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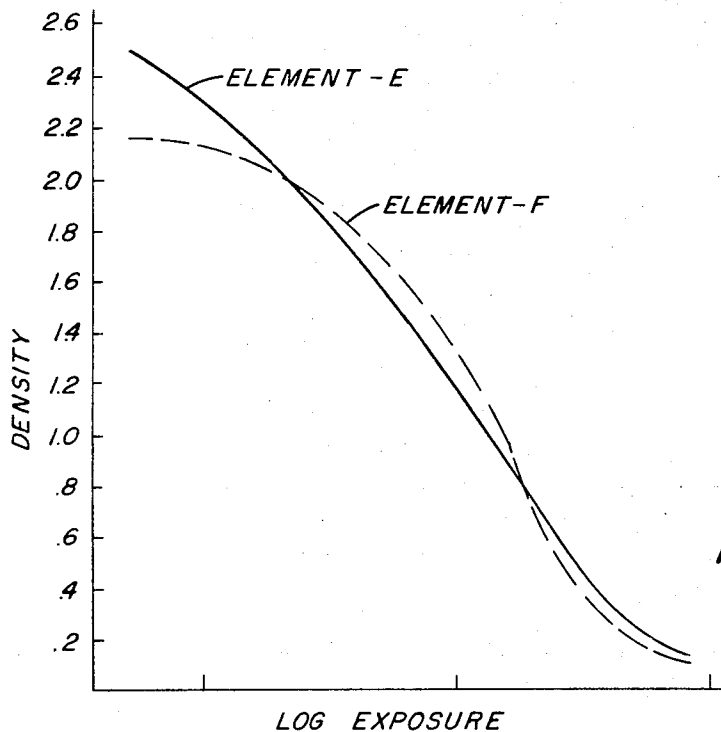
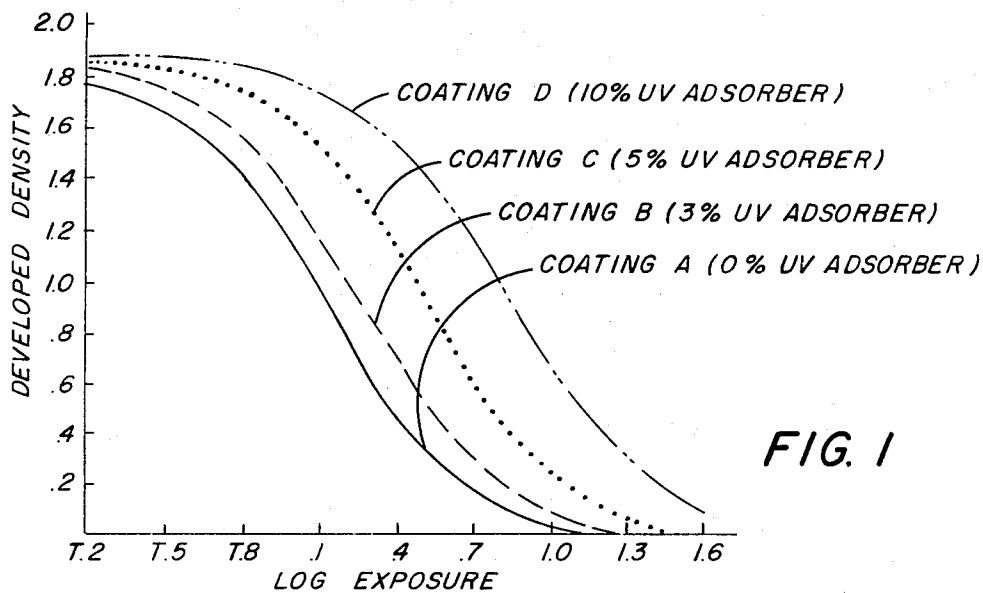
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DIAZOTYPE PHOTOGRAPHIC ELEMENTS HAVING EXTENDED EXPOSURE

LATITUDE WITH SPECIFIC U-V ABSORBER

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DIAZOTYPE PHOTOGRAPHIC ELEMENTS HAVING EXTENDED EXPOSURE LATITUDE WITH SPECIFIC U-V ABSORBER

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4 Claims

ABSTRACT OF THE DISCLOSURE

Diazotype photographic elements having stratified light-sensitive layers including a diazonium salt and a coupler compound which can react with the diazonium salt to produce an azo dye are able to reproduce high-light and shadow details of continuous tone images under widely varying exposure conditions and without background stain by the inclusion therein of an alkaline-bleachable ultraviolet absorber layer which is positioned such that it intercepts activating exposing radiation not later than its passage through the terminally irradiated light-sensitive layer. Advantageous ultraviolet absorber materials include substituted pyrylium salts and substituted thiapyrylium salts such as 2,4,6-triphenylthiapyrylium fluoroborate. Additionally, duplicating characteristics including the print speed and image quality of subsequent generation copies are improved.

This invention relates to photography and in particular to light-sensitive diazotype photographic elements which are capable of yielding stain-free continuous tone image reproductions in successive print generations and under widely varying exposure conditions.

Two-component diazotype photographic elements normally include a resinous matrix containing at least one diazonium salt and at least one coupler compound which can react with the diazonium salt, typically in an alkaline medium to form an azo dye. Such media can exist as monolayer elements or as multilayer elements wherein each light-sensitive layer includes at least one diazonium salt and at least one coupler compound. In addition, there can be present various other additives, such as ultraviolet absorbers, acid stabilizers to prevent premature coupling of the diazonium salt and the coupler as well as additional known addenda. These diazotype compositions or azo dye-forming systems have been employed generally as duplicating media. Their use typically involves an imagewise exposure to activating radiation, e.g., light, through an original, whereby the transmitted light decomposes a diazonium salt. After exposure the film is usually treated with an alkaline medium such as aqueous ammonia vapor to promote coupling of the undecomposed diazonium salt and coupler compound, thereby forming an azo dye in the unexposed areas to provide a positive image corresponding to that of the original.

Diazotype elements are generally utilized to produce high contrast copies. They are adapted to the preparation of high contrast reproductions such as line drawings, book print and other solid black-on-white copy situations such as half-tone dot patterns, since impingement by activating radiation generally results in total decomposition of the diazonium salt in light-struck areas. This characteristic usually renders diazotype elements unsuited for continuous tone reproduction due especially to their inability to reproduce detail in highlight areas.

Numerous attempts have been made to improve the tonal gradation reproduction characteristics of diazotype elements. In one of the attempts at producing a more nearly linear sensitometric curve, multiple diazonium

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salts of differing light-absorbitivity have been coated in a composite diazotype element. The more light-sensitive member of what is typically a diazonium salt pair is more rapidly destroyed so that contrast in high-density image areas (shadow region) is increased. The slower member of a pair tends to remain undestroyed at longer exposures and thereby contributes towards producing a lower contrast in low density highlight areas.

This method, however, suffers from several fundamental disadvantages. Usually, any pair of diazonium salts which are sufficiently varied in their chemical construction to have widely differing light sensitivities and in turn produce significant contrast-mitigating sensitometric effects are also very likely to produce dyes of widely differing colors and also to couple to produce these dyes at widely differing rates. These factors, especially in combination, tend to produce a two-toned effect with a dye color being produced in regions of high density which is different from that dye color which is produced in regions of low density. An additional disadvantage resides in the fact that printing speed is adversely effected by the presence of the more slowly printing diazonium salt.

An additional attempt at mitigating the high contrast effects of diazotype elements has been to mix finely divided pigments such as barium sulfate, calcium sulfate, etc., into the diazotype coating formulation. Although improvements in continuous tone reproduction are effected by this method, much of the improvement results through a reduction in dye density due to the whitening effect of the pigment. Such whitening often tends to produce a chalky appearance in the ultimate print, and therefore, is not suitable for many reproduction situations.

Additionally, it has been proposed to introduce a yellow dye into diazotype compositions to bring about an overall softening of their sensitometric characteristics. In carrying out this technique, however, considerable amounts of yellow dye are required in order to gain the desired softening of contrast. This amount of dye reduces printing speed and additionally causes a degradation of overall contrast in subsequent prints due to the background stain produced by the yellow dye. Moreover, the presence of the yellow dye in a diazotype layer depresses contrast not only in the highlight region but also in the shadow region of the image where contrast is initially low. The most recent attempt at producing a diazotype material which is adapted to reproduce continuous tone images (those images not composed of discrete dots) is described in U.S. Patent 3,069,268, wherein a stratified diazotype element of two layers is utilized, that element including an upper layer sensitized with a light-sensitive diazonium salt and a coupler compound and a lower layer sensitized with the same or similar light-sensitive components but also including an ultraviolet absorber which intercepts the exposing radiation after its passage through the upper light-sensitive layer and before or during its passage through the lower light-sensitive layer. In this fashion the upper light-sensitive layer, i.e., that which is first struck by the printing light, receives the shadow detail of the continuous tone image to be printed and the lower light-sensitive layer receives the highlights of such images.

This method, however, has the undesirable result of residual background stain (generally of a yellow or buff color) in the finished print caused by the presence of the ultraviolet absorber. This stain produces a consequent decrease in image quality in the first generation print due to unwanted background coloration, especially in highlight areas. Additionally, the presence of U.V. absorber in the developed transparency makes that image extremely opaque to actinic and ultraviolet light rays which results

in undesirably extended auto-generation exposure intervals.

Accordingly, it is an object of this invention to produce a new light-sensitive diazotype photographic element for high quality reproduction of continuous tone images.

It is an additional object of this invention to produce a novel light-sensitive diazotype photographic element having extended exposure latitude and which produces high-quality, stain-free continuous tone azo dye images.

Another object of this invention is to provide a novel light-sensitive diazotype photographic element which incorporates a removable ultraviolet absorber.

Still another object of the present invention is to produce a new light-sensitive diazotype photographic element, including a bleachable ultraviolet absorber, which has extended exposure latitude and produces stain-free continuous tone azo dye images having improved duplicating characteristics.

Yet an additional object of this invention is to produce a novel light-sensitive diazotype photographic element having extended exposure latitude, which element also has multiple light-sensitive layers each including at least one diazonium salt and at least one coupler compound as well as an alkaline bleachable ultraviolet absorber layer located therein such that it intercepts exposing radiation after its passage through the first-irradiated light-sensitive layer and not later than its passage through the last-irradiated light-sensitive layer.

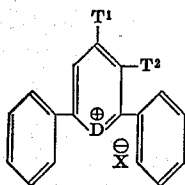
Still an additional object of the instant invention is to provide a new photographic process.

These and other objects of the present invention will become additionally apparent from a reading of the following specification and appended claims.

The objects of the present invention are accomplished with light-sensitive diazotype photographic elements having extended exposure latitude, which elements include a support having coated thereon multiple layers including a light-sensitive diazonium salt and a coupler component which can react with the diazonium salt to form an azo dye, which element also has therein an alkaline bleachable ultraviolet absorber layer to reduce the effective photographic speed of subsequently irradiated light-sensitive layers which ultraviolet absorber layer is located such that it intercepts exposing light-radiation after its passage through the first-irradiated light-sensitive layer and not later than its passage through the last irradiated light sensitive layer.

The alkaline bleachable ultraviolet absorber layers which are advantageous in the practice of this invention include colored materials, usually organic dyes, which absorb light in the ultraviolet, actinic and near blue portions of the spectrum. Such dyes are bleached to a colorless form upon contact with an alkaline medium such as, for example, ammonia. In such fashion, the ultraviolet absorber is effectively removed from the diazotype element.

Organic dyestuffs which possess the requisite absorption characteristics and are alkaline bleachable include a wide variety of pyrylium and thiapyrylium salt dyestuffs as are described in detail in U.S. Pat. 3,250,615, generally from column 2, line 27, to column 4, line 25. Especially advantageous alkaline labile or alkaline bleachable ultraviolet absorbers include certain pyrylium and thiapyrylium dye salts having the formula:



wherein:

(1) T¹ represents a member which is either an alkyl

radical having from 1 to about 15 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl, amyl, isoamyl, hexyl, octyl, nonyl, decyl, dodecyl penta-decyl and the like, an alkoxy radical having from 1 to about 8 carbon atoms like methoxy, ethoxy, propoxy, butoxy, amyloxy, hexoxy, octoxy, etc., or an aryl radical of the benzene series such as phenyl, naphthyl, etc., with phenyl being preferred and including substituted aryl radicals such as alkylphenyl radicals like 4-ethylphenyl, 4-propylphenyl, etc., alkoxyphenyl radicals like 4-ethoxyphenyl, 4-methoxyphenyl, 2-hexoxyphenyl, 3,4-dimethoxyphenyl, 2-hydroxyethoxyphenyl and the like as well as additional substituted aryl radicals like 4-hydroxyphenyl, 3,4-dichlorophenyl, 3,4-dibromophenyl, 4-chlorophenyl, 2,4-dichlorophenyl, etc.

(2) T² represents a member which is either a hydrogen atom, an alkyl radical having from 1 to about 15 carbon atoms such as those described hereinabove in conjunction with the T¹ substituent, an alkoxy radical having from 1 to about 8 carbon atoms as those described in relationship to T¹ or an aryl radical also as those described above with reference to T¹, phenyl being preferred.

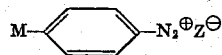
(3) D represents either an oxygen atom or a sulfur atom, and

(4) X⁻ represents an anion including conventional stabilizing anions such as, for example, fluoroborate, perchlorate, chloride, p-toluene sulfonate, sulfate, ferric chloride, zinc chloride, etc., with any stabilizing anion being advantageous.

Exemplary advantageous alkaline bleachable ultraviolet absorbers include such pyrylium and thiapyrylium dyes as:

a 2,4,6-triphenylpyrylium salt,
a 2,4,6-triphenylthiapyrylium salt,
a 2,6-diphenyl-4-n-propylpyrylium salt,
a 2,6-diphenyl-4-n-decylthiapyrylium salt,
a 2,6-diphenyl-4-ethoxythiapyrylium salt,
a 2,6-diphenyl-4-octoxythiapyrylium salt,
a 2,6-di(4-hydroxyphenyl)-3-n-decyl-4-(4-ethylphenyl) thiapyrylium salt,
a 2,6-di(3,4-dichlorophenyl)-3-phenyl-4-amyloxy-pyrylium salt,
a 2,6-di(4-bromophenyl)-3-pentadecyl-4-ethoxy-thiapyrylium salt,
a 2,4,6-tri(3,4-diethylphenyl)pyrylium salt,
a 2,4,6-triphenyl-3-ethoxythiapyrylium salt,
a 2,4-di(4-ethoxyphenyl)-3-n-octoxy-4-n-octoxy-pyrylium salt, and
a 2,4-diphenyl-4-(2-hydroxyethoxyphenyl)pyrylium salt.

In the light-sensitive diazotype elements of this invention, alkaline bleachable ultraviolet light absorbers are used in conjunction with one or more light-sensitive diazonium salts and a coupler compound or compounds constituting a coupler component which can react with the diazonium salt to form an azo dye. Useful diazonium salts include benzene diazonium salts such as those having the formula:



wherein M is either:

(1) a hydrogen atom,
(2) a halogen atom,
(3) an aryl radical,
(4) an amino radical including substituted amino radicals such as those having the formula



wherein R and R⁰ are the same or different and can be a hydrogen atom, an aliphatic alkyl radical (aliphatic alkyl radicals are defined herein to include straight and branched

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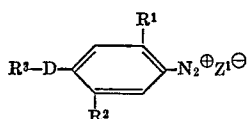
chain alkyl radicals having from 1 to 8 carbon atoms such as methyl, ethyl, isopropyl, tert-butyl, n-amyl, octyl and the like) or an aryl radical such as phenyl or naphthyl, or

(5) an alkyl or aryl thioether radical, and

(6) $Z^{\ominus}$ is an acid anion.

These compounds can also be substituted on one or more of the nuclear benzene carbons with, for example, at least one of either a halogen atom, an aliphatic alkyl radical, an alkoxy radical, an acyl radical, a carbamyl radical, a carboxyl radical or a nitro radical.

Particularly useful diazonium salts include p-aminobenzene diazonium salts having the above formula wherein M is either an amino radical including substituted amino radicals or a thioether radical as described above, and wherein the benzene nucleus is unsubstituted or substituted in at least one of the 2-position and the 5-position with either an aliphatic alkyl radical or an alkoxy radical. This class of useful diazonium salts can be represented by the formula:



wherein:

(1) D is either a sulfur atom or a radical having the formula NR^4 ,

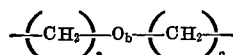
(2) R^3 , when taken alone, is either a hydrogen atom when D is NR^4 , or a lower aliphatic alkyl radical, a lower alkoxy radical, an acyl radical having the formula



wherein T is either an aryl radical or an alkyl radical as described elsewhere herein, or a phenyl radical when D is either a sulfur atom or NR^4 ,

(3) R^4 , when taken alone, is either a hydrogen atom, a lower alkyl radical or a lower alkoxy radical,

(4) R^3 and R^4 , when taken together, complete a divalent radical having the formula:

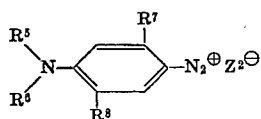


wherein b is an integer having a value of 0 or 1, each of a and c is a positive integer, and the sum of a, b and c has a value of 5,

(5) R^1 and R^2 are each either a hydrogen atom, a halogen atom, a lower aliphatic alkyl radical (preferably methyl or ethyl) or a lower alkoxy radical (preferably methoxy or ethoxy), and

(6) $Z^{\ominus}$ is an acid anion.

Preferred p-aminobenzene diazonium salts include substituted aminobenzene diazonium salts having the formula:



wherein:

(1) each of R^5 and R^6 , when taken alone, is a lower alkyl radical,

(2) R^5 and R^6 , when taken together, are the number of carbon and hetero oxygen atoms necessary to complete a morpholino radical,

(3) each of R^7 and R^8 is a hydrogen atom, a halogen atom, a lower alkyl radical or a lower alkoxy radical, and

(4) $Z^{\ominus}$ is either a chlorozincate anion, a fluoroborate anion, a sulfate anion, a phosphate anion, or a chlorostannate anion.

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The most preferred benzene diazonium salts are the fluoroborate salts wherein:

(1) R^7 and R^8 are alkoxy radicals when R^5 and R^6 complete a morpholino radical, and

(2) R^7 and R^8 are each a hydrogen atom when R^5 and R^6 are each a lower alkyl radical.

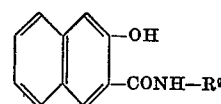
Illustrative of the subject diazonium salts are such compounds as the salts of

- 1-diazo-2,5-dimethoxybenzene;
- 1-diazo-2,5-diethoxybenzene;
- 1-diazo-4-chloro-2,5-diethoxybenzene;
- 4-diazo-2,5-dimethoxybiphenyl;
- 4-diazo-2,5,4'-triethoxybiphenyl;
- 1-diazo-4-dimethylaminobenzene;
- 1-diazo-4-(diethoxyamino)benzene;
- 1-diazo-4-[bis(hydroxypropyl)amino]benzene;
- 1-diazo-4-(N-methyl-N-allylamino)benzene;
- 1-diazo-4-(diamylamino)benzene;
- 1-diazo-4-(oxazolidino)benzene;
- 1-diazo-4-(cyclohexylamino)benzene;
- 1-diazo-4-(9-carbazolyl)benzene;
- 1-diazo-4-(dihydroxyethylamino)-3-methylbenzene;
- 1-diazo-4-dimethylamino-3-methylbenzene;
- 1-diazo-2-methyl-4-(N-methyl-N-hydroxypropylamino)benzene;
- 1-diazo-4-dimethylamino-3-ethoxybenzene;
- 1-diazo-4-diethylamino-3-chlorobenzene;
- 1-diazo-2-carboxy-4-dimethylaminobenzene;
- 1-diazo-3-(2-hydroxyethoxy)-4-pyrrolidinobenzene;
- 1-diazo-2,5-diethoxy-4-acetoxyaminobenzene;
- 1-diazo-4-methylamino-3-ethoxy-6-chlorobenzene;
- 1-diazo-2,5-dichloro-4-benzylaminobenzene;
- 1-diazo-4-phenylaminobenzene;
- 1-diazo-4-morpholinobenzene;
- 1-diazo-4-morpholino-3-methoxybenzene;
- 1-diazo-4-morpholino-2,5-dimethoxybenzene;
- 1-diazo-4-morpholino-2-ethoxy-5-methoxybenzene;
- 1-diazo-4-morpholino-2,5-dibutoxybenzene;
- 1-diazo-2,5-diethoxy-4-benzoylaminobenzene;
- 1-diazo-2,5-dibutoxy-4-benzoylaminobenzene;
- 1-diazo-4-ethylmercapto-2,5-diethoxybenzene;
- 1-diazo-4-tolylmercapto-2,5-diethoxybenzene

and the like, as well as mixtures thereof.

Azo dye couplers which can be reacted with the diazonium salt to form an azo dye include a wide variety of chemical species such as those disclosed by Kosar, "Light-Sensitive System," John Wiley & Sons, Inc., New York (1965), pp. 220-240. Phenolic couplers are preferred, however, with particularly preferred classes including:

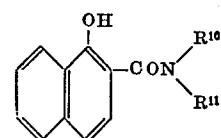
(1) as blue couplers, 2-hydroxy-3-naphthanilides having the formula:



wherein R^9 is a phenyl radical, and preferably a phenyl radical substituted with at least one of either a lower alkyl radical or a lower alkoxy radical or a halogen atom,

(2) as blue couplers, ortho naphthalenediols,

(3) as yellow couplers, 1-hydroxy-2-naphthamides having the formula:



wherein:

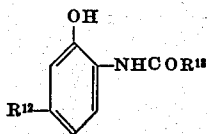
(a) each of R^{10} and R^{11} , when taken alone, is a hydrogen atom or an aliphatic alkyl radical including substituted aliphatic alkyl radicals such as

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those described herein, a cycloalkyl radical, an aryl radical and like hydrocarbon or substituted hydrocarbon radicals,

(b) R¹⁰ and R¹¹, when taken together, represent the carbon and oxygen atoms necessary to complete a six-membered hetero piperidino or morpholino radical, and

(4) as yellow couplers, 2-acylamido-5-substituted phenols having the formula:



wherein R¹² is either an alkyl radical or an alkoxy radical and R¹³ is an aliphatic alkyl radical, an aryl radical, an aralkyl radical or an aralkoxy radical.

Illustrative of the subject couplers are such compounds as for example,

2-hydroxy-3-naphthanilide;
2-hydroxy-2'-methyl-3-naphthanilide;
2-hydroxy-2',2'-dimethoxy-5'-chloro-3-naphthanilide;
2-hydroxy-2'-dimethoxy-3-naphthanilide;
2-hydroxy-2',5'-dimethoxy-4'-chloro-3-naphthanilide;
2-hydroxy-1'-naphthyl-3-naphthanilide;
2-hydroxy-2'-naphthyl-3-naphthanilide;
2-hydroxy-4'-chloro-3-naphthanilide;
2-hydroxy-3-naphthanilide;
2-hydroxy-2',5'-dimethoxy-3-naphthanilide;
2-hydroxy-2',4'-dimethyl-3-naphthanilide;
2,3-naphthalenediol;
1-hydroxy-2-naphthamide;
N-methyl-1-hydroxy-2-naphthamide;
N-butyl-1-hydroxy-2-naphthamide;
N-octadecyl-1-hydroxy-2-naphthamide;
N-phenyl-1-hydroxy-2-naphthamide;
N-methyl-N-phenyl-1-hydroxy-2-naphthamide;
N-(2-tetradecyloxyphenyl)-1-hydroxy-2-naphthamide;
N-[4-(2,4-di-tert-amylphenoxy)butyl]-1-hydroxy-2-naphthamide;
1-hydroxy-2-naphthopiperidide;
N-(3,5-dicarboxyphenyl)-N-ethyl-1-hydroxy-2-naphthamide;
N,N-dibenzyl-1-hydroxy-2-naphthamide;
N-(2-chlorophenyl)-1-hydroxy-2-naphthamide;
N-(4-methoxyphenyl)-1-hydroxy-2-naphthamide;
1-hydroxy-2-naphthopiperizide;
1,3-bis(1-hydroxy-2-naphthamidobenzene);
2-acetamido-5-methylphenol;
2-acetamido-5-pentadecylphenyl;
2-butyramido-5-methylphenol;
2-(2,4-di-tert-amylphenoxyacetamido)-5-methylphenol;
2-benzamido-5-methylphenol

and the like, as well as mixtures thereof.

In addition to the various alkyl, alkoxy and aryl radicals described herein, it is noted that lower aliphatic alkyl and alkoxy radicals are deemed to refer to aliphatic alkyl and alkoxy radicals having from 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, isobutyl, tert-butyl and like alkyl radicals as well as alkoxy radicals such as methoxy, ethoxy, propoxy, tert-butoxy and the like.

For ease of coating and stability of the coated layer, the diazotype composition is generally dispersed in a resinous matrix such as those described hereinbelow, conventionally in an amount of from about 20 to about 40 parts by weight per 100 parts of matrix vehicle.

In addition to the dye-forming components and alkaline bleachable ultraviolet absorbers described in this invention, the diazotype composition can contain and usually does contain other additives such as stabilizers and the like to advantageously modify its photographic and chemi-

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cal properties. A preferred class of additives includes acid stabilizers which operate to prevent premature coupling of the diazonium salt and coupler compound. These acid stabilizers include organic acids such as 5-sulfosalicylic acid and the like as well as numerous other organic and inorganic acids. In general, an acid stabilizer is preferably present in all of the diazotype reproduction media of this invention with the amount normally varying from about 1 part to about 6, and preferably from about 2 to about 5 parts by weight per 100 parts of polymeric matrix. Additionally, metal salts such as zinc chloride can also be present as a development accelerator or dye brightener, generally in an amount of from about 0.5 to about 1.5 parts by weight per 100 parts of matrix vehicle.

Another, and especially desirable, class of additives for diazotype compositions comprises hindered phenols containing in the 2-position either an alkyl or a cycloalkyl radical and in the 4-position an alkyl radical, an alkoxy radical, a hydroxyl radical or a thioether radical, which with the hindered phenolic moiety completes a hindered bithiophenol and more generally a symmetrical bithiophenol. These hindered phenols restrain fading of the developed azo dye image. Such advantages hindered phenols are described in detail in the copending U.S. Patent Application Ser. No. 663,470 filed July 31, 1967, now Pat. No. 3,591,381.

The diazotype compositions, including all supplemental addenda, are typically carried in a film-forming hydrophobic polymeric matrix or binder when preparing photographic elements, both for ease of coating and physical stability of the resultant light-sensitive layers. Advantageous matrix vehicles include a wide variety of polymeric substances such as, for example, cellulosic ethers such as ethyl cellulose, butyl cellulose as well as cellulose esters such as cellulose acetate, cellulose triacetate, cellulose propionate, cellulose acetate propionate, cellulose butyrate and cellulose acetate butyrate; vinyl polymers such as poly(vinyl acetate), poly(vinylidene chloride), poly(vinyl butyral), copolymers of vinyl chloride and vinyl acetate, polystyrenes, poly(methyl methacrylate), copolymers of alkylacrylates and acrylic acid, etc.; polyesters such as the esterification product of p-cyclohexanedicarboxylic acid and 2,2,4,4-tetramethylcyclobutane-1,3-diol, as well as additional polymers such as polyphenylene oxides, terpolymers of ethylene glycol, isophthalic acid and terephthalic acid and terpolymers of p-cyclohexane dicarboxylic acid, isophthalic acid and cyclohexylenebismethanol.

In the preparation of diazotype photographic elements of the present invention, a support material such as described hereinbelow is coated with a plurality of stratified, light-sensitive layers positioned in a superposed relationship with respect to one another such that they are exposed sequentially by light rays, each layer including at least one light-sensitive diazonium salt and at least one coupler compound which can react with the diazonium salt to form an azo dye. Also included in the composite photographic element is an alkaline bleachable ultraviolet absorber layer including at least one of the above-described ultraviolet absorber compounds, which ultraviolet absorber layer is positioned such that it intercepts exposing radiation not later than its passage through the terminally or last-irradiated light-sensitive layer.

Advantageous support materials include conventional photographic film base materials, for example, cellulose esters such as cellulose acetate, cellulose triacetate, cellulose acetate butyrate, etc., poly- α -olefins such as polyethylene and polypropylene, polyesters such as poly(ethylene terephthalate), polystyrenes, polycarbonates, as well as metals such as zinc and aluminum and paper including polyethylene and polypropylene coated papers. Other support materials that are suitable for use herein are known in the art. It is advantageous that the support be transparent or substantially so if the image is to be viewed or copied via transmitted light.

Coating is typically by solvent coating means since it offers the potential for rapid, convenient, continuous operation and alternative coating techniques such as immersion, flow coating, whirl coating, brushing, doctor blade coating, hopper coating and the like can be used if desired. Coating is generally effected by first dissolving the photographic image-forming composition in a suitable solvent along with a matrix polymer if desired. Exemplary matrix polymers are described hereinabove. The coating solution conventionally contains from about 5 to about 20 weight percent solids and preferably from about 8 to about 15 percent solids. In that solution when a matrix polymer is utilized, the photographic image-forming components are typically included in an amount of from about 20 to about 50 parts by weight per 100 parts of polymeric binder with concentrations in the range of from about 25 to about 45 parts per 100 parts of matrix polymer being preferred. Wider variations are possible where desired, but the above-mentioned ratios are typical for most conventional preparations. After coating by such means as whirl coating, brushing, doctor blade coating, hopper coating or the like, typically at a wet thickness of from about 25 microns to about 125 microns, the coated material is dried to prepare a composite photographic element of this invention.

The alkaline bleachable ultraviolet absorber layer, as noted elsewhere herein, is positioned in the photographic element such that it contacts or intercepts exposing radiation after its passage through the first-irradiated light-sensitive layer and not later than its passage through the last-irradiated light-sensitive layer. By such a technique, at least the first-irradiated light-sensitive layer has a typical high photographic speed, and at least the last-irradiated light-sensitive layer has a decreased photographic speed (since certain activating ultraviolet and actinic rays are screened out by the ultraviolet absorber layer) and is capable of registering detail in highlight areas by producing decreased contrast in those image regions. The first exposed, higher speed light-sensitive layer or layers then can record the lower light shadow detail of continuous tone images with photographic speeds being advantageously balanced by controlling the filtering action of the ultraviolet absorber layer between the light-sensitive layers to produce both shadow and highlight details. In this fashion, high-quality image reproduction can be obtained with virtually any combination of diazonium salts and coupler compounds of the types described hereinabove. These results are obtained over a wide variety of exposure conditions. This is to be distinguished from diazotype elements not utilizing an ultraviolet absorber wherein a level of exposure sufficient to produce detail in shadow areas would overexpose the remaining areas virtually eliminating nominal density gradations in highlight areas and vice versa. Additionally, with the alkaline bleachability of the ultraviolet absorbers of this invention, the developed image does not exhibit background stain and, as such, does not exert a filtering effect on exposing radiation for subsequent generation prints or transparencies so that desirably brief auto-generation exposure times are maintained.

In one aspect, the support material can be coated with superimposed, contiguous light-sensitive layers, at least the lowermost of which having an alkaline bleachable ultraviolet absorber of the type described herein included therein as part of the image-forming coating composition. When so included, the ultraviolet absorber material is advantageously present in an amount of from about 1 to about 20 percent by weight of the total coating solids and preferably from about 5 to about 15 percent by weight. In this case, the ultraviolet absorber layer coincides with a light-sensitive layer and acts on exposing rays during their passage through that and underlying light-sensitive layers. In a second aspect, the ultraviolet absorber layer can be coated as a discrete layer interposed between two superposed light-sensitive layers.

When coated in such a fashion, the absorber material is conveniently placed in solution and either dispersed in or codissolved with a resinous vehicle such as those described hereinabove as hydrophobic, film-forming matrices. In yet a third aspect, and using techniques recited herein, the ultraviolet absorber layer can be coated as a discrete layer onto a transparent or substantially transparent support material after which at least one light-sensitive layer can then be coated over the ultraviolet absorber layer and at least one other light-sensitive layer can be coated on the opposite side of the transparent support material to complete a composite photographic element.

Exposure is advantageously to a source of light radiation which is rich in ultraviolet and actinic rays such as a mercury arc lamp. Where elements are structured according to the above-recited second and third aspects, and where the support is transparent or substantially so, exposure can be advantageously accomplished with either side of the support material positioned towards the source of exposing radiation.

After exposure, which can be, for example, through a continuous tone photographic transparency, the element is suitably treated or contacted with an alkaline medium such as one including aqueous ammonia vapor or anhydrous ammonia gas to produce a colored, azo dye image in unexposed areas and thereby forming a positive copy corresponding to the original. During image development, the alkaline medium bleaches the ultraviolet absorber to a colorless form and for photographic purposes effectively secures its removal from the system. Therefore, in the production of subsequent generation copies, substantially the entire spectrum of exposing rays is available for image formation which achieves a commensurate high printing speed in subsequent generation copies. With non-bleachable, non-removable ultraviolet absorbers, exposure times for subsequent prints or transparencies are undesirably extended since that portion of the spectrum to which the diazonium salts exhibit the greatest response, ultraviolet and actinic rays, are filtered out by the background ultraviolet absorber still remaining in the diazotype "original."

Additionally, with conventional, non-removable ultraviolet absorber materials, image, quality in subsequent generation prints (i.e., copies made from copies) is impaired due to the residual stain caused by the still present ultraviolet absorber. Such background staining is not present in the diazo-type photographic elements of this invention.

The following examples are excluded for a further understanding of the invention.

EXAMPLE 1

A coating composition containing:

Cellulose acetate butyrate	g--	14.82
4-diethylaminobenzenediazonium fluoroborate	g--	
1-hydroxy - 2 - naphthopiperidide	g--	2.10
2-hydroxy - 3 - naphth-o-anisidide	g--	1.02
5-sulfosalicylic acid	g--	1.46
Ethanol/acetone 20:80	ml--	.60
		180

is divided into four coating portions (coatings A, B, C and D). The bleachable ultraviolet absorber dye 2,4,6-triphenylthiapyrylium fluoroborate is added to coatings B, C and D in amounts of 3%, 5% and 10% respectively of total solids. No ultraviolet absorber is added to coating portion A which serves as a control. Each coating portion is then coated, using a doctor blade coater, onto separate portions of a subbed poly(ethylene terephthalate) support material to prepare corresponding coatings A, B, C and D. Each coating is then exposed for 40 seconds through a .3 density increment silver step tablet (approximating a continuous tone image) to the U.V. rays of a mercury arc lamp in a Filmsort 086 processor manufactured by Minnesota Mining and Manufacturing. They are

then processed by contact with moist ammonia vapors at 145° F. and 14 p.s.i. on the same Filmsort unit. After image development, density measurements at various exposure levels are obtained on a Macbeth Densitometer Model TD-102. Comparative density values and relative speed loss over the straight-line portion of the characteristic curve for coatings B, C and D, as compared to coating A as a control, are summarized below in tabular form. This comparative data illustrates the speed losses (relative) obtained by inclusion of ultraviolet absorber into a diazo-type element.

PORTION A (0% U.V. ABSORBER)

Log exposure	Developed density	Relative speed loss (log E)
1.0	.03	Control
.7	.15	Control
.4	.47	Control
.1	.93	Control

1.8 1.39 Control

PORTION B (3% U.V. ABSORBER)

1.0	.1	.14
.7	.28	.16
.4	.68	.16
.1	1.16	.16

1.8 1.54 .14

PORTION C (5% U.V. ABSORBER)

1.6		
1.3		
1.0	.23	.40
.7	.63	.42
.4	1.08	.42
.1	1.5	.40

1.8 1.72 (1)

PORTION D (10% U.V. ABSORBER)

1.6		
1.3		
1.0	.72	.76
.7	1.16	.76
.4	1.54	.74
.1	1.73	(1)

1 Not recorded in shoulder portion.

A comparison of the results appearing in the above tables is graphically presented in the accompanying drawing, FIG. 1. In the graph, the vertical axis is calibrated to record developed image density. The horizontal axis is calibrated to record the log exposure. The resultant curves are conventional characteristic curves of the type widely used in the sensitometric analysis of photographic elements. From the curves, and using coating A as a reference, relative speed losses for coatings B, C and D are obtained. The recorded reductions in photographic speed are inversely related to ultraviolet absorber level, and it is easily seen that a reduction in photographic speed is produced by the presence of an ultraviolet absorber material.

EXAMPLE 2

A subbed poly(ethylene terephthalate) support material is extrusion hopper coated with a first layer of a coating composition including:

Cellulose acetate butyrate	32.4
Cellulose acetate	39.6
Acetone	540.0
Methanol	260.0
Methoxyethanol	100.0
4-diethylaminobenzenediazonium fluoroborate	10.4
2-hydroxy-3-naphth-o-anisidide	7.1
1-hydroxy-2-naphthopiperidide	4.9
5-sulfosalicylic acid	2.8
2,4,6-triphenylthiapyrylium fluoroborate	2.8

to provide a dry coverage of .41 g./ft.². The coated layer is thoroughly dried. A second layer of a coating composition including:

n-Butanol	800.0
Water	100.0
Cellulose butyrate	68.7
2,5-diethoxy-4-morpholinobenzenediazonium fluoroborate	14.5
2-hydroxy-3-naphth-o-anisidide	8.2
1-hydroxy-2-naphthopiperidide	5.6
5-sulfosalicylic acid	3.0

is coated over and contiguous to the first layer and at a dry coverage of .20 g./ft.² to prepare a composite, multi-layer diazotype photographic element incorporating a bleachable ultraviolet absorber. The composite element is divided into two portions (elements E and F). Element E is exposed for 60 seconds and processed, as in Example 1, with the bar gamma being 1.2 and the exposure scale being 1.9. The developed image in element E is then used as an original to expose element F which is exposed and processed as is element E to yield comparative results. The exposure time for element F is 74 seconds. On development the ultraviolet absorber material is bleached to a colorless form by the alkaline processing medium, and for this reason the exposure times for elements E and F are substantially equivalent, the entire spectrum of exposing radiation being transmitted to the light-sensitive element. In low density image areas there is also no background staining caused by residual ultraviolet absorber. The similar sensitometric characteristics of developed elements E and F are graphically illustrated in the accompanying drawing (FIG. 2). As noted above, each element includes a bleachable ultraviolet absorber which is removed during processing, thereby avoiding detrimental sensitometric and other image characteristics.

EXAMPLE 3

Photographic elements are made as in Example 2, except that like amounts of the following alkaline bleachable ultraviolet absorbers are used in lieu of 2,4,6-triphenylthiapyrylium fluoroborate:

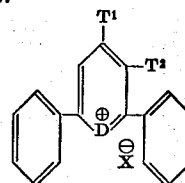
- 2,6-diphenyl-4-p-tolylthiapyrylium fluoroborate
- 2,6-diphenyl-4-methylpyrylium perchlorate
- 2,4,6-triphenyl-3-n-tridecylpyrylium perchlorate
- 2,4,6-triphenyl-3-methylpyrylium perchlorate
- 2,4,6-tri(p-chlorophenyl)-3-n-hexylthiapyrylium fluoroborate

Exposure and processing is accomplished in a like fashion and comparable results are obtained.

The 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. A light-sensitive diazotype photographic element having extended exposure latitude, said element comprising a support having coated thereon two light-sensitive layers, each layer comprising a light-sensitive diazonium salt, a coupler component which can react with the diazonium salt to form an azo dye, and an acidic stabilizer to prevent premature coupling, said element also having therein, to reduce the effective photographic speed of subsequently irradiated light-sensitive layers, a layer comprising an ultraviolet absorber that is bleached to a colorless form on contact with an ammonia developing medium, said ultraviolet absorber comprising a compound having the formula:



wherein:

- (a) T¹ represents a member selected from the group consisting of an alkyl radical having from 1 to 15 carbon atoms, an alkoxy radical having from 1 to 8 carbon atoms and a phenyl radical,
- (b) T² represents a member selected from the group consisting of a hydrogen atom, an alkyl radical having from 1 to 18 carbon atoms and a phenyl radical,
- (c) D represents an oxygen atom or a sulfur atom, and
- (d) X[⊖] represents an anion,

which ultraviolet absorber layer is located such that it intercepts exposing light radiation after its passage through the first-irradiated light-sensitive layer and not later than its passage through the last-irradiated light-sensitive layer.

2. A light-sensitive diazotype photographic element as described in claim 1 wherein said ultraviolet absorber is present in the last-irradiated light-sensitive layer.

3. A light-sensitive diazotype photographic element, as described in claim 1 wherein the alkaline bleachable ultraviolet absorber is selected from the group consisting of:

- 2,4,6-triphenylthiapyrylium fluoroborate,
- 2,6-diphenyl-4-p-tolylthiapyrylium fluoroborate,
- 2,6-diphenyl-4-methylpyrylium perchlorate,
- 2,4,6-triphenyl-5-tridecylpyrylium perchlorate, and
- 2,4,6-triphenyl-5-methylpyrylium perchlorate.

4. A light-sensitive diazotype photographic element comprising a support having coated thereon a first light-

sensitive layer comprising the light-sensitive diazonium salt 4 - diethylaminobenzenediazonium fluoroborate, the coupler compounds 2' - methoxy - 2 - hydroxy - 3 - naphthanilide and 1 - hydroxy - 2 - naphthopiperidide, and the alkaline bleachable ultraviolet absorber 2,4,6 - triphenylthiapyrylium fluoroborate and, coated over the first layer, a second light-sensitive layer comprising the light-sensitive diazonium salt 2,5 - diethoxy - 4 - morpholinobenzenediazonium fluoroborate and the coupler compounds 2' - methoxy - 2 - hydroxy - 3 - naphthanilide and 1-hydroxy-2-naphthopiperidide.

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