed, this does not interfere with seeing the existing visible image. The photoreductant is specifically chosen to yield a reducing agent precursor that is light in color and, preferably, substantially colorless, so that a sharp visible contrast exists between the formazan dye image and the background areas.

It is another distinct advantage of the photographic elements of this invention that they exhibit stable, low density backgrounds when stored in the atmosphere over extended periods. Since the atmosphere is free of basic substances, the reducing agent precursor is not converted to a reducing agent during storage of the photographic element in contact with the atmosphere. Similarly, there is no direct atmospheric reduction of the tetrazolium salt on storage of the photographic elements. Over an extended period of time atmospheric oxygen can oxidize the latent image of reducing agent precursor, thereby entirely eliminating the possibility of unwanted image formation. Thus, in marked contrast to photographic elements that contain dye precursors which form visible dyes on oxidation, the photographic elements of the present invention are notably free of background printout.

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 reducing agent precursor could, if desired, be brought into contact with a basic solution for activation as a reducing agent, according to the preferred practice of this invention the reducing agent precursor is contacted with gaseous ammonia to produce the active reducing agent. In one form the gaseous ammonia can be generated "in situ". Beyond this, in the image recording layer each of the components and each of the reaction products formed, except for the formazan dye, are of low optical density. This avoids any need for rinsing or processing baths to remove or alter any of the components or reaction products formed within the image-recording layer.

Since the single processing step of exposure to gaseous ammonia can be performed in commercially available equipment sold for this purpose and since no resort to comparatively cumbersome conventional photographic processing techniques, such as processing baths, uniform or 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.

Fleming, Manthey and Brongo in concurrently filed, commonly assigned application Ser. No. 384,859, titled TETRAZOLIUM SALT PHOTOREDUCTIVE IMAGING broadly disclose the use of tetrazolium salts in combination with a photoreductant and labile hydrogen atoms to produce a formazan dye image. The tetrazolium salts employed in the practice of this invention produce formazan dyes of enhanced stability by utilizing substituents to the tetrazole nucleus which, collectively, exhibit electronegative Hammett sigma values in excess of a predetermined minimum, as is hereinafter more fully explained.

A wide variety of tetrazolium salts are known to the art including bis-tetrazolium salts linked directly or indirectly 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, oxazoyl, thiazolyl, quinolinyl, benzoxazolyl, benzothiazolyl, etc.) substituents in the 2 and 3 positions of the tetrazole nucleus. The tetrazolium salts of the present invention are either known to the art or can be readily produced using conventional synthesis and substitution procedures for forming tetrazolium salts.

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.

It is Applicant's discovery that tetrazolium salts having tetrazole nucleus substituents the algebraic sum of whose Hammett sigma values is collectively greater than 0.78 and, preferably, greater than 1.00 are useful in combination with photoreductants and labile hydrogen to produce formazan dye images of enhanced stability. Applicant has further discovered that 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 advantges 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 essen-

tially subtractive in effect. For example, two like ortho substituents to 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 electronegative 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.

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), cyanide, azide, 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), sulfoxide (e.g., methylsulfoxide), sulfonium (e.g., dimethyl sulfonium), silane (e.g., trimethylsilane) and trioether (e.g., methyl mercaptide) 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 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 I.

TABLE I

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

Exemplary preferred tetrazolium salts having predominately electronegative tetrazole nucleus, substituents are set forth in Table II. 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 II

Exemplary Preferred Tetrazolium Salts for forming Dyes of Enhanced Stability

	Tetrazolium Salt
T- 1	2-(4-methylthiophenyl)-3-(3,5-dichlorophenyl)-5-(3-nitrophenyl)2H-tetrazolium hexafluorophosphate
T- 2	2(4-cyanophenyl)-3-(3-benzamidophenyl-5-(3,4-dichlorophenyl)-2H-tetrazolium perchlorate
T- 3	2-(2-naphthyl)-3-(3-nitro-5-chloro-phenyl)-5-(4-cyanophenyl)-2H-tetrazolium sulfate
T- 4	2-(4-bromo-1-naphthyl)-3-(4-cyanophenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium chloride
T- 5	2-(3-pyridyl)-3-phenyl-5-(4-chlorophenyl)-2H-tetrazolium bromide
T- 6	2-(2,4-dichlorophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T- 7	2-(2,4,5-trichlorophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T- 8	2-(2,4,5-trichlorophenyl)-3-(4-phenylsulfonyl phenyl)-5-phenyl-2H-tetrazolium chloride
T- 9	2-(2,3,4,5-tetrachlorophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium iodide
T-10	2-(2-trifluoromethyl-5-chlorophenyl)-3-(4-cyanophenyl)-5-phenyl-2H-tetrazolium bromide
T-11	2-(4-pyridyl)-3-(2-trifluoromethylphenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-12	2-(2-chloro-5-5-trifluoromethylphenyl)-3-(3,4-dichlorophenyl)-5-phenyl-2H-tetrazolium hexafluorophosphate
T-13	2-(2-chloro-5-nitrophenyl)-3-(4-acetyl phenyl)-5-(3-nitrophenyl)-2H-tetrazolium chloride
T-14	2-(2-chloro-4-cyanophenyl)-3-(4-benzoyl-phenyl)-5-(3-chlorophenyl)-2H-tetrazolium perchlorate
T-15	2-(2-nitro-4-chlorophenyl)-3-(4-phenylazophenyl)-5-(4-chlorophenyl)-2H-tetrazolium chloride
T-16	2-[4-(4-nitrophenyl)thiophenyl]-3-(2-chloro-5-trifluoromethylphenyl)-5-(3-nitrophenyl)-2H-tetrazolium bromide
T-17	2-(4-phenylsulfonylphenyl)-3-(2-chloro-5-trifluoromethyl phenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium bromide
T-18	2-(4-benzylphenyl)-3-(2,4-dichlorophenyl)-5-(4-nitrophenyl)-2H-tetrazolium sulfate
T-19	2-(4-phenylsulfonylphenyl)-3-(2-chloro-4-cyanophenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium chloride
T-20	2-(2-methoxy-4-nitrophenyl)-3-(4-cyanophenyl)-5-phenyl-2H-tetrazolium chloride
T-21	2-(3-propionylphenyl)-3-(2,4-dichlorophenyl)-5-(3-nitrophenyl)-2H-tetrazolium chloride
T-22	2-(2-biphenyl)-3-(3,4-dichlorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium chloride
T-23	2-(4-nitrophenyl)-3-(3-pyridyl)-5-phenyl-2H-tetrazolium perchlorate
T-24	2-(2-chloro-4-cyanophenyl)-3-(2-chloro-5-trifluoromethylphenyl)-5-(3-chlorophenyl)-2H-tetrazolium tetrafluoroborate
T-25	2-(4-pyridyl)-3-(2,3,4,5-tetrafluorophenyl)-5-phenyl-2H-tetrazolium hexafluorophosphate
T-26	2-(2-benzoylphenyl)-3-(2,4-dichlorophenyl)-5-(3-nitrophenyl)-2H-tetrazolium hexafluorophosphate
T-27	2-(1-nitro-2-naphthyl)-3-(2-methyl-4-nitrophenyl)-5-(4-chlorophenyl)-2H-tetrazolium chloride
T-28	2-(3-phenylformamidophenyl)-3-(2-nitro-4-chlorophenyl)-5-(3-chlorophenyl)-2H-tetrazolium tetrafluoroborate
T-29	2-(anthraquinone-2-yl)-3-(2-nitro-4-chlorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium tetrafluoroborate
T-30	2-(2,5-dichlorophenyl)-3-phenyl-5-(4-nitrophenyl)-2H-tetrazolium tetrafluoroborate
T-31	2-(2,4-dibromophenyl)-3-(4-nitrophenyl)-5-methyl-2H-tetrazolium chloride
T-32	2-(2,5-dichlorophenyl)-3-(2-methoxy-4-nitrophenyl)-5-(4-methoxyphenyl)-2H-tetrazolium chloride
T-33	2-(2,4,5-trichlorophenyl)-3-(3-nitrophenyl)-5-ethyl-2H-tetrazolium bromide
T-34	2-(4-trifluoromethylphenyl)-3-(4-cyanophenyl)-5-n-propyl-2H-tetrazolium bromide
T-35	2-(2-phenoxy-4-chlorophenyl)-3-(4-nitrophenyl)-5-n-hexyl-2H-tetrazolium tetrafluoroborate
T-36	2-(2-bromophenyl)-3-(2-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-37	2,3-di(4-nitrophenyl)-5-methyl-2H-tetrazolium hexafluorophosphate
T-38	2-(4-bromophenyl)-3-(4-nitrophenyl)-5-tert-butyl-2H-tetrazolium tetrafluoroborate
T-39	2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride
T-40	2-(2-nitro-1-naphthyl)-3-(4-cyanophenyl)-5-methyl-2H-tetrazolium tetrafluoroborate
T-41	2-(2-nitro-4-chloro-1-naphthyl)-3-(4-trifluoromethylphenyl)-5-methyl-2H-tetralzolium perchlorate
T-42	2-(2-bromo-4-cyano-1-naphthyl)-3-(4-nitrophenyl)-5-n-propyl-2H-tetrazolium chloride

TABLE II-Continued

Exemplary Preferred Tetrazolium Salts for forming Dyes of Enhanced Stability

	Tetrazolium Salt
T-43	2-(1-bromo-4-nitro-2-naphthyl)-3-(3,4-dichlorophenyl)-5-ethyl-2H-tetrazolium hexafluorophosphate
T-44	2-(3,6,7-trichloro-1-naphthyl)-3-(4-nitrophenyl)-5-n-hexyl-2H-tetrazolium hexafluorophosphate
T-45	2-(5-nitro-2-naphthyl)-3-(2,4,5-trichlorophenyl)-5-isobutyl-2H-tetrazolium hexafluorophosphate
T-46	2-(5,8-dichloro-1-naphthyl)-3-(4-nitrophenyl)-5-methyl-2H-tetrazolium sulfate
T-47	2-(3,5-dibromo-2-naphthyl)-3-(4-chlorophenyl)-5-propyl-2H-tetrazolium iodide
T-48	2,3-di(2-chlorophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-49	2-(2-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-50	2-(2-chloro-4-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-51	2-(2-chlorophenyl)-3-phenyl-5-(3-nitrophenyl)-2H-tetrazolium tetrafluoroborate
T-52	2-(2,4-dinitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-53	2,3,5-tri(4-nitrophenyl)-2H-tetrazolium chloride
T-54	2-(2-methyl-4-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-55	2-(4-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate
T-56	2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-57	2-(4-nitrophenyl-3-phenyl-5-(4-chlorophenyl)-2H-tetrazolium tetrafluoroborate
T-58	2,3-di(4-nitrophenyl)-5-phenyl-2H-tetrazolium tetrafluoroborate
T-59	2,5-di(4-nitrophenyl)-3-phenyl-2H-tetrazolium tetrafluoroborate
T-60	2,3-di(4-nitrophenyl)-5-(4-methoxyphenyl)-2H-tetrazolium tetrafluoroborate
T-61	2-(3-chlorophenyl)-3-(4-cyanophenyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium iodide
T-62	2-(4-phenylsulfonyl phenyl)-3-(3,5-dichlorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium chloride
T-63	2-(4-diphenyl)-3-(3,5-dinitrophenyl)-5-(4-trimethylammonium phenyl)-2H-tetrazolium dichloride
T-64	2-(4-acetylphenyl)-3-(3-trifluoromethyl-4-chlorophenyl)-5-(4-nitrophenyl)-2H-tetrazolium bromide

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 I and II. Any one of these anions can be incorporated in place of any other anion in any of the tetrazolium salts set forth in Tables I and II. 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, noted above, suggests the use 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, 2-quinolinyl and 2-azolyl (e.g., 2-thiazolyl, 2-benzothiazolyl, 2-oxazolyl, 2-benzoxazolyl, etc.) ring structures, for example.

It is specifically contemplated that in addition to formazan dye stabilization through the use of electronegative tetrazolium salt substituents the formazan dye image can be further stabilized by forming a formazan dye chelate. While such stabilized formazan dye chelates can be bidentate chelates, it is recognized that highest stabilities due to chelation are obtained when the formazan dye is a tridentate chelate. Certain exemplary tetrazolium salts which are electronegatively substituted in accordance with the teachings of this invention and which are additionally capable of producing highly stable tridentate formazan dye chelates are set forth in Table III.

TABLE III

Exemplary Preferred Tetrazolium Salts for Forming Tridentate Formazan Dye Chelates

T-65	2-(2-pyridyl)-3-(4-chlorophenyl)-5-phenyl-2H-tetrazolium nitrate
T-66	2-(2-quinolinyl)-3-phenyl-5-(3-nitrophenyl)-2H-tetrazolium tetrafluoroborate
T-67	2-(2-pyridyl)-3-(2-tolyl)-5-(4-cyanophenyl)-2H-tetrazolium hexafluorophosphate
T-68	1,5-naphthalene-bis[3-[2-(2-pyridyl)-5-(3,4-dichlorophenyl)-2H-tetrazolium tetrafluoroborate]
T-69	2-(2-pyridyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium nitrate
T-70	2-(benzothiazol-2-yl)-3,5-di(4-chlorophenyl)-2H-tetrazolium chloride
T-71	2-(benzothiazol-2-yl)-3-(3-nitrophenyl)-5-(4-iodophenyl)-2H-tetrazolium tetrafluoroborate
T-72	2-(benzothiazol-2-yl)-3-(2-fluorophenyl)-5-(4-cyanophenyl)-2H-tetrazolium tetrafluoroborate
T-73	2-(4,5-dimethylthiazol-2-yl)-3-(3-trifluoromethylphenyl)-5-(4-bromophenyl)-2H-tetrazolium tetrafluoroborate
T-74	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.

If a metal salt is incorporated within the imaging layer for the purpose of chelating, some increase in background density can occur upon prolonged re-exposure to actinic radiation, unless the residual photoreductant, the remaining chelating metal salt, the unreduced tetrazolium salt or all of these are removed from the non-image areas. This can be accomplished, for example, by washing the photographic element in a suitable solvent, such as a polar solvent, like water, which does not attack or leach the formazan dye. To obtain minimal background densities and to avoid processing the photographic element after image formation, it is preferred to utilize tetrazolium salts with electronegative substituents that produce stabilized formazan dyes rather than to incorporate chelating metal salts. Where extended re-exposure to actinic radiation is not contemplated or where increasing background densities can be tolerated, the formazan dyes can be chelated and the photoreductant, the tetrazolium salt and the unreacted metal salt in the background areas can be left in the photographic element. In other words, processing after image formation can be omitted.

As employed herein, the term "photoreductant" designates a material capable of molecular photolysis or photo-induced rearrangement to generate a reducing agent precursor. The term "reducing agent precursor" designates a compound which is not capable of reducing a tetrazolium salt employed in combination therewith, but which can be activated by a base to become a reducing agent capable of reducing the tetrazolium salt.

Exemplary of the photoreductants which can be utilized in the practice of this invention are disulfides capable of being photolytically cleaved at the S—S bond to form a mercaptan in the presence of labile hydrogen atoms. A variety of such disulfides presence of labile hydrogen atoms. A variety of such disulfides are known in the art. It is preferred to employ hydrocarbon disulfides and, more specifically, aryl disulfides. The aryl disulfides preferred are the alkyl aryl disulfides having from 1 to 20 (preferably 1 to 6) alkyl carbon atoms and diaryl disulfides. Either single or fused aromatic ring structures can be employed—e.g. phenyl, naphthyl, anthryl and similar ring structures. It is also contemplated that aromatic disulfides that incorporate non-basic heterocyclic aromatic rings can be utilized. Typical of such disulfides are those incorporating 5 and 6 membered aromatic rings having oxygen and/or sulfur heteroatoms.

In addition to the disulfides set forth above, phenazinium salts can be utilized as photoreductants in the practice of this invention. Also useful as photoreductants are diazoanthrones, β-ketosulfides and nitroarenes. The arene ring can be any aromatic carbocyclic ring structure—e.g. phenyl, naphthyl, anthryl and similar ring structures. It is specifically contemplated that the nitroarenes can incorporate substituents having labile hydrogen atoms and that these labile hydrogen atoms can be used in converting the photoreductant to a reducing agent precursor. For example, the nitroarenes can incorporate hydroxyalkyl substituents to provide labile hydrogen atoms.

Specific exemplary disulfides, phenazinium salts, diazoanthrones, β-ketosulfides and nitroarenes are set forth in Table IV.

TABLE IV

Exemplary Photoreductants

PR- 1	2-nitrobenzyl alcohol
PR- 2	4-bromonitrobenzene
PR- 3	2-(1-hydroxyethyl)-1-nitronaphthalene
PR- 4	2-nitroanthracene
PR- 5	4-hexoxynitrobenzene
PR- 6	2,5-diethoxynitrobenzene
PR- 7	2-nitronaphthalene
PR- 8	2-ethoxy-1-nitronaphthalene
PR- 9	2-isopropylnitrobenzene
PR-10	2-benzylnitrobenzene
PR-11	1-methyl-4-nitropyridinium tetrafluoroborate
PR-12	1-naphthyl-1'-phenethyl disulfide
PR-13	β-naphthyl disulfide
PR-14	9-anthryl disulfide
PR-15	cyclohexyl 2-naphthyl disulfide
PR-16	diphenylmethyl 2-naphthyl disulfide
PR-17	2-dodecyl 1'-naphthyl disulfide
PR-18	4,4'-dihexyldiphenyl disulfide
PR-19	2,2'-bis(hydroxymethyl)diphenyl disulfide
PR-20	4,4'-dinitrodiphenyl disulfide
PR-21	3-phenyl-3H-naphtho[1,2-c]-1,2-dithiole
PR-22	phenazinium 4-toluenesulfonate
PR-23	N-methyl phenazinium bromide
PR-24	2-methoxyphenazinium hexafluorophosphate
PR-25	2-nitrophenazinium tetrafluoroborate
PR-26	1-(hydroxymethyl)phenazinium chloride
PR-27	1-isopropoxy-10-methylphenazinium tetrafluoroborate
PR-28	2,3,9-trimethylphenazinium chloride

TABLE IV-Continued

Exemplary Photoreductants	
PR-29	2,3-dimethyl-5-nitrophenazinium methyl sulfate
PR-30	2,3-dichlorophenazinium chloride
PR-31	2-cyanophenazinium tetrafluoroborate
PR-32	1,2-benzophenazinium 4-toluenesulfonate
PR-33	10-diazoanthrone
PR-34	2-methoxy-10-diazoanthrone
PR-35	3-nitro-10-diazoanthrone
PR-36	3,6-diethoxy-10-diazoanthrone
PR-37	3-chloro-10-diazoanthrone
PR-38	4-ethoxy-10-diazoanthrone
PR-39	4-(1-hydroxyethyl)-10-diazoanthrone
PR-40	2,7-diethyl-10-diazoanthrone
PR-41	2-(4-tolyl)thiochromanone
PR-42	7-methyl-2-tolylthiochromanone
PR-43	2-(2,4,6-trimethylphenylthio)-1-tetralone
PR-44	2-benzylthio-1-tetralone
PR-45	2-(4-tolyl)thio-1-tetralone
PR-46	4-tolylthioacetone
PR-47	3-phenyl-2-(4-tolyl)thiopropiophenone
PR-48	2-ethylthio-3-phenylpropiophenone
PR-49	3-phenyl-2-phenylthiopropiophene
PR-50	3-phenyl-1-(4-tolyl)thio-2'-propionaphthone
PR-51	4'-methoxy-3-phenyl-2-phenylthiopropiophenone
PR-52	3,3-diphenyl-2-phenylthiopropiophenone

Quinones are useful as photoreductants in the practice of this invention. Useful quinones include ortho and para-benzoquinones, diphenoquinones, ortho and para-naphthoquinones, phenanthrenequinones and anthraquinones. The quinones may be unsubstituted or incorporate any substituent or combination of substituents that do not interfere with the conversion of the quinone to the corresponding reducing agent precursor—e.g., hydroquinone. A variety of such substituents are known to the art and include, but are not limited to, primary, secondary and tertiary alkyl, alkenyl and alkynyl, aryl, alkoxy, aryloxy, aralkoxy, alkaryloxy, hydroxyalkyl, hydroxyalkoxy, alkoxyalkyl, acyloxyalkyl, aryloxyalkyl, aroyloxyalkyl, aryloxyalkoxy, alkylcarbonyl, carboxyl, primary and secondary amino, aminoalkyl, amidoalkyl, anilino, piperidino, pyrrolidino, morpholino, nitro, halide and other similar substituents. Such aryl substituents are preferably phenyl substituents and such alkyl, alkenyl and alkynyl substituents, whether present as sole substituents or present in combination with other atoms, typically incorporate twenty (preferably six) or fewer carbon atoms.

Specific exemplary quinones intended to be used in combination with a separate source of labile hydrogen atoms are set forth in Table V.

TABLE V

Exemplary Quinones Useful with External Hydrogen Source	
PR-53	Anthraquinone
PR-54	2-Methylanthraquinone
PR-55	2-t-Butylanthraquinone
PR-56	1,4-Dimethylanthraquinone
PR-57	2-Piperidinoanthraquinone
PR-58	2-Methyl-1,4-anthraquinone
PR-59	N-methyl-1-aminoanthraquinone
PR-60	2,5-Dimethyl-1,4-benzoquinone
PR-61	Phenanthrenequinone
PR-62	Duroquinone
PR-63	2,5-Di-t-butyl-1,4-benzoquinone
PR-64	2-Methyl-1,4-benzoquinone
PR-65	2,3,5-Trimethyl-6-bromo-1,4-benzoquinone
PR-66	2-Phenyl-1,4-benzoquinone
PR-67	1,4-Naphthoquinone
PR-68	2-Methyl-1,4-naphthoquinone
PR-69	2,3-Dimethyl-1,4-naphthoquinone
PR-70	2,3-Dichloro-1,4-naphthoquinone
PR-71	2-Thiomethyl-1,4-naphthoquinone
PR-72	2-Methyl-3-(methylthio)-1,4-naphthhoquinone
PR-73	2,3-Dithiomethyl-1,4-naphthoquinone

TABLE V-Continued

Exemplary Quinones Useful with External Hydrogen Source	
PR-74	2-Amino-3-chloro-1,4-naphthoquinone
PR-75	2-(Acetylthiomethyl)-3-methyl-1,4-naphthoquinone

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 purpose of providing a ready source of labile hydrogen atoms are those set forth in Table VI. Compounds known to be useful in providing labile hydrogen atoms are also disclosed in U.S. Pat. No. 3,383,212, issued May 14, 1968, the disclosure of which is here incorporated by reference.

TABLE VI

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

TABLE VI-Continued

Exemplary External Hydrogen Source Compounds	
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)

The compounds of Table VI capable of providing labile hydrogen atoms are referred to as external hydrogen source compounds. The external hydrogen source compounds are incorporated within the photographic elements of the present invention and can, in fact, perform more than one function. For example, the external hydrogen source polymers of Table VI can also be used as binders as well as to provide a source of labile hydrogen atoms. These compounds are designated as external hydrogen source compounds only to point up that the labile hydrogen atoms are not incorporated in the photoreductant. As specifically noted above in connection with useful nitroarenes, the photoreductants can themselves incorporate labile hydrogen atoms which facilitate their conversion to reducing agent precursors. Such photoreductants are herein referred to as "internal hydrogen source photoreductants".

A preferred class of internal hydrogen source photoreductants are the internal hydrogen source quinones disclosed and claimed by Fleming, Manthey and Brongo in commonly assigned concurrently filed application Ser. No. 384,861 titled PHOTOGRAPHIC ELEMENTS AND PROCESSES FOR INCORPORATED HYDROGEN SOURCE PHOTOREDUCTION IMAGING.

It has been discovered that quinones incorporating labile hydrogen atoms are more easily photoreduced than quinones which do not incorporate labile hydrogen atoms. Even when quinones lacking labile hydrogen atoms are employed in combination with an external hydrogen source while incorporated hydrogen source quinones are similarly employed without external hydrogen source compounds, the internal hydrogen source quinones continue to exhibit greater ease of photoreduction. When internal hydrogen source quinones are employed with external hydrogen source compounds, their ease of photoreduction can generally be further improved, although the improvement is greater for those internal hydrogen source quinones which are less effective when employed without an external hydrogen source compound.

Using quinones exhibiting greater ease of photoreduction results in photographic elements which exhibit improved image densities for comparable exposures and which produce comparable image densities with lesser exposure times. Hence, incorporated hydrogen source quinones can be employed to achieve greater photographic speeds and/or image densities.

Particularly preferred internal hydrogen source quinones are 5,8-dihydro-1,4-naphthoquinones having at least one hydrogen atom in each of the 5 and 8 ring positions. Other preferred incorporated hydrogen source quinones are those which have a hydrogen atom bonded to a carbon atom to which is also bonded the oxygen atom of an oxy substituent or a nitrogen atom of an amine substituent with the further provision that the carbon to hydrogen bond is the third or fourth bond removed from at least one quinone carbonyl double bond. As employed herein the term "amine substituent" is inclusive of amide and imine substituents. Disubstituted amino substituents are preferred. 1,4-Benzoquinones and naphthoquinones having one or more 1' or 2'-hydroxyalkayl, alkoxy (including alkoxyalkoxy--particularly 1' or 2'-alkoxyalkoxy, hydroxyalkoxy, etc.), 1' or 2'-alkoxyalkyl, aralkoxy, 1' or 2'-acyloxyalkyl, 1' or 2'-aryloxyalkyl, aryloxyalkoxy, 1' or 2'-aminoalkyl (preferably a 1' or 2'-aminoalkyl in which the amino group contains two substituents in addition to the alkyl substituent, at least one of which is an electronegative or aryl substituent), 1' or 2'-aroyloxyalkyl, alkylarylamino, dialkylamino, 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, pyrrolino, pyrrolidino, piperidino, and/or morpholino substituents in the 2 and/or 3 position are particularly preferred. Other substituents can, of course, be present. Unsubstituted 5,8-dihydro-1,4-naphthoquinone and 5,8-dihydro-1,4-naphthoquinones substituted at least in the 2 and/or 3 position with one or more of the above-listed preferred quinone substituents also constitute preferred internal hydrogen source quinones. It is recognized that additional fused rings can be present within the incorporated hydrogen source quinones. For example, 1,4-dihydro-anthraquinones represent a useful species of 5,8-dihydro-1,4-naphthoquinones useful as incorporated hydrogen source quinones. The aryl substituents and substituent moieties of incorporated hydrogen source quinones are preferably phenyl or phenylene while the aliphatic hydrocarbon substituents and substituent moieties preferably incorporate twenty or fewer carbon atoms and, most preferably, six or fewer carbon atoms. Exemplary preferred internal hydrogen source quinones are set forth in Table VII.

TABLE VII

Exemplary Internal Hydrogen Source Quinones	
PR-76	5,8-dihydro-1,4-naphthoquinone
PR-77	5,8-dihydro-2,6,7-trimethyl-1,4-naphthoquinone
PR-78	5,8-dihydro-6,7-dimethyl-2-phenyl-1,4-naphthoquinone
PR-79	5,8-dihydro-2,5,8-trimethyl-1,4-naphthoquinone
PR-80	2,5-bis(dimethylamino)-1,4-benzoquinone
PR-81	2,5-dimethyl-3,6-bis(dimethylamino)-1,4-benzoquinone
PR-82	2,5-dimethyl-3,6-bispyrrolidino-1,4-benzoquinone
PR-83	2-ethoxy-5-methyl-1,4-benzoquinone
PR-84	2,6-dimethoxy-1,4-benzoquinone
PR-85	2,5-dimethoxy-1,4-benzoquinone
PR-86	2,6-diethoxy-1,4-benzoquinone
PR-87	2,5-diethoxy-1,4-benzoquinone
PR-88	2,5-bis(2-methoxyethoxy)-1,4-benzoquinone
PR-89	2,5-bis(β-phenoxyethoxy)-1,4-benzoquinone
PR-90	2,5-diphenethoxy-1,4-benzoquinone
PR-91	2,5-di-*n*-propoxy-1,4-benzoquinone
PR-92	2,5-di-isopropoxy-1,4-benzoquinone
PR-93	2,5-di-*n*-butoxy-1,4-benzoquinone
PR-94	2,5-di-sec-butoxy-1,4-benzoquinone
PR-95	2-(N-ethylacetamidomethyl)-5-tert-butyl-1,4-benzoquinone
PR-96	bis[2-(5-methyl-1,4-benzoquinone-2-yl)ethyl]ether
PR-97	2-methyl-5-morpholinomethyl-1,4-benzoquinone
PR-98	2,3,5-trimethyl-6-morpholinomethyl-1,4-benzoquinone
PR-99	2,5-bis(morpholinomethyl)-1,4-benzoquinone
PR-100	2-(1-hydroxy-2-methyl-*n*-propyl)-5-methyl-1,4-benzoquinone
PR-101	2-hydroxymethyl-3,5,6-trimethyl-1,4-benzoquinone
PR-102	2-(1-hydroxyethyl)-5-methyl-1,4-benzoquinone

TABLE VII-Continued

	Exemplary Internal Hydrogen Source Quinones
PR-103	2-(1-hydroxy-*n*-propyl)-5-methyl-1,4-benzoquinone
PR-104	2-(1-hydroxy-n-octyl)-5-methyl-1,4-benzoquinone
PR-105	2-(1,1-dimethyl-2-hydroxyethyl)-5-methyl-1,4-benzoquinone
PR-106	2-(1-acetoxyethyl)-5-methyl-1,4-benzoquinone
PR-107	2-(1-methoxyethyl)-5-methyl-1,4-benzoquinone
PR-108	2-(1-ethoxyethyl)-5-methyl-1,4-benzoquinone
PR-109	2-(1-isopropoxyethyl)-5-methyl-1,4-benzoquinone
PR-110	2-chloro-3-n-octylamino-1,4-naphthoquinone
PR-111	1,4-dihydro-1,4-dimethylanthraquinone
PR-112	1,4-dihydro-2,3-dimethylanthraquinone
PR-113	2-dimethylamino-1,4-naphthoquinone
PR-114	2-methoxy-1,4-naphthoquinone
PR-115	2-benzyloxy-1,4-naphthoquinone
PR-116	2-methoxy-3-chloro-1,4-naphthoquinone
PR-117	2,3-dimethoxy-1,4-naphthoquinone
PR-118	2,3-diethoxy-1,4-naphthoquinone
PR-119	2-ethoxy-1,4-naphthoquinone
PR-120	2-phenethoxy-1,4-naphthoquinone
PR-121	2-(2-methoxyethoxy)-1,4-naphthoquinone
PR-122	2-(2-ethoxyethoxy)-1,4-naphthoquinone
PR-123	2-(2-phenoxy)ethoxy-1,4-naphthoquinone
PR-124	2-ethoxy-5-methoxy-1,4-naphthoquinone
PR-125	2-ethoxy-6-methoxy-1,4-naphthoquinone
PR-126	2-ethoxy-7-methoxy-1,4-naphthoquinone
PR-127	2-n-propoxy-1,4-naphthoquinone
PR-128	2-(3-hydroxypropoxy)-1,4-naphthoquinone
PR-129	2-isopropoxy-1,4-naphthoquinone
PR-130	7-methoxy-2-isopropoxy-1,4-naphthoquinone
PR-131	2-n-butoxy-1,4-naphthoquinone
PR-132	2-*sec*-butoxy-1,4-nephthoquinone
PR-133	2-n-pentoxy-1,4-naphthoquinone
PR-134	2-n-hexoxy-1,4-naphthoquinone
PR-135	2-n-heptoxy-1,4-naphthoquinone
PR-136	2-actetoxymethyl-3-methyl-1,4-naphthoquinone
PR-137	2-methoxymethyl-3-methyl-1,4-naphthoquinone
PR-138	2-(β-acetoxyethyl)-1,4-naphthoquinone
PR-139	2-N,N-bis(cyanomethyl)aminomethyl-3-methyl-1,4-naphthoquinone
PR-140	2-methyl-3-morpholinomethyl-1,4-naphthoquinone
PR-141	2-hydroxymethyl-1,4-naphthoquinone
PR-142	2-hydroxymethyl-3-methyl-1,4-naphthoquinone
PR-143	2-(1-hydroxyethyl)-1,4-naphthoquinone
PR-144	2-(2-hydroxyethyl)-1,4-naphthoquinone
PR-145	2-(1,1-dimethyl-2-hydroxyethyl)-1,4-naphthoquinone
PR-146	2-bromo-3-isopropoxy-1,4-naphthoquinone
PR-147	2-ethoxy-3-methyl-1,4-naphthoquinone
PR-148	2-chloro-3-piperidino-1,4-naphthoquinone
PR-149	2-morpholino-1,4-napthoquinone
PR-150	2,3-dipiperidino-1,4-naphthoquinone

To form a radiation-sensitive composition useful in the present invention it is merely necessary to bring together the photoreductant and the tetrazolium salt 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 clement 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 tetrazolium salt 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; 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 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 external hydrogen sources to supplement or replace other hydrogen sources as described above. For example, any of the polymers set forth in Table VI can be used both as binders and as external 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 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 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 a 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% by weight of the radiation-sensitive layer, but is typically employed in proportions of from 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 con-

centration of at least 1×10^{-6} moles per square decimeter and, most preferably, in a concentration of from 1×10^{-5} to 8×10^{-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* 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. Negative images can be formed by exposure through a positive stencil or transparency while positive images can be formed by exposure through a negative stencil or transparency.

To avoid direct printout on exposure with the consequent necessity of fixing where uniform re-exposure to actinic radiation is contemplated, the radiation-sensitive layer is maintained significantly less basic than is required to convert the reducing agent precursor to the reducing agent. While the exact degree of permissible basicity of the radiation-sensitive layer will vary somewhat as a function of the specific reactants chosen, it is generally preferred to avoid the incorporation of strongly basic reactants in the radiation-sensitive layer. For this reason components of the radiation-sensitive layer are chosen to be free of strongly basic moieties. It is preferred, for maximum protection against premature and/or background printout, that the radiation-sensitive layer be maintained neutral or on the acid side of neutrality.

The latent image that is produced in the photographic element on exposure is easily developed using gaseous ammonia processors, such as those which release moist ammonia vapors at ambinet pressure or those which use high pressure anhydrous ammonia gas. Other volatile bases, such as methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine, triethyl amine, propyl amine, butyl amine, etc., can be used. Although wet processing is not preferred, it is also contemplated that the photographic elements of this invention can be developed using aqueous alkaline solultions. It is comtemplated that the radiation-sensitive layer or an adjacent layer of the photographic element can contain a base source which is convertible to a base at will. For example, it is contemplated that the radiationsensitive layer can contain a compound that will release ammonia on exposure to heat or other activating energy.

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

EXAMPLES 1 and 2

A solution containing 13.5 g. of acetone, 1.5 g. of cellulose acetate butyrate, 0.037 g. of poly(ethylene glycol) (commercially available under the trademark Carbowax 600), 0.18 g. of phenazine and 0.76 g. of 4-toluenesulfonic acid was mixed with a solution of 0.33 g. of 2,3,5-triphenyl-2H-tetrazolium chloride (herein designated TC—1) in 5.0 g. of methanol. This mixture was coated on a paper support at room temperature and on a poly-(ethylene terephthalate) film base at 38°C with a 150 micron coating blade. Both coatings were contact exposed with a silver negative using a high pressure mercury light source and were then processed in a commercial diazo ammonia processor. A dark reddish-brown positive image on a buff background was produced in in both instances. The exposed and processed elements were held under normal office light conditions for several days without any substantial increase in background coloration. Similar results could have been achieved using a tetrazolium salt containing electronegative substituents according to this invention.

EXAMPLE 3

A mixture was prepared by dissolving the following components in an ethylene chloride-methanol solvent blend of 9.0 and 2.5 cc of respective solvents:

2-(1-hydroxyethyl)-5-methyl-1,4-benzoquinone (PR-102)	1.0 mmole
2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (T-39)	1.0 mmole
styrene-butadiene random copolymer consisting essentially of 78% by weight styrene and 22% by weight butadiene (sold commercially under the trademark KRO-3 by Phillips Petroleum)	1.0 g

A coating of approximately 100 microns wet thickness of the mixture was formed on a poly(ethylene terephthalate) film support and samples were exposed from

8 seconds through a step tablet and developed in a commercial diazo ammonia processor. Intense red negative prints were obtained with an average green density of 1.77. The results are included in Table VIII.

EXAMPLE 4

Two mixtures were prepared of 1 mmole of 2-methyl-1,4-naphthoquinone PR-68), and equal molar amount of 2,3,5-triphenyl-2H-tetrazolium chloride (TPC), and 0.660 g of a binder, dissolved in 11.5 cc of a solvent blend consisting essentially of ethylene chloride and methanol in a 1.4:1 weight ratio. A coating of approximately 100 microns wet thickness was formed from each mixture on a film support and exposed and developed as described in Example 1. One mixture contained poly(vinyl butyral) (HS—6) as the binder while the other mixture contained cellulose acetate butyrate (HS—10) as the binder. No hydrogen source other than the binders was present in either instance. Sensitometric curves for the two elements formed showed the poly(vinyl butyral) containing film to have a photographic speed 2 to 4 times greater than that of the cellulose acetate butyrate containing film. Similar results can be achieved using a tetrazolium salt containing electronegative substituents according to this invention with the further advantage that formazan dye images of enhanced stability can be formed.

EXAMPLES 5 and 6

To a mixture of 0.33 g. of 2,3,5-triphenyl-2H-tetrazolium chloride (TC-1) in 5.0 g. of methanol was added a solution of a photoreductant as set forth in Table IX below and 1.50 g. of cellulose acetate butyrate in 13.5 g. of acetone. The mixture was coated on a paper support with a 150 micron blade at room temperature and then exposed as in Example 1. In Example 5 a dark orange image was obtained on a light yellow background. In Example 6 a dark red image was obtained on a light buff background. Similar results can be achieved using a tetrazolium salt containing electronegative substituents according to the invention with the further advantage that formazan dye images of enhanced stability can be formed.

TABLE IX

Photoreductant	Amount Used	Ex. No.
phenanthrenequinone (PR-61)	0.20 g.	5
1,4-naphthoquinone (PR-65)	0.16 g.	6

EXAMPLES 7 through 13

To a mixture containing 0.33 g. of cellulose acetate butyrate, 0.69 g. phenyl-1,2-ethanediol (HS—2), 0.167 g. of 2,3,5-triphenyl-2H-tetrazolium chloride (TC—1), 1.85 g. of methanol, and 2.64 g. of acetone was added 0.50 millimoles of a photoreductant. The mixture was coated onto a poly(ethylene terephthalate) film base with a 100 micron coating blade at 22°C. All of the coatings were exposed and processed as in Example 1, except that the coatings of Examples 7, 8 and 9 were exposed through a 0.3 log E step tablet. Six steps were visible in Example 7; 3 in Example 8 and 2 in Example 9. In Example 7 a red image was obtained on a clear background. In both Examples 8 and 9 a dark red image was obtained on a light yellow background. See Table VIII for maximum and minimum green densities and for the photoreductants chosen. Generally similar results can be obtained using a tetrazolium salt containing electronegative substituents according to the present invention with the further advantage that formazan dye images of enhanced stability can be formed.

EXAMPLES 14 THROUGH 16

A mixture consisting of 0.25 g. of 2,3,5-triphenyl-2H-tetrazolium chloride (TC—1), 0.26 g. of 2-methyl-1,4-naphthoquinone (PR—68), 1.0 g. cellulose acetate butyrate (HS—10), 1.25 g. of methanol, and 7.95 g. of acetone was divided into three parts. One part was retained as a control. To another part was added 0.067 g. of nitriloacetonitrile (HS—3) and to the third part was added 0.069 g. of phenyl-1,2-ethanediol (HS—2). The three dopes were then coated onto a poly(ethylene terephthalate) film base with a 100 micron coating blade at 22°C and exposed and processed as in Example 7. In each instance a red image was obtained on a clear background. In Example 14, 4 steps were visible; Example 15, 5 steps; and in Example 16, 6 steps. Generally similar results could have been obtained using a tetrazolium salt containing electronegative substituents according to the present invention.

EXAMPLES 17 THROUGH 81

Each coating was made up by mixing 1.00 millimole of the tetrazolium salt with 1.00 millimole of the photoreductant and 0.660 g. of cellulose acetate butyrate binder. While the binder was capable of functioning to a limited degree as an external hydrogen source or hydrogen donor, the binder is not designated as a hydrogen source in Table VIII, except where no other hydrogen source was available. In some of the coatings, as designated in Table VIII, the high efficient external hydrogen source HS—2 was incorporated in a concentration of 1.00 millimole. In others of the coatings an internal hydrogen source photoreductant was employed. This is designated in Table VIII by the designation "Internal." In each instance the radiation-sensitive layer was coated onto a support from a solution formed with 11.5 cc. of a solvent. Two solvent systems were used. One solvent system was a mixture of 1.4 parts by volume ethylene chloride per part by volume of methanol. In the other solvent system 3.6 parts of acetone were present per part by volume of methanol. The radiation-sensitive coatings were in each instance 100 microns in thickness as coated.

Processing was accomplished by a 30 second exposure through a neutral density step tablet in an exposing unit of the type commercially available under the trademark Filmsort Uniprinter 086. Immediately after exposure the photographic elements were given three passes through a Keuffel and Esser Mercury Ammonia Chamber.

In Examples 24, 25 and 51 the fully processed photographic elements were uniformly re-exposed to actinic radiation in the exposure unit and then veiwed for background printout. No background printout was visible to the eye.

TABLE VIII

Exemplary Image and Background Qualities Produced by Various Photoreductants and Hydrogen Sources

Ex. No.	T-Salt	Photo-Reductant	Donor Hydrogen	Green Density Max.	Green Density Min.
3	T-39	PR-102	Internal only	1.77	N.R.
7	TC-1	PR-66	HS-2	1.02	0.08
8	TC-1	PR-70	HS-2	N.R.	N.R.
9	TC-1	PR-63	HS-2	N.R.	N.R.
10	TC-1	PR-55	HS-2	0.32	0.08
11	TC-1	PR-69	HS-2	0.39	0.08
12	TC-1	PR-62	HS-2	0.39	0.08
13	TC-1	PR-60	HS-2	0.70	0.08
17	T-39	PR-60	Binder	0.42	0.06
18	T-39	PR-61	Binder	0.48	0.09
19	T-39	PR-62	Binder	0.32	0.06
20	T-39	PR-63	Binder	0.78	0.06
21	T-39	PR-65	Binder	0.40	0.06
22	T-39	PR-67	Binder	1.06	0.46
23	T-39	PR-68	Binder	0.65	0.05
24	TC-1	PR-68	Binder	0.55	0.06
25	TC-1	PR-68	HS-2	1.02	0.06
26	T-39	PR-69	Binder	0.29	0.05
27	TC-1	PR-71	Binder	0.37	0.07
28	TC-1	PR-75	Binder	0.75	0.40
29	TC-1	PR-77	Internal	1.60	0.62
30	TC-1	PR-78	Internal	1.05	0.95
31	TC-1	PR-79	Internal	1.07	0.06
32	T-39	PR-79	Internal	1.60	0.06
33	TC-1	PR-83	Internal	1.01	0.04
34	TC-1	PR-86	Internal	0.92	0.04
35	TC-1	PR-87	Internal	1.50	0.05
36	TC-1	PR-87	HS-2/Int.	1.54	N.R.
37	TC-1	PR-88	Internal	1.01	0.08
38	TC-1	PR-90	Internal	1.48	0.06
39	TC-1	PR-91	Internal	1.40	0.07
40	TC-1	PR-92	HS-2/Int.	1.77	N.R.
41	TC-1	PR-92	Internal	1.82	0.08
42	T-39	PR-92	Internal	2.63	0.05
43	TC-1	PR-94	Internal	1.90	0.06
44	T-39	PR-95	Internal	1.00	0.12
45	T-39	PR-96	Internal	0.70	0.05
46	T-39	PR-97	Internal	3.97	0.51
47	TC-1	PR-98	Internal	1.01	0.05
48	T-39	PR-98	Internal	3.00	0.04
49	T-39	PR-99	Internal	2.51	0.34
50	T-39	PR-101	Internal	2.59	0.06
51	T-39	PR-102	Internal	3.42	0.13
52	T-39	PR-103	Internal	3.22	0.10
53	T-39	PR-104	Internal	1.87	0.17
54	T-39	PR-105	Internal	1.86	0.06
55	T-39	PR-107	Internal	2.66	0.10
56	T-39	PR-108	Internal	2.12	0.06
57	T-39	PR-109	Internal	1.86	0.00
58	T-39	PR-111	Internal	1.66	0.05
59	TC-1	PR-114	Internal	0.90	0.06
60	TC-1	PR-114	HS-2/Int.	0.99	0.06
61	T-39	PR-117	Internal	1.42	0.06
62	TC-1	PR-119	Internal	1.30	0.06
63	TC-1	PR-119	HS-2/Int.	1.30	0.06
64	TC-1	PR-120	Internal	1.33	0.07
65	TC-1	PR-122	Internal	1.27	0.06
66	TC-1	PR-123	Internal	1.04	0.06
67	TC-1	PR-126	Internal	1.28	0.08
68	TC-1	PR-128	Internal	1.44	0.05
69	TC-1	PR-129	Internal	1.39	0.05
70	TC-1	PR-129	HS-2/Int.	1.44	0.06
71	TC-1	PR-135	Internal	1.19	0.07
72	TC-1	PR-137	Internal	2.67	0.09
73	TC-1	PR-138	Internal	2.00	0.20
74	TC-1	PR-139	Internal	2.31	0.20
75	TC-1	PR-140	Internal	2.79	0.09
76	TC-1	PR-141	Internal	3.07	0.20
77	TC-1	PR-142	Internal	2.91	0.05
78	TC-1	PR-143	Internal	3.00	0.10
79	TC-1	PR-144	Internal	3.20	0.13
80	TC-1	PR-146	Internal	1.65	0.05
81	T-39	PR-146	Internal	2.40	0.05

N.R. = No record was kept which could be located for inclusion in this table.

EXAMPLES 82 THROUGH 114

A mixture was prepared in each instance using 65 g. of acetonitrile, 25 g. of methanol, 10 g. of cellulose acetate butyrate binder and either 7.5 millimoles of 2-(1-hydroxyethyl)-5-methyl-1,4-benzoquinone (PR—102) or 2-isopropoxy-1,4-naphthoquinone (PR—129). To 6 grams of each mixture was added a tetrazolium salt. Those tetrazolium salts lacking electronegative substituents as required by the present invention and incorporated for the purpose of comparison are set forth below in Table X.

TABLE X

T-Salt	Control Designation
2,3,5-triphenyl-2H-tetrazolium chloride	TC-1
2-(2-methylphenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate	TC-2
2-(4-chlorophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate	TC-3
2,3-diphenyl-5-(4-chlorophenyl)-2H-tetrazolium tetrafluoroborate	TC-4
2-(4-iodophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate	TC-5
2-(2-methoxyphenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate	TC-6
2,3-diphenyl-5-(2-chlorophenyl)-2H-tetrazolium iodide	TC-7
2-(2,4,6-trichlorophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate	TC-8
2,3-diphenyl-5-(3-nitrophenyl)-2H-tetrazolium tetrafluoroborate	TC-9
2-(3-nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate	TC-10
2,3-diphenyl-5-(4-nitrophenyl)-2H-tetrazolium tetrafluoroborate	TC-11

Those mixtures containing PR—102 received 0.2 millimoles of tetrazolium salt and those containing PR—129 received 0.4 millimoles of tetrazolium salt. The mixture was agitated and coated with a 150 micron coating blade onto a 100 micron poly(ethylene terephthalate) film support. Contact exposure for 8 seconds on an exposure unit commercially available under the trademark IBM Microcopier II was followed by development with anhydrous ammonia at 75 psi. At this point the image green densities were measured. These are set out in Table XI. The developed images were placed on a desk top in a room lighted by two banks of three GE F400W Cool White fluorescent lights six and eight feet from the desk surface. The half-life reported in Table XI is the time elapsed before the dye had irreversibly faded to destroy one half of the formazan dye initially present.

TABLE XI

Exemplary Image Qualities Produced by Various Tetrazolium Salts

Ex. No.	T-Salt	Photo-Reductant	Summed Substituent Sigma Values	Initial Image Green Density	Half-life (days)
82	TC-1	PR-129	0.0	1.7	8
83	TC-2	PR-129	−0.13	1.8	10
84	TC-3	PR-129	+0.24	2.1	12
85	TC-4	PR-129	+0.24	1.7	12
86	TC-5	PR-129	+0.30	1.9	9
87	TC-6	PR-129	+0.24	1.8	12
88	TC-7	PR-129	+0.24	0.7	21
89	TC-8	PR-102	+0.72	1.9	3
90	TC-9	PR-129	+0.71	2.0	N.R.
91	TC-10	PR-102	+0.71	1.5	5
92	TC-10	PR-129	+0.71	1.5	25
93	TC-11	PR-102	+0.78	0.5	6
94	TC-11	PR-129	+0.78	1.5	21
95	T-48	PR-102	+0.48	2.2	90
96	T-36	PR-102	>1.05	2.3	145
97	T-36	PR-129	>1.05	1.6	150
98	T-48	PR-102	>0.78	1.6	90
99	T-48	PR-129	>0.78	1.5	80
100	T-49	PR-102	>1.02	2.8	80
101	T-49	PR-129	>1.02	2.0	100
102	T-51	PR-102	+0.95	1.9	80
103	T-51	PR-129	+0.95	1.7	86
104	T-52	PR-102	>1.56	N.R.	180
105	T-54	PR-102	>0.65	2.7	18
106	T-55	PR-102	>0.78	3.0	8
107	T-55	PR-129	>0.78	2.2	33
108	T-56	PR-102	>1.08	3.7	12
109	T-56	PR-129	>1.08	2.0	N.R.
110	T-57	PR-102	>1.02	2.6	17
111	T-58	PR-102	>1.56	3.9	20
112	T-58	PR-129	>1.56	2.0	N.R.
113	T-59	PR-102	>1.56	2.4	21
114	T-60	PR-102	+1.40	2.5	13

EXAMPLES 116 AND 117

In each instance a solution was prepared containing 1.25 ml methanol, 4.5 ml ethylene chloride, 0.33 g. of cellulose acetate butyrate, 0.25 millimoles of a tetrazolium salt, and 0.10 g. 2-isopropoxy-1,4-naphthoquinone (PR—129). In one instance 0.28 millimoles of cadmium nitrate was included while in a second instance it was omitted. This solution was coated with a 100 micron coating blade on a 100 micron poly(ethylene terephthalate) film support. Each element was given a contact exposure through a 0.05 neutral density filter for 10 seconds on a commercial exposure unit sold under the trademark Filmsort Uniprinter 086 followed by development in a Keuffel and Esser Mercury Ammonia Chamber. The coating containing cadmium nitrate exhibited a red image density of 1.14 while the coating lacking this chelating agent exhibited a blue density of 1.06.

EXAMPLES 118 THROUGH 120

In a 5.5 g. portion of a mixture containing 10 g. cellulose acetate butyrate, 70 g. methyl ethyl ketone, 20 g. of methanol and 1.23 g. of 2-(1-hydroxyethyl)-5-memthyl-1,4-benzoquinone (PR102) was dissolved 0.25 millimoles of 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl tetrazolium tetrafluoroborate and 0.99 g. of copper cyclohexylbutyrate. The mixture was coated with a 150 micron coating blade. The initial neutral density after an 8 second exposure on an exposure unit commercially available under the trademark Microcopier II and 1 second ammonia development at 75 psi and 1.62. These results are summarized below in Table XII. Similar runs with different tetrazolium salts are also set out in Table XII.

TABLE XII

Exemplary Densities of Elements Incorporating Bidentate Formazans

Ex. No.	T-Salt	Area	Neutral Density
118	T-56	Image	1.62
		Background	0.07
119	T-52	Image	1.12
		Background	0.07
120	T-58	Image	2.17
		Background	0.09

EXAMPLE 121

A coating was made up by mixing 6 grams of cellulose acetate butyrate (used as a binder), 36 grams of acetone, 12 grams of methanol, 6 grams of methoxyethanol and 0.90 grams of phenyl-1,2-ethanediol (HS—2). In 6 grams of this mixture were dissolved 0.164 grams of 2-nitrobenzyl alcohol (PR—1) and 0.196 grams of 2-(2.5-dichlorophenyl)-3-(2-methoxy-4-nitrophenyl)-5-(4-methoxyphenyl)-2H-tetrazolium tetrafluoroborate (T—32). A coating was prepared on poly(ethylene terephthalate) film support with a wet coating thickness of approximately 150 microns. Contact exposure for 8 seconds on an exposure unit commercially available under the trademark IBM Microcopier II was followed by development for one second with anhydrous ammonia at 75 psi. A negative purple image was obtained having a maximum green density of 1.02. The background areas exhibited a green density of 0.10.

EXAMPLE 122

The procedure of Examples 19 through 83 was repeated using 2-(4-tolyl)thiochromanone (PR—41as a photoreductant and as a tetrazolium salt 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (T—39). A reddish negative image was obtained on a colorless background.

EXAMPLE 123

A coating composition was prepared by mixing together 0.58 g of celluloe acetate butyrate, 5.00 grams of acetone, 1.92 grams of methanol, 0.051 grams of phenyl-1,2-ethanediol (HS—2), 0.065 grams of 10-diazoanthrone (PR—33), 0.40 grams of dimethylformamide, and 0.100 grams of 2,3,5-triphenyl-2H-tetrazolium chloride (TC—1). The composition was coated onto a poly(ethylene terephthalate) film support at a 100 microns wet coating thickness. The dried coating was given a 4 minute on-off exposure at a distance of 36 centimeters with a conventional exposure unit using a 2000 watt mercury lamp commercially available under the trademark Addalux type 1406—CI. Upon processing in a conventional diazo ammonia processor, a red negative image was obtained while unexposed areas remained yellow. Generally similar results can be obtained using electronegatively substituted tetrazolium salts according to the present invention with the further advantages that more stable formazan dye images can be formed.

EXAMPLE 124

A solution of 100 mg of 1-naphthyl-(1-phenethyl) disulfide (PR—12) and 1.0 gram of tricresyl phosphate was dispersed in 10 grams of a 5 percent by weight aqueous gelatin emulsion. Two drops of 40 percent by weight formalin was added to the emulsion, and the composition was coated on a poly(ethylene terephthalate) film support at a wet thickness of 100 microns.

A section of the dried coating was exposed in a xenon wedge spectrograph for 15 minutes and then developed in a dilute aqueous solution of ammonia and 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (T—39). A red image was produced on a pale background.

EXAMPLE 125

A mixture was prepared containing 6.6 grams of cellulose acetate butyrate, 90 ml of ethylene chloride and 25 ml methanol. In 7 grams of this mixture were dissolved 0.080 grams of phenyl-1,2-ethanediol (HS—2), 0.103 g of 4-bromonitrobenzene (PR—2) and 0.165 grams of 2,3,5-triphenyl-2H-tetrazolium chloride (TC—1). This was coated on a transparent poly(ethylene terephthalate) film support at a wet thickness of 100 microns. The film was exposed for 8 seconds on an exposure unit commercially available under the trademark IBM Microcopier II. Exposure was followed by development for one second with anhydrous ammonia at 75 psi. A negative red image was produced on a colorless background. Generally similar results can be obtained using electronegatively substituted tetrazolium salts according to the present invention with the further advantage that more stable formazan dye images can be formed.

In each of the foregoing examples, the processed photographic elements were handled in room light without fixing. In no instance did the background den-

sity increase to the point that the image was obscured, and, in most instances, no increase in background densities were visibly detectible.

While the foregoing examples are incorporated for the purpose of illustrating the scope of the present invention, it is recognized that the internal hydrogen source photoreductants constitute improvements on the present invention which are specifically disclosed and claimed in the above-referenced concurrently filed patent application of Fleming et al titled PHOTOGRAPHIC ELEMENTS AND PROCESSES FOR INCORPORATED HYDROGEN SOURCE PHOTOREDUCTION IMAGING.

This invention has been described in detail with particular reference to certain 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 at least one radiation-sensitive image recording layer thereon comprised of a source of labile hydrogen atoms, a tetrazolium salt capable of reduction to a formazan dye and a photoreductant capable of forming a base activatible reducing agent precursor on exposure to actinic radiation in the presence of said labile hydrogen atoms, the improvement in which said tetrazolium salt includes dye stabilizing tetrazole nucleus substituents which are, collectively, predominantly electronegative so that the algebraic sum of the Hammett sigma values of the tetrazole nucleus substituents are

a. in excess of 0.78 or

b. in excess of 0.40 when said tetrazole nucleus is provided with a ring substituent bonded to said tetrazole nucleus at a first ring position and including a single substituent ortho to said first ring position.

2. In a photographic element according to claim **1** the further improvement in which said source of labile hydrogen atoms in external of said photoreductant.

3. In a photographic element according to claim **2** the further improvement in which said external hydrogen source 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 is a polymer and also serves as a binder for said image recording layer.

5. In a photographic element according to claim **4** the further improvement in which siad 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 **4** the further improvement in which said polymer binder is a poly(vinyl acetal).

8. In a photographic element according to claim **7** the further improvement in which said polymer binder is poly(vinyl butyral).

9. In a photographic element according to claim **2** the further improvement in which said external hydrogen source is nitrilotriacetonitrile.

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

11. In a photographic element according to claim **2** the further improvement in which said external hydrogen source is a poly(alkylene glycol).

12. In a photographic element according to claim **11** the further improvement in which said external hydrogen source is poly(ethylene glycol).

13. In a photographic element according to claim **1** the further improvement in which said photoreductant is a nitroarene.

14. In a photographic element according to claim **13** the further improvement in which said photoreductant is a halonitroarene.

15. In a photographic element according to claim **14** the further improvement in which said photoreductant is a halonitrobenzene.

16. In a photographic element according to claim **15** the further improvement in which said photoreductant is a 4-halonitrobenzene.

17. In a photographic element according to claim **16** the further improvement in which said photoreductant is 4-bromonitrobenzene.

18. In a photographic element according to claim **1** the further improvement in which said photoreductant is a phenazinium salt.

19. In a photographic element according to claim **18** the further improvement in which said phenazinium salt is phenazinium 4-toluenesulfonate.

20. In a photographic element according to claim **1** the further improvement in which said photoreductant is a disulfide.

21. In a photographic element according to claim **20** the further improvement in which said photoreductant is an aryl disulfide capable of being cleaved at the S—S bond by actinic radiation to form a mercaptan.

22. In a photographic element according to claim **21** the further improvement in which said photoreductant is 1-naphthyl-1'-phenethyl disulfide.

23. In a photographic element according to claim **1** the further improvement in which said photoreductant is a diazoanthrone.

24. In a photographic element according to claim **23** the further improvement in which said diazoanthrone is a 10-diazoanthrone.

25. In a photographic element according to claim **1** the further improvement in which said photoreductant is a beta-ketosulfide.

26. In a photographic element according to claim **25** the further improvement in which said photoreductant is a thiochromanone.

27. In a photographic element according to claim **26** the further improvement in which said photoreductant is 2-(4-tolyl)thiochromanone.

28. In a photographic element according to claim **1** the further improvement in which said photoreductant is a quinone, a disulfide, a phenazinium salt, a beta-ketosulfide, a nitroarene, a diazoanthrone, or a mixture of two or more of these.

29. In a photographic element according to claim **1** the further improvement in which said tetrazolium salt contains 2 and 3 position tetrazole ring substituents chosen from the class consisting of pyridyl, quinolinyl, azolyl and aryl substituents.

30. In a photographic element according to claim **29** the further improvement in which said tetrazolium salt

is a 2,3-diaryl tetrazolium salt.

31. In a photographic element according to claim **30** the further improvement in which said tetrazolium salt is a 2,3,5-triaryltetrazolium salt.

32. In a photographic element according to claim **31** the further improvement in which said tetrazolium salt is a 2,3,5-triphenyltetrazolium salt.

33. In a photographic element according to claim **32** the further improvement in which said phenyl substituents are halogen or nitro substituted.

34. In a photographic element according to claim **33** the further improvement in which at least one of said phenyl substituents contains a single ortho substituent, which is a halogen or nitro substituent.

35. In a photographic element according to claim **34** the further improvement in which said tetrazolium salt is chosen from the class consisting of 2-(2-bromophenyl)-3-(2-nitrophenyl)-5-phenyl-2H-tetrazolium salt; 2,3-di(2-chlorophenyl)-5-phenyl-2H-tetrazolium salt; 2-(2nitrophenyl)-3,5-diphenyl-2H-tetrazolium tetrafluoroborate; 2-(2-chlorophenyl)-3-phenyl-5-(3-nitrophenyl)-2H-tetrazolium salt; and 2-(2,4-dinitrophenyl)-3,5-diphenyl-2H-tetrazolium salt.

36. In a photographic element according to claim **33** the further improvement in which said tetrazolium salt is a 2,3-di(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride.

37. In a photographic element according to claim **33** the further improvement in which said tetrazolium salt is a 2-(4-nitrophenyl)-3,5-diphenyl-2H-tetrazolium salt or a 2,3-di(4-nitrophenyl)-5-(4-alkoxyphenyl)-2H-tetrazolium salt.

38. In a photographic element according to claim **29** the further improvement in which said tetrazolium salt contains halogen or nitro substituents to said ring substituents.

39. In a photographic element according to claim **38** the further improvement in which said tetrazolium salt contains a 2-(2-pyridyl)-3-(4-halophenyl)-5-phenyl-2H-tetrazolium salt.

40. In a photographic element according to claim **29** the further improvement in which said tetrazolium salt contains at least one 2-pyridyl or 2-azolyl tetrazole nucleus substituent in the 2 or 3 position capable of forming a tridentate chelate.

41. In a photographic element according to claim **1** the further improvement additionally including means incorporated within said image recording layer capable of interacting with a formazan dye to form a chelate.

42. In a photographic element according to claim **41** the further improvement in which said chelating means is chosen from the class consisting of copper, zinc, mercury, cadmium, cobalt and nickel salts.

43. In a photographic element according to claim **41** the further improvement in which said chelating means is a metal carboxylate.

44. In a photographic element according to claim **1** the further improvement in which said tetrazolium salt is a tetrafluoroborate or a hexafluorophosphate.

45. In a photographic element according to claim **1** the further improvement in which from 0.1 to 10 moles of tetrazolium salt are present per mole of photoreductant.

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

47. 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 99 percent by weight.

48. In a photographic element according to claim **47** 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.

49. In a photographic element according to claim **45** the further improvement in which said photoreductant and said tetrazolium salt are present in substantially equal molar proportions.

50. In a photographic element having a support and at least one radiation-sensitive image recording layer thereon comprised of a source of labile hydrogen atoms, a tetrazolium salt capable of reduction to a formazan dye, a quinone photoreductant capable of forming a base activatible reducing agent precursor on exposure to actinic radiation in the presence of said labile hydrogen atoms, the improvement in which said tetrazolium salt includes dye stabilizing tetrazole nucleus substituents which are, collectively, predominantly electronegative so that the algebraic sum of the Hammett sigma values of the tetrazole nucleus substituents are

a. in excess of 0.78 or

b. in excess of 0.40 when said tetrazole nucleus is provided with a ring substituent bonded to said tetrazole nucleus at a first ring position and including a single substituent alpha to said first ring position, said alpha substituent being electronegative.

51. In a photographic element according to claim **50** the further improvement in which said quinone incorporates at least one alkyl, alkenyl, alkynyl, aryl, alkoxy, aryloxy, alkaryloxy, hydroxyalkyl, alkylcarbonyl, carboxyl, amino, aminoalkyl, amidoalkyl, anilino, piperidino, pyrrolidino, morpholino, nitro or halide substituent.

52. In a photographic element according to claim **51** the further improvement in which said quinone incorporates at least one phenyl or phenoxy substituent.

53. In a photographic element according to claim **52** the further improvement in which each of said alkyl, alkenyl and alkynyl substituents, whether present as separate substituents or in combination with other substituents, incorporate twenty or fewer carbon atoms.

54. In a photographic element according to claim **53** the further improvement in which each of said alkyl, alkenyl and alkynyl substituents, whether present as separate substituents or in combination with other substituents, incorporate six or fewer carbon atoms.

55. In a photographic element according to claim **50** the further improvement in which said quinone is a benzoquinone.

56. In a photographic element according to claim **55** the further improvement in which said benzoquinone is a 1,4-benzoquinone.

57. In a photographic element according to claim **56** the further improvement in which said 1,4-benzoquinone is 2,5-dimethyl-1,4-benzoquinone; duroquinone; 2,5-di-t-butyl-1,4-benzoquinone; 2,3,5-trimethyl-6-bromo-1,4-benzoquinone; or 2-phenyl-1,4-benzoquinone.

58. In a photographic element according to claim **50** the further improvement in which said quinone is a naphthoquinone.

59. In a photographic element according to claim 58 the further improvement in which said naphthoquinone is a 1,4-naphthoquinone.

60. In a photographic element according to claim 59 the further improvement in which said 1,4-naphthoquinone is 2-methyl-1,4-naphthoquinone; 2,3-dimethyl-1,4-naphthoquinone; 2,3-dichloro-1,4-naphthoquinone; 2-thiomethyl-1,4-naphthoquinone; 2-acetylthiomethyl-3-methyl-1,4-naphthoquinone; or 1,4-naphthoquinone.

61. In a photographic element according to claim 50 the further improvement in which said quinone is an anthroquinone.

62. In a photographic element according to claim 61 the further improvement in which said anthroquinone is 2-t-butylanthraquinone.

63. In a photographic element having a support and at least one radiation-sensitive image recording layer thereon comprised of a source of labile hydrogen atoms, a tetrazolium salt capable of reduction to a formazan dye and a quinone photoreductant capable of forming a base activatible reducing agent precursor on exposure to actinic radiation in the presence of said labile hydrogen atoms, the improvement in which said tetrazolium salt includes dye stabilizing 2 and 3 position tetrazole nucleus substituents chosen from the class consisting of pyridyl, azolyl, quinolinyl and aryl substituents which are, collectively, predominantly electronegative, with the algebraic sum of the Hammett sigma values of all tetrazole nucleus substituents being in excess of 1.00.

64. In a photographic element having a support and at least one radiation-sensitive image recording layer thereon comprised of a source of labile hydrogen atoms, a tetrazolium salt capable of reduction to a formazan dye and a quinone photoreductant capable of forming a base activatible reducing agent precurson on exposure to actinic radiation in the presence of said labile hydrogen atoms, the improvement in which said tetrazolium salt includes dye stabilizing 2 and 3 position tetrazole nucleus phenyl substituents which are, collectively, predominantly electronegative, with the algebraic sum of the Hammett sigma values of all tetrazole nucleus substituents being in excess of 0.50 when at least one of said 2 and 3 position phenyl substituents are singly ortho substituted.

65. An image recording process comprising converting a photoreductant capable of forming a base activatible reducing agent precursor on exposure to actinic radiation, within a selected areal portion of a radiation-sensitive layer of a photographic element, to a reducing agent precursor by imagewise exposing the photoreductant to actinic radiation while in reactive contact with labile hydrogen atoms,

activating the precursor with a base to form a reducing agent; and

reducing to produce a formazan dye of enhanced stability a tetrazolium salt including dye stabilizing tetrazole nucleus substituents which are, collectively, predominantly electronegative so that the algebraic sum of the Hammett sigma values of the tetrazole nucleus substituents are

a. in excess of 0.78 or

b. in excess of 0.40 when the tetrazole nucleus is provided with a ring substituent bonded to the tetrazole nucleus at a first ring position and including a single substituent ortho to the first ring position.

66. An image recording process according to claim 65 comprising utilizing the base in the gaseous phase.

67. An image recording process according to claim 65 in which the precursor is activated by ammonia.

68. An image recording process according to claim 65 comprising chelating the formazan dye.

69. An image recording process according to claim 65 in which the radiation-sensitive layer of the photographic element is exposed to visible light.

70. An image recording process according to claim 65 in which the radiation-sensitive layer of the photographic element is exposed to ultra-violet radiation.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,887,372

DATED : June 3, 1975

INVENTOR(S) : David S. Bailey

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

Column 3, line 14, "expopsed" should read --exposed--. Column 4, line 65, "advantges" should read --advantages--. Column 7, line 8, that part of formula reading "benzamidophenyl-5" should read --benzamidophenyl)-5--; line 23, that part of formula reading "chloro-5-5" should read --chloro-5--. Column 15, line 48, "clement" should read --element--. Column 18, line 6, "ambinet" should read --ambient--; line 19, "radiationsensitive" should read --radiation-sensitive--. Column 19, line 8, "PR-68)" should read --(PR-68)--. Column 21, lines 5-6, "Donor Hydrogen" should read --Hydrogen Donor--. Column 23, line 24, that part of formula reading "memthyl" should read --methyl--; line 24, "PR102" should read --PR-102--; line 57, that part of formula reading "(2.5" should read --(2,5--. Column 24, line 3, "(PR-41" should read --PR-41)--; line 11, "celluloe" should read --cellulose--; line 29, "advantages" should read --advantage--. Column 25, line 53, "siad" should read --said--. Column 27, line 20, that part of formula reading "(2nitrophenyl)" should read --(2-nitrophenyl)--. Column 29, line 37, "precurson" should read --precursor--.

Signed and Sealed this

thirteenth Day of April 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks