United States Patent Office **3,542,555**
Patented Nov. 24, 1970

3,542,555
PHOTOGRAPHIC SILVER HALIDE ELEMENTS CONTAINING TETRAKISAZO DYES

Jonas J. Chechak, Brockport, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Sept. 15, 1967, Ser. No. 668,174
Int. Cl. G03c *1/40*
U.S. Cl. 96—73 **4 Claims**

ABSTRACT OF THE DISCLOSURE

Certain tetrakisazo dyes are readily bleached in the presence of a silver image, and when they are coated on a support contiguous to the silver halide of at least one light-sensitive silver halide emulsion layer, a photographic element results which can be processed by known dye-bleach techniques to provide positive, colored dye images.

This invention relates to photography, and in particular, to dyes which are readily bleached in the presence of a silver image and to photographic elements and processes utilizing such dyes.

It is known in the art to produce photographic mono and multicolored positive dye images by dye-bleach techniques. In a single color element, a support material is coated with a light-sensitive layer that contains a silver halide emulsion and a bleachable azo dye. A typical multicolor element involves three such light-sensitive layers sensitized to red, green and blue light and having in association therewith, respectively, amounts of bleachable cyan colored, magenta colored and yellow colored azo dyes. After an imagewise exposure, such elements, both single color and multicolor, are developed in a typical black-and-white developer solution to product photographic silver images in the areas which have been impinged upon by activating radiation. The elements bearing such silver image or images are then treated with a suitable bleaching solution which causes the colored azo dyes to be reduced to colorless forms in the areas corresponding to the silver image, thereby producing colored dye images which are positive reproductions of the original. Bleaching solutions can be either alkaline, such as a sodium hydroxide solution of stannous chloride, or acidic, such as acidic thiourea.

It is an object of this invention to provide, for photographic purposes, new azo dyes which can be bleached readily in the presence of a silver image.

Another object of this invention is to provide, for photographic purposes, novel azo dyes which are readily bleached by both acidic and alkaline bleaching solutions in the presence of a silver image.

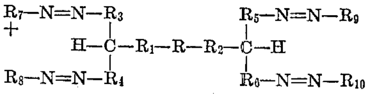
An additional object of the present invention is to provide new photographic elements which, when processed by acidic or alkaline dye-bleach techniques, produce positive colored dye images.

Still another object of this invention is to provide a new photographic dye-bleach process.

These and other objects of the instant invention will become apparent from a consideration of the following specifications and appended claims.

The objects of the present invention are accomplished with tetrakisazo dyes which are readily bleached in the presence of a silver image. Such tetrakisazo dyes can be coated upon a support, contiguous to the silver halide of a silver halide emulsion, to form a light-sensitive photographic element which can be processed by known dye-bleach techniques to provide positive dye images.

The tetrakisazo dyes of this invention include dyes having the formula:



$$\begin{array}{ccc} R_7-N{=}N-R_3 & & R_5-N{=}N-R_9 \\ | & & | \\ H-C & -R_1-R-R_2- & C-H \\ | & & | \\ R_8-N{=}N-R_4 & & R_6-N{=}N-R_{10} \end{array}$$

wherein:

(a) R represents a ureylene radical,
(b) each of R_1 through R_6 represents a phenylene radical, and
(c) each of R_7 thorugh R_{10} represents either a monovalent sulfonated aryl alcohol radical or a monovalent sulfonated aryl amine radical.

The radiacls described herein and designated by R_1 through R_6 can be substituted. Typical substituents are, for example, hydroxyl radicals; halogen atoms such as bromine, iodine and chlorine; alkyl radiacls having 1 to about 14 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, octyl dodecyl, tetradecyl and the like; alkoxy radicals having from 1 to about 12 carbon atoms such as methoxy, ethoxy, propoxy, octoxy, dodecoxy and the like; and carboxylic acid ester radicals having from 1 to about 14 carbon atoms such as propionoyloxy, benzoyloxy, octanoyloxy, decanoyloxy, lauroyloxy and the like acyloxy and aracyloxy, radicals. Other advantageous substituents include sulfamino, aryl sulfonamido and other substituted amino radicals such as alkacylamino, acetamino for example, and aracylamino radicals such as benzoylamino.

The nonvalent sulfonated aryl alcohol radicals and arylamine radicals, as represented by R_7, R_8, R_9 and R_{10}, are typically mono or disulfonated and can be additionally substituted. Typical sulfonated aryl alcohols are, for example, sulfonated phenols. These subject phenols can be substituted with either a halogen atom, an alkyl radical such as methyl, ethyl, propyl, isopropyl, hexyl, octyl, dodecyl and the like alkyl radicals, generally varying between 1 and 14 carbon atoms, or an amino radical such as those described above for R_1 through R_6. Other typical sulfonated aryl alcohols are sulfonated naphthols. Paricular illustrations of subsituents typically attached to the sulfonated naphthols are an amino radical and substituted amino radicals such as acylamino, alkylamino, alkacylamino and aracylamino. The presence on the amino radical of either straight chain acyl groups having from 1 to about 14 carbon atoms or branched chain acyl groups having from 3 to about 14 carbon atoms tends to prevent diffusion of the dye.

Specific examples of the many sulfonated phenols and naphthols which can be employed in preparing the subject tetrakisazo dyes are:

p-cresol-2-sulfonic acid,
2-hydroxy-4-aminophenyl sulfonic acid,
2-hydroxy-5-chlorophenyl sulfonic acid,
2-hydroxy-5-n-propylphenyl sulfonic acid,
2-naphthol-3,6-disulfonic acid,
1-amino-8-naphthol-4-sulfonic acid,
2-amino-8-naphthol-6-sulfonic acid,
1-amino-8-naphthol-3,6-disulfonic acid,
1-amino-8-naphthol-2,4-disulfonic acid,
1-benzoylamino-8-naphthol-3,6-disulfonic acid,
1-acetylamino-8-naphthol-3,6-disulfonic acid,
1-lauroylamino-8-naphthol-3,6-disulfonic acid,
1-ethylamino-8-naphthol-3,6-disulfonic acid,
1-(N,N-propylpropionoyl)amino-8-naphthol-3,6-disulfonic acid,

1-(N,N-phenylbutyroyl)amino-8-naphthol-3,6-disulfonic acid,
1-ethylamino-8-naphthol-2,4-disulfonic acid,
1-(N,N-propylpropionoyl)amino-8-naphthol-2,4-disulfonic acid, and
1-(N,N-phenylbutyroyl)amino-8-naphthol-2,4-disulfonic acid.

Typical monovalent, sulfonated arylamines useful in this invention include such compounds as sulfonated phenylamines and sulfonated naphthylamines. Illustrative of such compounds are 1-aminonaphthalene-4-sulfonic acid and 1-aminobenzene-4-sulfonic acid. Additionally, the amino group can be advantageously substituted in a similar fashion to the amino groups noted hereinabove, with such typical substituents as alkyl groups, acyl groups, alkacyl groups and aracyl groups.

The tetrakisazo dyes of the present invention are susceptible of preparation by well-known chemical syntheses. For example, the dyes can be formed by first tetraazotizing a di-(4-aminophenyl) methylbenzene which essentially constitutes one-half of a final symmetrical tetraamine, which tetraazotized diamine is then coupled with, for example, a sulfonated phenol, naphthol or naphthylamine such as those described herein, to produce a diazo compound having two azo linkages. The tetrakisazo dyes of this invention are then obtained by linking two units of the described diazo compound by a urea residue. A typical method is to obtain free amino substitution on the carbon atoms between which the two diazo units will be linked, such as by the reduction of a nitro group. The diazo compound can then be reacted with phosgene in the presence of sodium carbonate until a test for free amino is no longer positive, thus forming the desired tetrakisazo dye. The dye so obtained is then typically salted out of solution by treatment with, for example, sodium chloride and purified by known techniques, typically filtration and washing in a solvent such as ethyl alcohol.

Alternatively, a tetraamine can be preformed and then coupled with the desired sulfonated phenol or sulfonated naphthol to form the tetrakisazo dye directly, thus avoiding the necessity to subsequently join two diazo compounds. Purification can be obtained in the fashion described herein.

Tetrakisazo dyes which are so produced can, depending upon the structure of the chromophoric chain, absorb light at essentially any point along the entire visible spectrum and are advantageously employed in the preparation of photographic layers and elements which can be developed by well-known dye-bleach techniques to produce positive, monochromatic or polychromatic dye images. Such photographic elements are prepared by coating a support with at least one light-sensitive layer which typically includes a silver halide emulsion and at least one of the tetrakisazo dyes of this invention. Alternatively, the silver halide emulsion and subject tetrakisazo dye can be coated in separate, but contiguous layers. Any of the conventional photographic silver halides can be used such as silver bromide, silver chloride, silver bromoiodide, silver chlorobromoiodide etc. Gelatin, polyvinyl alcohol or other hydrophilic photographic binders, as well as other conventional photographic silver halide emulsion addenda such as chemical sensitizers, antifoggants, hardeners, coating aids etc., are also typically included in the coated light-sensitive layer. Where dye solubility or dye migration makes it advantageous, whether because of the dye characteristics or the type of dye-bleach system, a polymeric mordanting material can be used in the dye-containing layers to inhibit such dye migration. Typical such materials are cationic mordants like poly(styrene-maleimide) mordants as described in U.S. Ser. No. 655,758, filed July 25, 1967 and presently copending herewith or poly-α-methyl-allyl-N-guanidyl ketimine glycolate, described in United States Pat. 2,882,156.

Other azo dyes which are bleachable in the presence of a silver image can be utilized conjunctively with the subject tetrakisazo dyes to produce the described photographic elements. Exemplary of such additional azo dyes are those derived from 4,4′-di(p-aminobenzoylamino)diphenyl-3,3′-disulfonic acid by tetraazotization and coupling with suitable couplers, such as the sulfonated aryl alcohols and sulfonated arylamines described herein. Any known coupler, however, can be used, and the dyes so produced can range in color from yellow to magenta.

Coating can be accomplished by a wide variety of techniques known to those skilled in the art, with doctor blade coating and hopper coating being typically employed means. As coated in any layer, the dye is preferably incorporated in an amount ranging from about 2.5 mg. to about 50 mg. per 100 mg. of hydrophilic binder material. The concentration of silver halide is susceptible of wide variation, but need only be sufficient to provide a silver image which will permit advantageous bleaching, since the subject dyes are bleached in situ with a photographic silver image.

A silver coverage of about 20 to 30 mg./ft.^{2} is sufficient to promote suitable dye bleaching, and the additional silver halide is present to provide sufficient photosensitivity. Typically, silver coverages of from about 50 mg./ft.^{2} to about 150 mg./ft.^{2} are used; coverages of 200 mg./ft.^{2} and higher can be used, but such heavy silver coverages are not generally practical since, in most mases, an excess of unreacted silver halide is obtained.

The support upon which the light-sensitive layer or layers are coated can be extensively varied according to usual practice. Conventional polymeric film supports, for example, cellulose esters such as cellulose acetate, cellulose nitrate and cellulose acetate butyrate and also poly (ethylene terephthalate) are advantageously employed. Papers, including polyethylene and polypropylene coated paper, as well as titanium dioxide and baryta pigmented paper, are also typical support materials. Additional support materials such as polystyrene can also be used.

The subject photographic elements can involve a support coated with one of the above-described light-sensitive layers. Such a layer is advantageously colored with at least one of the subject bleachable tetrakisazo dyes, and when such a photographic elements is imagewise exposed and bleached by well-known techniques of the photographic dye-bleach art, a positive, monochromatic dye image of the original is produced. Alternatively, a photographic element prepared as described above can involve multiple light-sensitive layers to prepare a multicolor silver dye-bleach element. Such an element typically includes three silver halide emulsion layers separately sensitized to red, green and blue light radiation and having associated therewith, respectively, a bleachable cyan, magenta and yellow colored azo dye. The tetrakisazo dyes of this invention can be advantageously used in the same or different layers with other azo dyes, such as monoazo, diazo and triazo dyes. When such a multicolor element is developed by well-known dye-bleach techniques, a positive, multicolored dye image is produced.

The above described photographic elements, of both single layer and multilayer types, are imagewise exposed and processed to produce the previously noted positive, colored dye images. Processing comprehends first developing a negative silver image by treating the imagewise exposed element in a black-and-white silver halide developer solution, and second, treating the photographic element bearing a negative silver image with a bleaching composition which causes the reduction of the subject tetrakisazo dyes to colorless products.

Bleaching solutions can be either alkaline or acidic in characted. A typical alkaline bleaching solution is stannite (alkaline stannous chloride) which operates to reductively destroy an azo dye, such as the subject dyes, in the presence of silver as a catalyst.

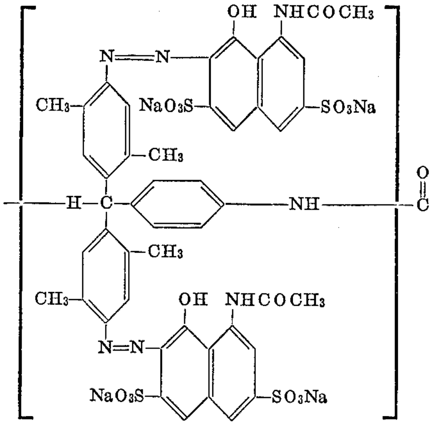
Acidic bleaching solutions utilize the photographic silver image as the reducing agent. Additionally, complexing agents such as thiourea can be added to increase the reducing power of the metallic silver, and accelerators such as phenazines can be present in acidic bleaching solutions to hasten the operation by their catalytic action. A typical acid bleaching composition has the formula

Concentrated HCl: 100 ml.
Thiocrea 125 g.
2-hydroxy-3-amino-phenazine: .15 g.
Water to make 1 liter.

The following examples serve as additional illustrations of particular embodiments of the present invention and should not be considered as expressions of limitation.

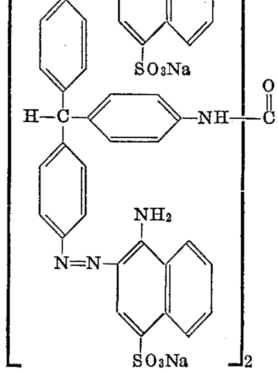
EXAMPLE I

One mole (4,4′-diamino-2,2′,5,5′-tetramethyldiphenyl-4″-nitrophenyl)methane is tetraazotized and coupled in a dilute aqueous sodium carbonate solution with 2 moles of acetyl H-acid (1-acetamido-8-naphthol-3,6-disulfonic acid). The resultant disazo dye is reacted with one mole of dextrose and sufficient sodium hydroxide to raise the pH to 12 for 2 hours at 25° C., which reaction operates to reduce the nitro group to free amino without reducing the azo linkages. This is then reacted with phosgene in the presence of sodium carbonate until a test for free amino is no longer positive. The dye so obtained is salted out of solution by the introduction of sodium chloride, and removed by filtration. Purification of the dye is effected by multiple washing in ethanol, yielding one mole of a magenta colored tetrakisazo dye having the formula:



EXAMPLE II

A dye of the invention is prepared according to the procedure described in Example I, except that one mole of (4,4′-diaminodiphenyl-4″-nitrophenyl) methane is coupled with two moles of NW acid (1-naphthol-4-sulfonic acid. One mole of an orange colored tetrakisazo dye results, having the formula:



EXAMPLE III

A photographic element is prepared by coating poly(ethylene-terephthalate) film support material with a light-sensitive emulsion layer comprising gelatin coated at a coverage of 300 mg./ft.^{2}, silverbromoiodide coated at a silver coverage of 125 mg./ft.^{2} and the magenta-colored tetrakisazo dye described in Example I coated at a coverage of 30 mg./ft.^{2}. The coating is then dried. The photographic element so prepared is exposed in an Eastman 1B sensitometer through a standard .15 log E step wedge and is then developed in a black-and-white developer having the formula

Elon: 3 g.
Sodium sulfite, desicated: 45 g.
Hydroquinone: 12 g.
Sodium carbonate, monohydrated: 80 g.
Potassium bromide: 2 g.
Water to make 1 liter.

to which is added 2 g. of potassium thiocyanate and .05 of 5-methylbenzotriazole per liter of developer solution. After conventional fixing in aqueous potassium thiosulfate to remove undeveloped silver halide, dye-bleaching is accomplished by a 30 second immersion in a solution of 10 percent aqueous sodium hydroxide to which is added 10 g./liter of stannous chloride. Ferricyanide bleaching and fixation in hypo remove residual silver. After the dye-bleaching, the developed coating exhibits a positive magenta dye image corresponding in dye density to the step wedge increments.

EXAMPLE IV

Another photographic element is prepared and exposed according to the procedure described in Example III, except that the tetrakisazo dye used is the orange colored dye described in Example II. It is developed in a black-and-white developer as in Example III. Dye-bleaching is accomplished by a 30 second immersion in a solution having the formula

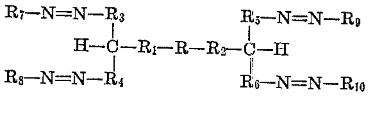
Thiourea: 125 g.
2-hydroxy-3-aminophenazine: .15 g.
Concentrated HCl: 100 ml.
Distilled water to make 1 liter.

Ferricyanide bleaching and fixation in hypo remove residual silver. After such processing, a positive, orange colored dye image is produced, corresponding in dye density to the step-wedge increments.

The invention has been described above in considerable detail, with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described above and as defined in the appended claims.

I claim:

1. A photographic element comprising a support having coated thereon at least one light-sensitive layer comprising silver halide emulsion and a bleachable tetrakisazo dye having the formula:



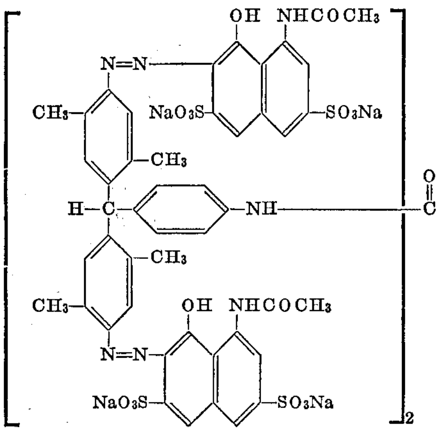
$$\begin{array}{ccc} R_7-N=N-R_3 & & R_5-N=N-R_9 \\ \quad\quad\quad\ | & & | \quad\quad\quad \\ H-C-R_1 & -R- & R_2-C-H \\ \quad\quad\quad\ | & & | \quad\quad\quad \\ R_8-N=N-R_4 & & R_6-N=N-R_{10} \end{array}$$

wherein:

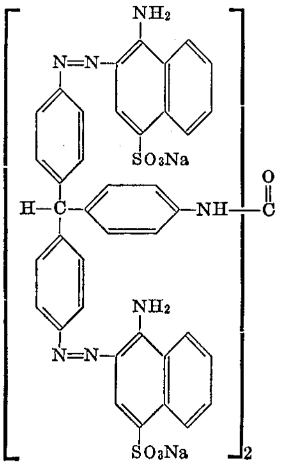
(a) R is a ureylene radical,
(b) each of R_1 through R_6 is a phenylene radical, and
(c) each of R_7 through R_{10} is a monovalent radical selected from the group consisting of a sulfonated 1-naphthol radical and a sulfonated 1-naphthylamine radical..

2. A photographic element as described in claim **1**, wherein the said sulfonated 1-naphthol radical and the said sulfonated 1-naphthylamine radical are each bonded to the said azo linkage at the 2-position.

3. A photographic element as described in claim **1**, wherein the tetrakisazo dye has the formula:



4. A photographic element as described in claim **1**, wherein the tetrakisazo dye has the formula:



References Cited

UNITED STATES PATENTS

2,470,769	5/1949	Gaspar	96—99
2,644,753	7/1953	Gaspar et al.	96—99

J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—53, 99