

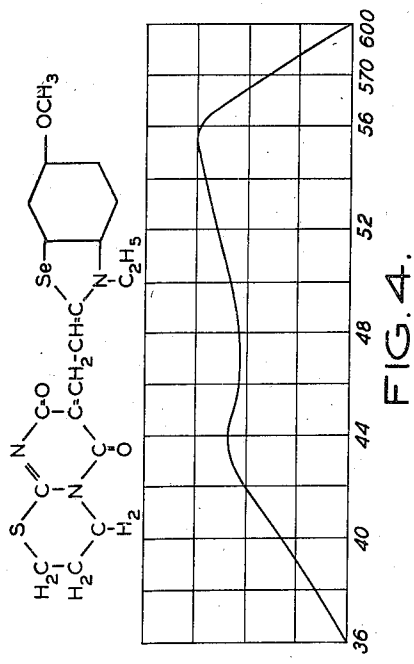
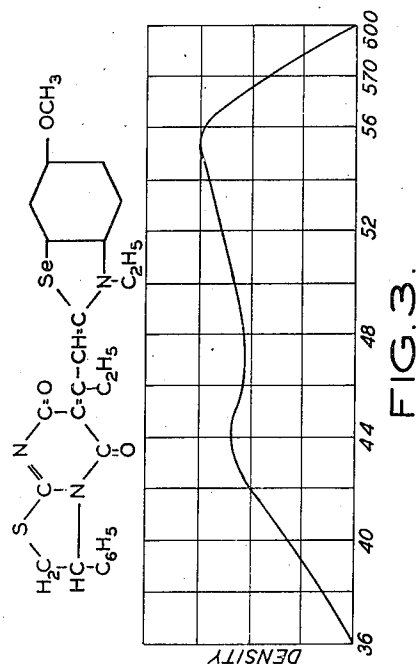
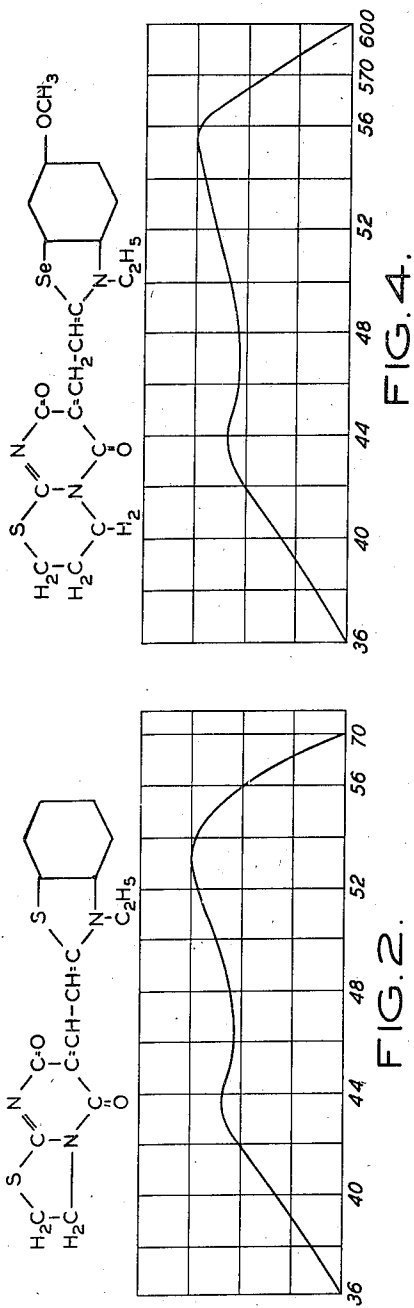
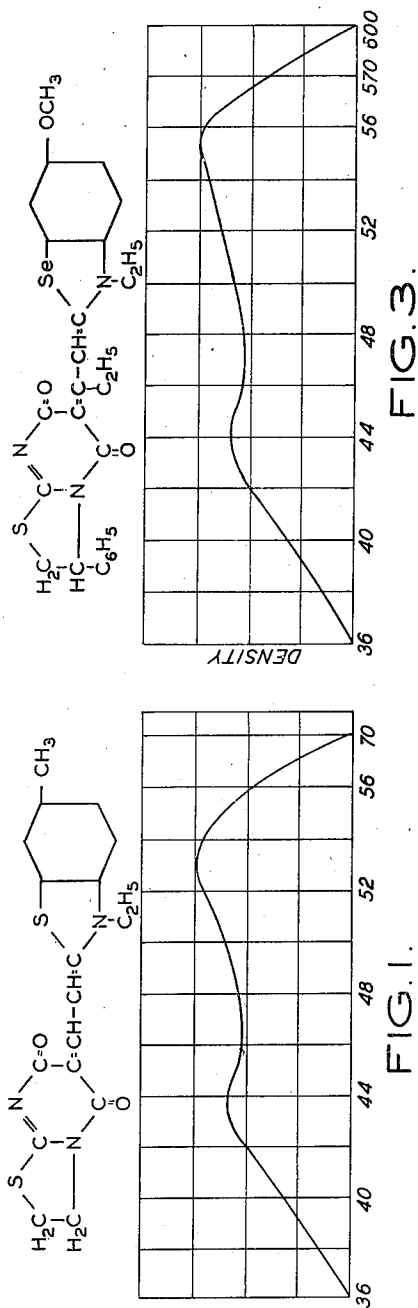
March 22, 1949.

A. W. ANISH
DYE-SENSITIZED PHOTOGRAPHIC
SILVER HALIDE EMULSION

2,464,780

Filed Dec. 7, 1945

2 Sheets-Sheet 1



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ATTORNEY

UNITED STATES PATENT OFFICE

2,464,780

DYE-SENSITIZED PHOTOGRAPHIC SILVER
HALIDE EMULSION

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a corporation of Delaware

Application December 7, 1945, Serial No. 633,539

6 Claims. (Cl. 95—7)

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The present invention relates to photographic preparations such as emulsions, plates and films coated by such emulsions. More particularly, the invention relates to silver halide emulsions which contain sensitizing dyes of a new type.

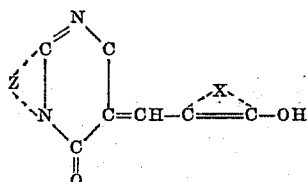
It is among the objects of my invention to produce novel and highly improved sensitized photographic emulsions. It is a further object of my invention to produce photographic emulsions which have a strong sensitivity.

It has heretofore been proposed to employ as sensitizers in photographic emulsions dyes of the merocyanine type. However, in the dyes heretofore proposed the keto-methylene structure is part of a monocyclic molecule.

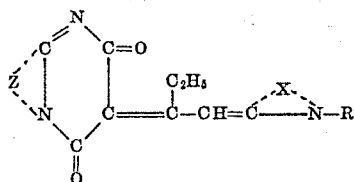
According to my invention, I have found that a silver halide emulsion sensitized with a merocyanine dye having a diketo-pyrimidine structure in a polycyclic molecule yields an emulsion of strong sensitivity.

The sensitizing dyes employed can be represented by the following formulae:

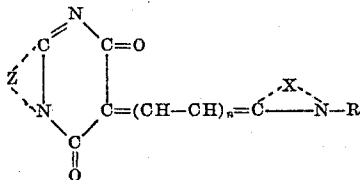
IIa



b



c



In the formulae, X and Z represent the non-metallic atoms necessary to complete a heterocyclic nucleus, n represents a positive integer ranging from 1 to 3, and R stands for a radical selected from the group consisting of aliphatic, cycloaliphatic, aryl and aralkyl groups.

More particularly, X, for example, represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing, for instance, a member of the oxazole series, e. g. benzoxazole; or a member of the thiazole series, e. g. benzothiazole; or a member of the thiazoline series, e. g. thiazoline; or a member of the pyridine series, e. g. pyridine; or of the quinoline series, e. g.

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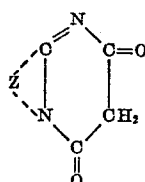
benzoquinoline; or of the selenazole series, e. g. benzelenazole; or of the selenazoline series, e. g. selenazoline, or of the indolenine series, e. g. 3,3-dimethyl indolenine.

More particularly, Z represents, for instance, the non-metallic atoms necessary to complete a heterocyclic nucleus such as of the thiazoline or selenazoline series, e. g. thiazoline or selenazoline; or of the benzthiazole series, hexahydrobenzthiazole; or of the pyrazolone series, e. g. 3-phenylpyrazolone; or of the pyridine or quinoline series, e. g. pyridine or quinoline or of the thiazine series, e. g. thiazine. n is a positive integer, for instance, from 1 up to and including 9. More particularly, R may represent methyl, ethyl, butyl, isopropyl, allyl, benzyl, n -amyl, β -ethoxyethyl and cyclohexyl, phenyl, etc.

The merocyanine dyes of Formula II can be prepared from bicyclic compounds which may be represented by the following general formula wherein Z has the same significance as in II.

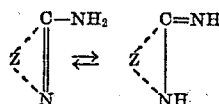
I.

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Any heterocyclic compound substituted by a primary amine group which readily undergoes the following tautomeric imino form, will yield the corresponding bicyclic compound,

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Z has the same significance as above.

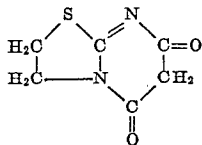
In practice, the starting compounds illustrated by Formula I can be obtained by condensing the aforementioned amino substituted heterocyclic compounds with ethyl malonate according to the procedure of Masters & Bogert, Journal of American Chemical Society, vol. 64 (1942), page 2709 or by the method described in Berichte, vol. 57 (1924), page 1170.

More particularly, the process involved in preparing the intermediates of structure I comprises condensing amino substituted heterocyclic compounds with ethyl malonate in the presence of alcoholic sodium ethylate. As examples of amino substituted heterocyclic compounds which may be so converted into polycyclic compounds having the structure I, there may be mentioned 2-amino thiazoline, 2-amino selenazoline, 2-amino dihydrothiazine, 2-amino-5-methyl-thiazoline, 2-amino-4-phenylthiazoline, 2-amino hexahydrobenzthiazole, 3-phenyl-5-amino pyrazolone and 2-amino pyridine. When these compounds are

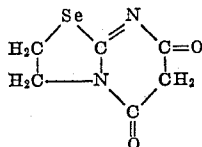
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condensed with ethyl malonate in the manner described, they result in compounds which may be represented by the following structural formulas:

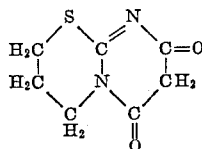
From 2-amino thiazoline



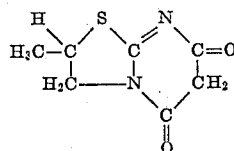
From 2-amino selenazoline



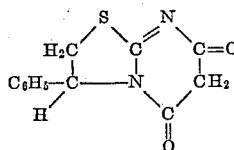
From 2-amino dihydrothiazine



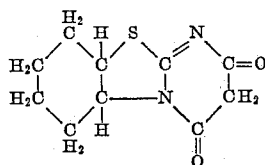
From 2-amino-5-methylthiazoline



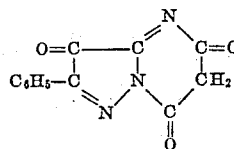
From 2-amino-4-phenylthiazoline



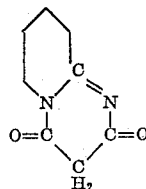
From 2-amino hexahydrobenzthiazole



From 3-phenyl-5-amino pyrazolone



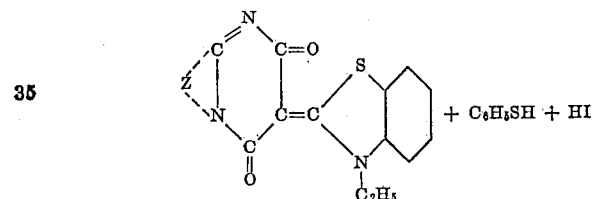
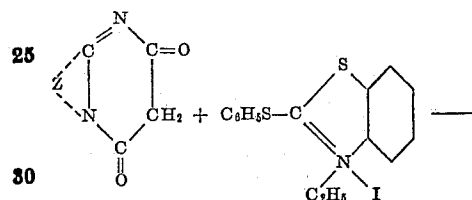
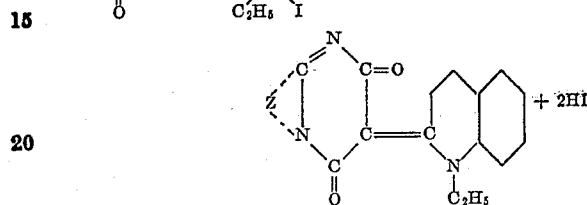
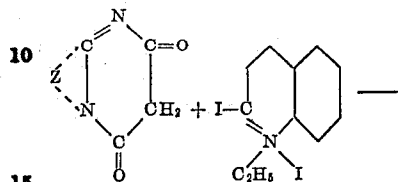
From 2-amino pyridine



The new dyes of the above Formulae II may, in general, be prepared by condensing in the presence of a suitable condensing agent a polycyclic diketopyrimidine of structure I with a heterocyclic nitrogen compound containing a reactive group. Thus, where in the above Formu-

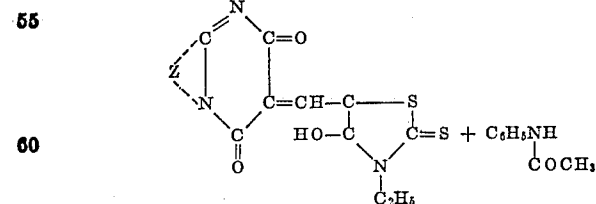
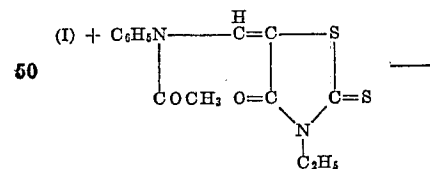
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lae II n is 1, the heterocyclic compound may be the cyclammonium quaternary salt having in its so-called reactive positions, namely, the 2- or 4-position, an iodo atom, a cyano group, or an aryl or alkyl mercapto group. The formation of such a dye may be illustrated by the following equations:



The new merocyanine dyes of the structure IIa, may be prepared by condensing the pyrimidine of structure I with a heterocyclic compound having an acetanilido methylene- group in one of the so-called reactive positions.

As illustrative of the method, the following equation is given:

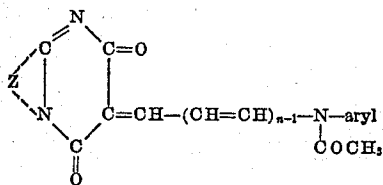


The new merocyanine dyes having the structures IIb and IIc, that is, the dimethine and polymethine merocyanines of these formulae, may be prepared by condensing the diketopyrimidine of structure I with a β -anilino vinyl, β -acetanilido vinyl derivative of a cyclammonium quaternary salt, or omega-aldehyde, or omega-ketone derivatives, such as acetylmethylene derivatives, or β -alkylmercaptovinyl, or β -alkylmercapto- β -alkylvinyl derivatives thereof, in the so-called reactive position. The procedure involving the use of omega-ketone and β -alkyl or arylmercapto

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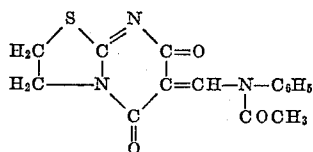
β -alkyl or aryl vinyl derivatives results in dyes having an alkyl or aryl group attached to the methine chain.

In an alternate method for the preparation of the new merocyanine dyes, the intermediate used in the dye condensation, may be the acetanilido-methylene derivative of compounds having the structure I. Such acetanilidomethylene derivatives may be characterized by the following formula:



where aryl is a hydrocarbon radical of the benzene or naphthalene series, Z has the hereinbefore mentioned significance and n represents a positive integer not greater than 3.

These derivatives, which are claimed in my application Serial No. 633,538, filed on December 7, 1945 now U. S. Patent No. 2,423,218, issued July 1, 1947, may be readily formed by reacting equimolecular amounts of a compound of structure I and a diarylformamidine, such as, for example, diphenylformamidine, or arylamino acrolein anils, e. g., β -anilinoacrolein anil hydrochloride; or ω -aryl amino- Δ 2,4-pentadienal anils, e. g., glutaconic aldehyde dianilide hydrochloride, in the presence of acetic anhydride. For instance, if this reaction is carried out on the 2,3-dihydro-5H-thiazolo[3,2-a]pyrimidine-5,7(6)-dione, a compound having the following structure results:



These acetanilidomethylene intermediates may be readily condensed with a cyclammonium quaternary salt having a methyl group in the reactive position in the manner indicated above to form the new merocyanine dyes.

In general, the process of preparing the dyes is advantageously carried out in the presence of suitable condensing agents. Where acids are given off during the reaction, it is preferable to use a basic condensing agent. Where water is formed during the reactions, it is preferable to use water-binding agents such as organic acid anhydrides, as for example, acetic, propionic and butyric acid anhydrides. It is preferred to use strong organic bases, examples of which are triethylamine, tributylamine, triethanolamine, N-methylpiperidine. Other basic condensing agents may be utilized as for example, pyridine, sodium or potassium acetate, sodium ethylate and sodium propionate.

The reactions to form my new dyes may also be advantageously carried out in the presence of a diluent. Lower aliphatic alcohols are preferable for this purpose. Examples of such alcohols are ethyl, n-propyl and isopropyl alcohols. Pyridine may also serve as a diluent.

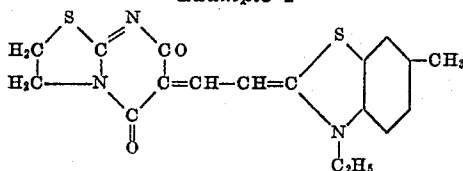
Heat facilitates the formation of my new dyes. Refluxing the reaction mixture is a convenient way of forming the dyes. The intermediates which are condensed to form my new dyes are ordinarily employed in equimolecular amounts

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although a slight excess of one or the other may be utilized. The basic condensing agent or water-binding agent is utilized in sufficient amount to bind the acid or water eliminated from the condensing compounds. While less may be utilized, it is preferred to use the condensing agent in excess.

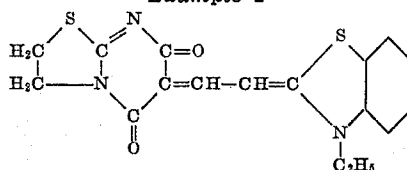
The following examples will serve to illustrate but are not intended to limit the invention:

Example 1



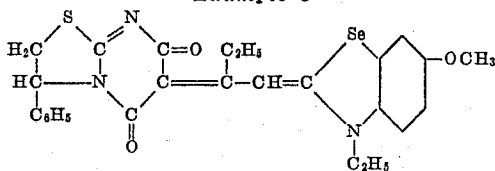
1.7 grams of 2,3-dihydro-5H-thiazolo[3,2-a]pyrimidine-5,7(6)-dione, prepared from 2-amino thiazoline and ethyl malonate in the presence of alcoholic sodium ethylate, and 3.4 grams of 2-(β -acetanilido vinyl) 6-methyl benzthiazole ethiodide were mixed in 30.0 cc. of isopropyl alcohol and 0.5 cc. of triethylamine added and the whole refluxed for 1 hour. The dye precipitates during the course of refluxing. The dye was filtered off after the reaction solution was brought to room temperature, washed with water, and the dye recrystallized from alcohol.

Example 2



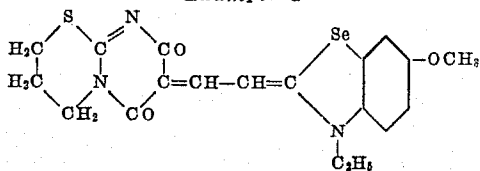
1.7 grams of 2,3-dihydro-5H-thiazolo[3,2-a]pyrimidine-5,7(6)-dione, made from 2-amino thiazoline and ethyl malonate, and 3.3 grams of 2-(β -acetanilido vinyl) benzthiazole ethiodide were suspended in 30.0 cc. of isopropyl alcohol and 0.5 cc. of triethylamine added. The mixture was refluxed for 1 hour. The dye which precipitated, was filtered after cooling and washed with water. The dye was purified by crystallizing from methyl alcohol.

Example 3



2.3 grams of 2,3-dihydro-3-phenyl-5H-thiazolo[3,2-a]pyrimidine-5,7(6)-dione made from 2-amino-4-phenyl thiazoline and ethyl malonate, and 3.1 grams of 2-(β -methylmercapto β -ethyl vinyl)-6-methoxy benzthiazole ethiodide and 0.5 cc. of triethylamine were refluxed in 30.0 cc. of n-propyl alcohol for 1 hour. The reaction mixture was cooled and the dye which separated was filtered off and recrystallized from methyl alcohol.

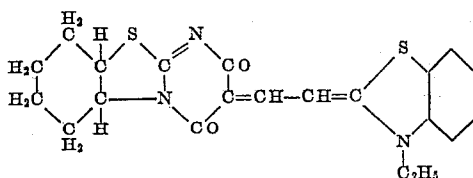
Example 4



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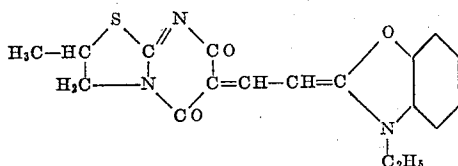
1.8 grams of 2,3-dihydro-6H-pyrimido[2,3-b]-1,3,4-thiazine-6,8(7)-dione prepared from 2-amino-dihydrothiazine and ethyl malonate and 4.7 grams of 2-(β -acetanilido vinyl)-6-methoxybenzselazole ethiodide, and 0.5 cc. of triethylamine were refluxed in 30.0 cc. of n-propyl alcohol for 1 hour. The dye was crystallized from methyl alcohol.

Example 5



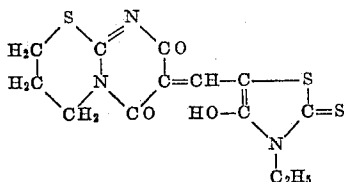
2.2 grams of 6,7,8,9,10,11-hexahydro-4H-pyrimido[2,1-b]benzothiazole-2,4(3)-dione prepared from 2-amino hexahydrothiazole and ethyl malonate were mixed with 3.3 grams of 2-(β -acetanilido vinyl) benzthiazole ethiodide and 0.5 cc. of triethylamine and the mixture refluxed in isopropyl alcohol for 1 hour. The dye, which separated out on cooling, was filtered off and recrystallized from alcohol.

Example 6



1.8 grams of 2,3-dihydro-2-methyl-5H-thiazolo[3,2-a]pyrimidine-5,7(6)-dione prepared from 2-amino-5-methyl thiazoline and ethyl malonate were mixed with an equimolecular amount of 2-(β -acetanilido vinyl) benzoxazole ethiodide and 0.5 cc. triethylamine and refluxed in isopropyl alcohol. The dye was recrystallized from ethyl alcohol.

Example 7



1.8 grams of 2,3-dihydro-6H-pyrimido[2,3-b]-1,3,4-thiazine-6,8(7)-dione, prepared from 2-amino dihydrothiazine and ethyl malonate, and 2.7 grams of 2-thio-3-ethyl-5-acetanilidomethylene dihydrothiazolidone-4 were mixed with 0.5 cc. of triethylamine in 30.0 cc. of pyridine and refluxed for 1 hour. The cooled reaction mixture was diluted with water and carefully precipitated with perchloric acid. The dye was filtered off, dissolved in 3 N caustic and again carefully precipitated with perchloric acid.

In practice, the new light sensitive emulsions are obtained by incorporating into silver halide emulsions usually employed in the photographic arts, a small amount of the sensitizing dyes. To facilitate the preparation of the sensitized emulsion, the dye is preferably dissolved in a suitable solvent such as methyl or ethyl alcohol, the solution being added to the emulsion so as to incorporate about 5 to 50 milligrams of the dye per kilogram of silver halide emulsion while stirring. The stirring is continued until the dye is uni-

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formly and practically homogeneously dispersed in the photographic emulsion. Amounts of dye usually ranging from 5 to 25 milligrams are sufficient to obtain the maximum sensitizing effect. Even lower amounts, however, may be employed because of the strong sensitizing action of my novel dyes. However, I do not intend to limit the invention to the quantities indicated since the most suitable and economical amount to be used in connection with any particular dye and emulsion will be understood to those skilled in the art upon making the usual and ordinary tests and observations customarily practiced in the art of emulsion making. In general, the dyes may be applied to the emulsion during any stage of its production. However, it is preferred to add the sensitizing dyes to the emulsion before it is cast.

As illustrative of my novel emulsions are the following examples:

Example 8

An ethyl alcohol solution of 20 milligrams of the dye of Example 1 was incorporated in one kilogram of a gelatino-silver chloride emulsion containing a small amount of silver bromide and a total content of 4 to 5 per cent of silver halide. The dye imparts a sensitivity to 570 mu with a maximum at 530 mu.

Example 9

An ethyl alcohol solution of 20 milligrams of the dye of Example 2 was incorporated in the same silver chloride emulsion as in Example 8. The dye sensitized to 570 mu with a maximum at 530 mu.

Example 10

An ethyl alcohol solution containing 20 milligrams of the dye of Example 3 was incorporated in the same silver chloride emulsion as in Example 8. The sensitivity imparted by the dye extended to about 600 mu with a maximum at 560 mu.

Example 11

When 20 milligrams of the dye of Example 4 were incorporated in a silver halide solution as in Example 8, the dye imparted a sensitivity to 600 mu with a maximum at 560 mu.

Example 12

In a similar manner, 20 milligrams of the following dyes were incorporated in the same silver halide emulsions as in Example 8:

(a) Dye of Example 5 sensitized to 575 mu with a maximum at 545 mu.

(b) Dye of Example 6 sensitized to 560 mu with a maximum at 525 mu, and

(c) Dye of Example 7 sensitized to 566 mu with a maximum at 530 mu.

The diagrammatic spectrograms constituting the accompanying drawing illustrate the regions of the spectrum to which the various types of thio- and seleno-carbocyanines containing a cyclic hydrocarbon substituted dioxy ring structure as part of the cyanine dye molecule disclosed herein will sensitize a gelatino silver-halide emulsion containing about 4-5% of silver-halide and the extent of the sensitization at various wavelengths. The seven figures of this drawing illustrate the sensitizing properties of the dyes in silver-halide emulsions in accordance with the preceding examples.

Figs. 1 to 4 inclusive illustrate the sensitizing

properties of the dyes of Examples 8 to 11 inclusive.

Figs. 5 to 7 inclusive illustrate the sensitizing properties of the dyes of Examples 12(a), 12(b), and 12(c).

Instead of incorporating the dyes in the emulsion during their manufacture or prior to the application of the emulsion to the support, the dyes may likewise, if desired, be added by bathing the photographic material on which the emulsion is cast in a bath or solution in which the dye has been dissolved. For example, the photographic material to be sensitized, such as a photographic film containing the usual gelatino silver emulsion layer, is bathed in a solution containing about one milligram of sensitizer in 50 cc. of an aqueous solution of methanol of 50% concentration, for about 5 minutes. The material is then dried, after which it is ready for use.

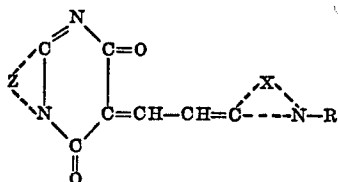
In addition to ethyl alcohol or methyl alcohol as a solvent, other suitable solvents such as, for example, acetone or pyridine may be utilized. The amount of dye which is incorporated in any given quantity of emulsion will, it is to be understood, vary from dye to dye and emulsion to emulsion. Accordingly, the regulation and selection will be apparent to those skilled in the art upon observing the sensitizing power of the particular dye for the particular emulsion being utilized. It is accordingly to be understood that the above proportions are only illustrative of the invention and are not to be taken as limiting the invention.

In general, the preferred method is to incorporate the dye in the emulsion prior to casting, rather than bathing the plate or film upon which emulsion has been coated. The claims are intended to cover any combination of my novel dyes with a photographic emulsion where the dye exerts a sensitizing action upon the emulsion. By the expression "gelatino-silver-halide emulsion" we intend to include all the silver halides usually employed in the photographic art and, in particular, the silver chloride and silver bromide emulsions or combinations thereof with one another or silver iodide. While my invention is particularly directed to the customarily employed gelatin emulsion, gelatin being the protective colloid in which the light sensitive salt is suspended, any other suitable carrier such as cellulose derivatives or synthetic resins may also be used as the carrier.

The sensitizing dyes as such and their method of production form the subject matter of my co-pending application Serial No. 633,537, filed December 7, 1945.

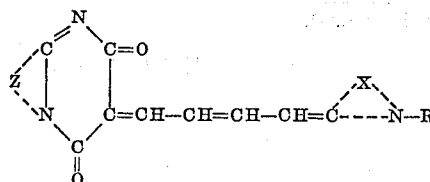
I claim:

1. A photographic gelatino-silver halide emulsion containing a sensitizing dye having the following general formula:



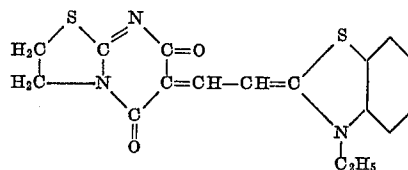
wherein X represents the non-metallic atoms necessary to complete a nitrogenous heterocyclic nucleus, Z represents a fused-on hydrogenated ring system selected from the class consisting of selenazoline, thiazoline, and thiazine and R represents an aliphatic radical.

2. A photographic gelatino-silver halide emulsion containing a sensitizing dye having the following general formula:

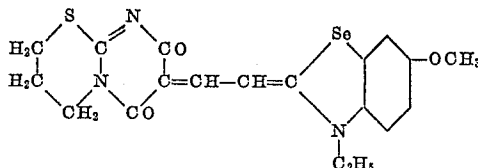


wherein X represents non-metallic atoms necessary to complete a nitrogenous heterocyclic nucleus, Z represents a fused-on hydrogenated ring system selected from the class consisting of selenazoline, triazoline, and thiazine and R represents an aliphatic radical.

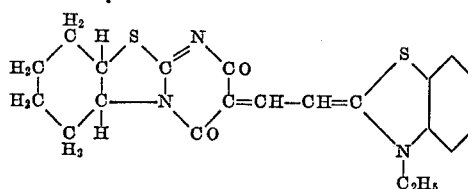
3. A photographic gelatino-silver halide emulsion containing a sensitizing dye having the following general formula:



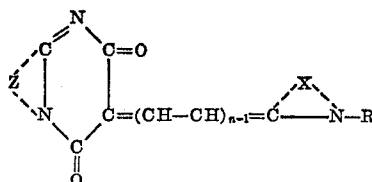
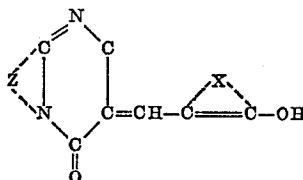
4. A photographic gelatino-silver halide emulsion containing a sensitizing dye having the following general formula:



5. A photographic gelatino-silver halide emulsion containing a sensitizing dye having the following general formula:



6. A photographic gelatino silver-halide emulsion containing a sensitizing dye selected from the group consisting of those represented by the following general formulae:



wherein X represents the atoms necessary to complete a nitrogenous heterocyclic nucleus, Z

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represents a fused-on hydrogenated ring system selected from the class consisting of selenazoline, thiazoline, and thiazine, n represents a positive integer ranging from 1 to 3, and R represents an aliphatic radical.

ALFRED W. ANISH.

12**REFERENCES CITED**

The following references are of record in the file of this patent:

UNITED STATES PATENTS**5**

Number	Name	Date
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