United States Patent Office 3,401,404
Patented Sept. 10, 1968

3,401,404

MEROCYANINE DYE-SENSITIZED PHOTOGRAPHIC MATERIALS COMPRISING SILVER HALIDE EMULSION LAYERS CONTAINING AZO-DYES

Bernhard Seidel, Cologne-Mulheim, and Oskar Riester, Leverkusen, Germany, assignors to Agfa-Gevaert Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

No Drawing. Filed Jan. 26, 1965, Ser. No. 428,205
Claims priority, application Germany, Feb. 13, 1964, A 45,221
3 Claims. (Cl. 96—99)

ABSTRACT OF THE DISCLOSURE

Particularly desirable sensitization of silver-dye-bleach silver halide emulsions is effected with certain substituted merocyanine dyes.

This invention relates to a merocyanine dye-sensitized photographic element comprising at least one silver halide emulsion layer uniformly dyed with an azo-dye for use in the silver dye bleach process.

Colored photographic images can be prepared by the silver dye bleach process in which a negative or a positive silver image is obtained, depending on the processing, by exposure and subsequent development of uniformly colored photographic layers. After further treatment, such as fixing and subsequent hardening, the azo-dye is bleached, generally in a strongly acidic bleach bath, in accordance with the silver image. In this way, dye image of the original is obtained. The dye image has a gradation opposite to the gradation of the silver image. The dyes generally employed are azo dyes, both water-soluble dyes and insoluble pigments.

One of the great disadvantages of the silver dye bleach process is that the sensitivity of the dyed photographic layers is very considerably reduced. This occurs in particular if the layers are sensitized in such a way, as is generally the case, that the blue-sensitive layer is dyed yellow, the green-sensitive layer magenta and the red-sensitive layer cyan. The reason for this is that the sensitization maxima coincide with the absorption maxima of the dyes. With respect to the sensitivity of the light-sensitive layers, the silver dye bleach process is inferior to other color photographic processes. Accordingly, one of the great difficulties of the silver dye bleach process is the preparation of sufficiently sensitive layers.

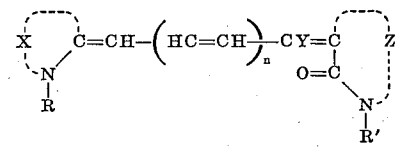
The sensitivity of photographic emulsions can be increased by the addition of suitable sensitizers. Sensitizers which are to be used in materials for the silver dye bleach process have to satisfy several requirements. In addition to good sensitizing properties the sensitizer must not deleteriously effect the stability of the emulsions, particularly in storage and under tropical conditions. Furthermore the sensitizing dyes have to be sufficiently soluble in the processing baths, so that the dye is readily washed out and no coloring of the support, for example paper, or the binding agent of the layer, for example gelatin, occurs. Furthermore, the sensitizer must adhere sufficiently firmly to the silver halide grains as not to be displaced by the azo-dyes, because otherwise the sensitizing action is decreased in the presence of azo-dyes. In particular because of the last mentioned requirement many of the sensitizers, which are operative in conventional silver halide photographic materials, are not suitable for the silver dye bleach process.

For instance basic cyanines are readily detached or removed from the silver halide grain by azo-dyes containing sulfonic acid groups and, for this reason, are not sufficiently effective in the silver dye bleach process. In some cases even a desensitizing effect can be observed of compounds which act as sensitizers in conventional photographic processes. It is known to employ betaine cyanines as sensitizers for photographic layers for use in the silver bleach process. These sensitizers are, however, of limited utility since they cannot be washed out sufficiently in the processing baths so that the image portions remain slightly discolored.

It is an object of the invention to provide sensitizing dyes for silver halide emulsion layers to be used in the silver dye bleach process. Another object is to provide photographic materials comprising at least one light-sensitive silver halide emulsion layer optically sensitized and containing an azo-dye. Other objects will become apparent from a consideration of the following description and examples.

We now have found that a particular class of merocyanine dyes are outstanding in their optically sensitizing properties for silver halide emulsion layers which contain uniformly distributed azo-dyes and which are to be used in the silver dye bleach process. The merocyanines of the present invention are characterized by two 5- or 6-membered heterocyclic rings which contain nitrogen as a ring member and which are linked together by way of 2 or 4 methine groups. Merocyanines of this type are generally known as zero-, di- or tetramethine merocyanines.

Particularly suitable are merocyanines of the following formula:



wherein:

X=represents the ring members necessary to complete a 5- or 6-membered heterocyclic ring, preferably of the following groups: thiazole, benzthiazole, napthothiazole, oxazole, benzoxazole, naphthoxazole, selenazole, benzselenazole, naphthoselenazole, benzimidazole, indoline, pyrrolidine, tetrazole, thiodiazole;

Y=hydrogen or alkyl preferably lower alkyl having up to 3 carbon atoms, such as methyl or ethyl;

Z=the ring members necessary for completing a 5-membered heterocyclic ring preferably such as thiazole, oxazole, selenazole, imidazole or pyrazole;

R=alkyl preferably lower alkyl having up to 5 carbon atoms in particular methyl or ethyl, whereby the alkyl groups can be substituted by carboxy, sulfo, hydroxy or chlorine;

R'=alkyl preferably alkyl up to 5 carbon atoms such as methyl or ethyl, olefinically unsaturated alkyl, preferably up to 5 carbon atoms such as allyl, cycloalkyl such as cyclohexyl, or aryl preferably phenyl;

n=0 or 1.

The above heterocyclic or aromatic rings can be substituted, for example, with alkyl preferably lower alkyl of up to 5 carbon atoms, alkoxy having up to 5 carbon atoms, hydroxy or halogen preferably chlorine.

The merocyanine dyes of the present invention are outstanding in their optically sensitizing action for silver halide emulsion layers containing an azo-dye. Furthermore they are superior to betain cyanines since the color images obtained by the process of the invention show very clear white portions of the images without any color stain.

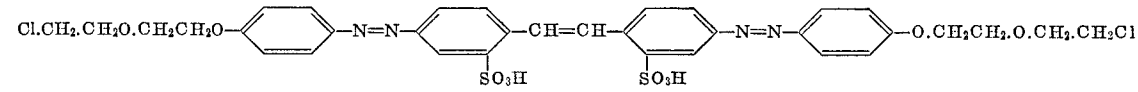
The above merocyanines are substantially inert both to the azo-dyes in the photographic layers for the silver dye bleach process and to other additives, in particular

stabilizers, mordants such as biguanides or guanides, wetting agents, agents for influencing the viscosity of azo-dyes in gelatin and/or photographic emulsions, hardening agents such as chrome alum, paraformaldehyde, or plasticizers such as glycerol.

The merocyanines of the instant invention are well known and described in the handbook of F. M. Hamer, "The Cyanine Dyes and Related Compounds," published by Interscience Publishers (1964), chapter XIV.

In the preparation of photographic emulsions the merocyanine dyes of the invention are preferably incorporated in the washed, finished silver halide emulsions before the azo-dyes are added and should be uniformly distributed throughout the emulsion. The methods of incorporating sensitizing dyes in light-sensitive emulsions are well known to those skilled in the art of emulsion making. Generally it is convenient to add the sensitizing dyes from solutions in appropriate solvents that should have no deleterious effect on the light-sensitive materials. Lower aliphatic alcohols such as methanol, ethanol or isopropanol, furthermore pyridine and the like, alone or in admixtures, for example with water, have proven satisfactory as solvents.

The silver halides of the emulsions comprise silver chloride, silver bromide or silver chlorobromide which



may contain a small amount of silver iodide, preferably not more than 10 mol percent.

The type of silver halide emulsions that can be sensitized with the merocyanines of the present invention include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides. These colloids include preferably gelatin which can be used in admixture with other hydrophilic colloids such as albumin, alginic acids and derivatives thereof, hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone and the like.

The concentration of the merocyanine dye and the light-sensitive emulsion can vary widely from about 5 to about 100 mg. per liter of emulsion. The suitable and most economical concentration for any given emulsion will be apparent to those skilled in the art upon making the tests customarily used in the art of emulsion making.

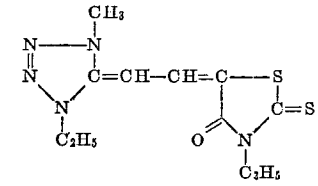
To prepare a silver halide emulsion sensitized with a merocyanine of the present invention, the following procedure is satisfactory: The desired quantity of the sensitizing dye is dissolved in a suitable solvent and a volume of this solution containing the desired amount of the dye is slowly added to the silver halide emulsion. Thereafter, the azo-dye is added preferably from a solution in a suitable solvent. With most of the merocyanine dyes of the present invention 10–30 mgs. of sensitizing dye per liter of emulsion are sufficient to produce the maximum sensitizing effect. The photographic emulsions may be coated on any of the photographic supports including paper, cellulose esters such as cellulose acetate or nitrate, polystyrene, polyesters in particular of polyethylene terephthalate, poly carbonates, preferably of bis-hydroxy phenyl alkanes, and the like.

Photographic silver halide emulsions containing the merocyanines of the invention can also contain such additives as chemical sensitizers, for instance, sulfo sensitizers, nobel metal compounds such as gold or palladium compounds, stabilizers such as benzotriazole compounds, heterocyclic mercapto compounds, mercury compounds or azaindenes; hardeners such as glyoxal, formaldehyde, acrolein or the like.

Azo-dyes which can advantageously be used in combination with the merocyanines of the invention comprise the customarily employed dyes which are known to be satisfactory for the silver dye bleach process. Preferred are those containing phenolic hydroxyl groups and/or sulfonic acid groups. Suitable dyes are described in the book of J. S. Friedman "History of Color Photography," published by The American Photographic Publishing Co., Boston, 1947, Chapter 24 or for instance in British patent specification Nos. 766,020, 899,758 or 953,622 or in German patent specification 1,039,840 or 1,041,355.

Example 1

500 g. of a silver bromide emulsion of average sensitivity are sensitized with 15 mg. of a dyestuff of the formula



dissolved in methanol. The preparation of the sensitizer is described in French patent specification No. 1,133,324. In addition to the usual coating additives and hardening agents, an aqueous solution containing gelatin and 4 g. of a yellow dyestuff of the formula

as described in British patent specification No. 766,020, Example 1, is added to the emulsion. The emulsion is then mordanted with 2 g. of diphenyl-4-4'-dibiguanide, as described in French patent specification No. 864,332 to increase the resistance to diffusion of the dye, and applied onto a baryta-coated paper. The resulting layer contains 1.5 g./m.^{2} of silver as silver bromide. For comparison purposes, a layer of exactly the same thickness is prepared but is not sensitized.

The two layers are exposed in a sensitometer behind a step wedge and processed as follows:

(1) Development in the following composition for 5 minutes

p-Methyl aminophenol	g.	1
Sodium sulfite anhydrous	g.	13
Hydroquinone	g.	3
Sodium carbonate (anhydrous)	g.	26
Potassium bromide	g.	1
Water	ml.	1000

(2) Rinsing for 1 minute.

(3) Fixing for 5 minutes in the following composition:

Sodium thiosulfate	g.	200
Potassium metabisulfite	g.	20
Water	ml.	1000

(4) Rinsing for 5 minutes.

(5) Hardening by treatment in a 4% aqueous formaldehyde solution for 5 minutes.

(6) Rinsing for 5 minutes.

(7) Bleaching of the azo-dye by treatment in the following solution for 20 minutes:

Ethanol	ml.	50
Thiourea	g.	50
Concentrated sulfuric acid	ml.	5
2,3-dimethyl quinoxaline	mg.	80
Water	ml.	910

(8) Rinsing for 5 minutes.

(9) Bleach-fixing for 15 minutes in the following bath:

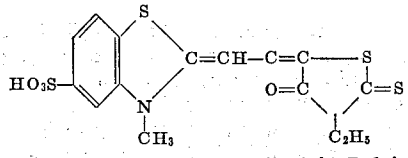
Tetrasodium ethylenediaminetetraacetate	g.	26
Sodium carbonate (anhydrous)	g.	24
Ferric chloride	g.	15
Sodium sulfite (anhydrous)	g.	13
Sodium thiosulfate	g.	200
Water	ml.	500

(10) Final rinsing for 20 minutes.

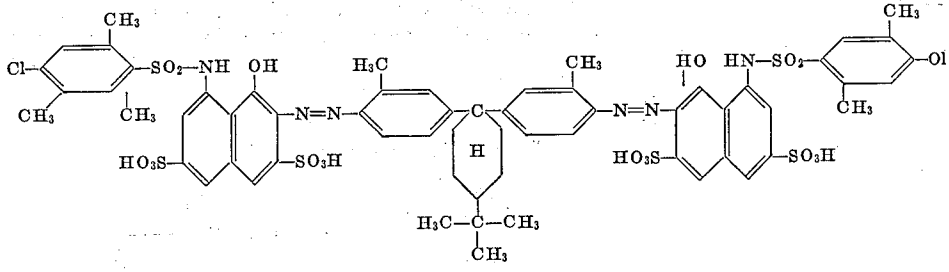
Two direct-positive color wedges are formed which are measured behind a blue filter. The difference in the sensitivity is 1.7 logarithmic units. The paper support is unstained.

Example 2

After melting with a small amount of 4-hydroxy-6-methyl-1,3,3a,7-tetraazainden as a stabilizer, 500 g. of a highly sensitive silver iodobromide emulsion is sensitized to green light by adding 15 mg. of the sensitizing dye of the formula



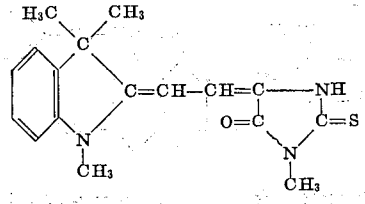
the preparation of which is described in Belgian patent specification 648,068. The usual additives are then incorporated, followed by the addition of 200 ml. of a 1% aqueous solution of the magenta azo dye of the formula



which is prepared in accordance with German patent specification No. 1,039,840. To improve its fastness to diffusion, a solution of 0.75 g. of bis-[3-anisidyl-4-biguanide] is added, and the emulsion is applied onto a support of cellulose triacetate as described in Example 1. A sample is exposed in a sensitometer behind a step wedge and yellow filter, and is then processed as described in Example 1 and compared with a standard sample which is not sensitized by sensitometric measurement behind a green filter the difference in the sensitivity of the two samples is found to be 1.7 logarithmic units. In the sensitized sample, the support is practically free from any coloring.

Example 3

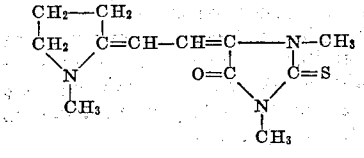
The procedure is the same as in Example 2, except that the sensitizer used in Example 2 is replaced by 15 mg. of a sensitizing dye of the formula



After exposure, processing and evaluation as in Example 2, the difference in sensitivity between the sensitized and unsensitized layers is 0.9 logarithmic units.

Example 4

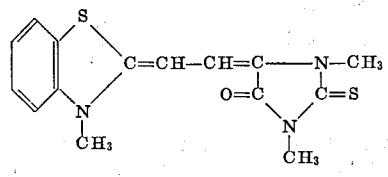
500 g. of a silver chloride emulsion are mixed as described in Example 1 with 15 mg. of the dye of the formula



(prepared according to German Patent No. 883,025) and with 300 ml. of a 1% aqueous solution of the mordanted azo-dye referred to in Example 1. The processing is performed as described in Example 1. The sensitized sample is more sensitive by 1.1 logarithmic units than the unsensitized emulsion.

Example 5

The procedure is the same as in Example 2, except that the dye used in that example is replaced by 15 mg. of the sensitizer of the formula

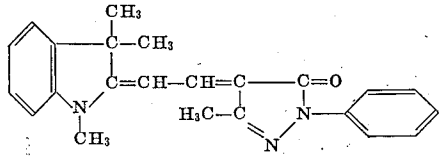


which may be prepared in accordance with British Patents Nos. 426,718 and 428,360.

The material is processed as described in Example 2. The sensitized sample has a sensitivity higher by 1.2 logarithmic units than that of the unsensitized sample.

Example 6

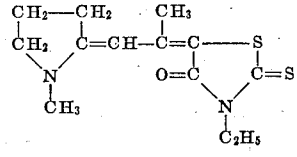
The procedure is the same as in Example 2, except that the sensitizer used in that example is replaced by 15 mg. of the dye of the formula



which may be prepared as described in British Patent No. 428,360. Contrary to Example 2, no mordant is used. The material is processed as described in Example 1. The sensitized sample has a sensitivity of 0.73 logarithmic units greater than the unsensitized sample.

Example 7

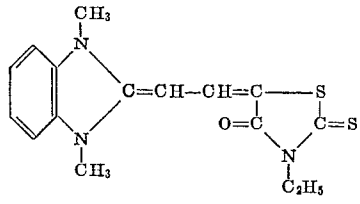
If the sensitizer referred to in Example 2 is replaced by 15 mg. of the dye



which may be obtained according to German Patent No. 883,025 and if the procedure described in Example 2 is followed, the resulting sensitized sample has a sensitivity 1.1 logarithmic units higher than that of the unsensitized sample.

Example 8

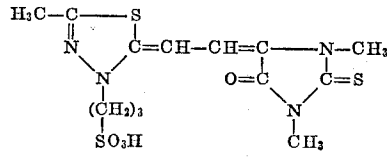
If the sensitizer mentioned in Example 2 is replaced by 15 mg. of the compound of the formula



which may be prepared according to J. Am. Chem. Soc. 73, 5332 (1951), and if the procedure described in Example 2 is followed, there is an increase in the sensitivity of the sensitized sample of 0.82 logarithmic units as compared with an identical unsensitized emulsion.

Example 9

The procedure is the same as in Example 2, except that the emulsion has a high silver content and, to obtain a suitable γ-value, is diluted with such a quantity of gelatin, that, after exposure and development, there is still sufficient silver left to bleach the azo-dye completely. A sensitizing dye of the formula



is added in a quantity of 30 mg. per kilogram of undiluted emulsion.

The resulting photographic element is processed as described in Example 1. The sensitized material is 0.7 logarithmic units more sensitive than an unsensitized mulsion which is otherwise identical.

The above sensitizer is prepared as follows:

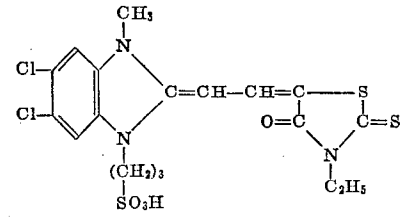
25 g. of the addition product of 2.5-dimethyl thiodiazole and propane sultone are heated at 100° C. for 1 hour with 25 g. of diphenyl formamidine and 50 ml. of acetic anhydride.

The reaction solution is taken up in acetone and the 2 - (phenylacetamino-ethylidene)-intermediate product which crystallizes out, is suction-filtered. Yield: 22.2 g. M.P. 286° C.

4 g. of this intermediate product are condensed for 3 hours on a steam bath with 3 g. of 1,3-dimethyl thiohydantoin in 20 ml. of cresol and 15 ml. of pyridine with 6 ml. of triethylamine. The resulting dye is dissolved in water and precipitated with potassium iodide. It is recrystallized from 150 ml. of water. Yield: 1.3 g.; M.P. above 290° C.

Example 10

The procedure is the same as in Example 9, except that the sensitizer dye has the formula



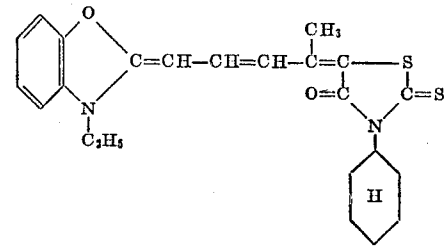
A simple is exposed and processed as described above. The sensitized sample is 1.4 logarithmic units more sensitive than an unsensitized comparison sample.

The sensitizing dye is prepared as follows:

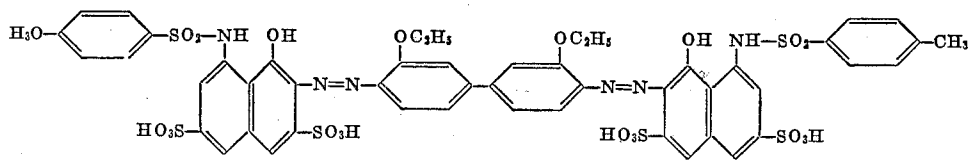
5 g. of 1-methyl-2-methylmercapto-5,6-dichlorobenzimidazole are heated at 130° C. for 15 minutes with 4 g. of propane sultone. After cooling to 100° C. the melt is dissolved in 20 ml. of pyridine while stirring. The resulting solution is stirred for 24 hours at 20° C. with 2 g. of 3-ethyl-5-ethylidene rhodanine and 6 ml. of triethylamine. The dye which crystallizes out is suction-filtered, dissolved in water and repreciptated with NaCl solution. It is then recrystallized from 700 ml. of methanol/chloroform (1:1). Yield: 0.5 g.; M.P. about 300° C.

Example 11

15 mg. of the sensitizing dye of the formula



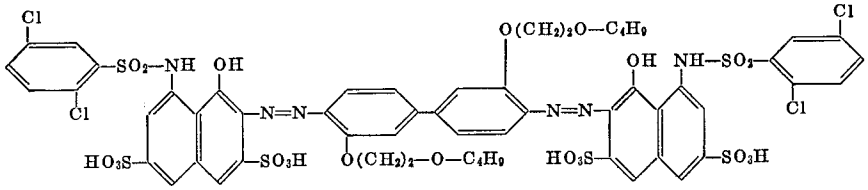
which is prepared by a method analogous to that described in J. Am. Chem. Soc. 73, 5337 (1951) "Merodicarbocyanine" are added to 500 ml. of a highly sensitive silver bromide emulsion containing 50 mg. of 1-phenyl-5-mercapto tetrazole as a stabilizer. After the addition of hardening agents such as 0.4 g. of chrome alum and 0.3 g. of paraformaldehyde, and wetting agents such as 20 ml. of a 5% solution of saponin the emulsion is mixed with 250 ml. of an aqeuous gelatin solution containing 1% of the cyan dye of the formula



which is obtained from 3,3'-ditheoxy-4,4'-diamino diphenyl by diazotisation and coupling with p-tosyl H acid. The dye is made resistant to diffusion by adding 0.5 g. of bis-(3-anisidyl-4-biguanide) in a 1% aqueous gelatin solution, and applied onto a baryta-coated paper base. The dried layer contains 1.5 g. of silver per square meter as silver halide. For comparison purposes, an otherwise identical unsensitized sample is prepared. The two samples are exposed in sensitometer behind a step wedge and a yellow filter, and are processed as in Example 1. The two cyan colored wedges obtained are measured behind red filters. The sensitized sample is more sensitive by 2.2 logaritmic units. In addition, the sensitized sample shows considerably less in the white portions of the image than the unsensitized comparison.

Example 12

The procedure is the same as in Example 11, except that the azo dye is replaced by the following cyan dye:



which is itself highly resistant to diffusion and, for this reason, does not require mordanting. This compound is prepared in accordance with Example 1 of German Patent No. 1,041,355. The comparison used is one from which the mordant, bis-(3-anisidyl-4-biguanide), has also been omitted. The samples are processed as described in Example 11. According to the measurement of the cyan colored wedges obtained the sensitized sample is more sensitive by 1.87 logaritmic units.

In the above examples differences in sensitivity are given in logarthmic units wherein a difference of sensitivty of 0.3 log. units correspond to a difference by a factor of 2 and 1.0 log. units correspond to a difference by a factor of 10.

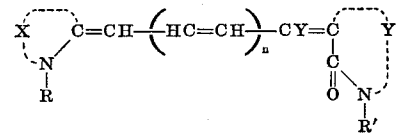
As has been mentioned before the essential steps of the processing of silver dye bleach materials consist in development of a silver image, bleaching of the dye according to the silver image and removing residual silver and silver halide by a bleaching and a fixing bath, both of which can be combined in one composition. Between developer and dye bleach bath other steps such as fixing or hardening baths can be included.

As developer compositions those containing for instance p-methyl aminophenol and hydroquinone may be used but other systems especially those containing 1-phenyl pyrazolidon are also useful.

For the purpose of the invention a wide variety of azo dye bleaching baths can be used. They may contain from 10 to 80 g. of thiourea, 20 to 80 g. of an alkali halide and 10 to 20 g. of a mineral acid per liter such as described in U.S. Patent No. 2,217,544. Other variations than those indicated are possible, including the omission of halide and the addition of organic solvents. Furthermore, dye bleaching baths on the basis of quinoline, hypophosphite, iodide and mineral acid as described in U.S. Patent No. 2,629,658 or combinations of iron salts and isothiocyanates are also useful. Besides the basic ingredients mentioned above, the bleaching bath in question normally also contains bleaching catalysts such as 2,3-dimethyl quinoxaline or other quinoxaline derivatives, 2-amino-3-hydroxy phenazine, 2,3-diamino phenazine, azines, oxazines, thiazines, cinnolines, indophenazines, ferro- or thienoquinoxalines and the like, which are usually added in amounts from 2 to 300 mg. per liter of bleaching solution. Silver bleach baths for use in the process of the process of the invention may, e.g., consist of copper chloride (10 to 50 g.) and potassium bromide (10–100 g.) together with hydrochloric acid (5 to 20 ml. per liter of solution). In this case an acidic thiosulfate both containing for instance 200 g. of sodium thiosulfate and 20 g. of potassium metabisulfite per liter of solution, will generally be used as a fixer. Combined bleaching and fixing baths are also very useful, however, and an example of such a composition comprising an Fe(III)-complex of ethylene diamine tetraacetic acid is described in Example 1.

We claim:

1. A light-sensitive photographic element, comprising at least one supported light-sensitive silver-dye-bleach silver halide emulsion layer which contains a silver-dye-bleach azo dye and is sensitized by a sensitizing amount of a merocyanine dye of the formula



wherein:

X represents the ring members necessary to complete a tetrazole, benzthiazole, indoline, pyrrolidine, benzimidazole, thiadiazole or benzoxazole ring;

Y stands for hydrogen or alkyl having up to 3 carbon atoms;

Z stands for the ring members necessary for completing a rhodanine, thiohydantoin or pyrazolone ring;

R stands for alkyl having up to 5 carbon atoms, carboxy-substituted alkyl in which the alkyl has up to 5 carbon atoms, sulfo-substituted alkyl having up to 5 carbon atoms, hydroxy-substituted alkyl having up to 5 carbon atoms or chloro-substituted alkyl having up to 5 carbon atoms;

R′ represents alkyl having up to 5 carbon atoms, cyclohexyl or phenyl and

n is 0 or 1.

2. A light-sensitive photographic element as defined in claim 1 wherein X and Z are substituted with alkyl having up to 5 carbon atoms, alkoxy having up to 5 carbon atoms, hydroxy or chlorine.

3. The combination of claim 1 in which the Z completes a rhodanine ring and is unsubstituted.

References Cited

UNITED STATES PATENTS

2,612,448	9/1952	Gaspar et al.	96—73
3,053,655	9/1962	Dreyfuss et al.	96—99
3,157,507	11/1964	Bruengger et al.	96—99

J. TRAVIS BROWN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

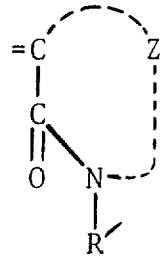
CERTIFICATE OF CORRECTION

Patent No. 3,401,404 September 10, 1968

Bernhard Seidel et al.

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

Column 10, lines 24 to 29, the right-hand portion of the formula should appear as shown below:



Signed and sealed this 10th day of March 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents