

April 27, 1937.

L. G. S. BROOKER

2,078,233

PHOTOGRAPHIC EMULSION

Filed Nov. 8, 1934

Fig. 1. 5-(2-ETHYL-1-BENZOXAZYLIDENE-ETHYLIDENE)-RHODANINE.

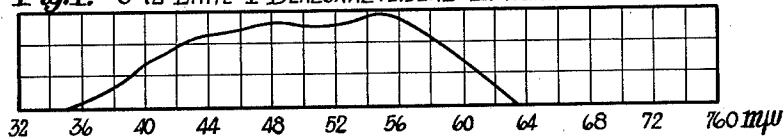


Fig. 2. 5-(2-ETHYL-1-BENZOTHIAZYLIDENE-ETHYLIDENE)-3-PHENYLRHODANINE.

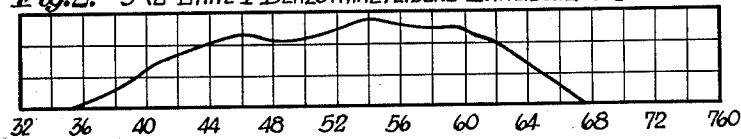


Fig. 3. 5-(1-ETHYL-2-QUINOLYLIDENE-ETHYLIDENE)-3-PHENYLRHODANINE.

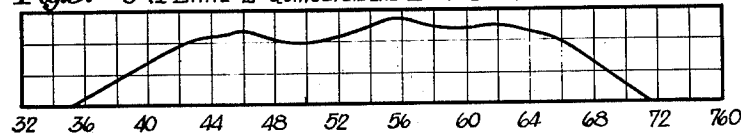


Fig. 4. 4-(2-ETHYL-1-BENZOXAZYLIDENE-ETHYLIDENE)-3-METHYL-1-PHENYL-5-THIOPYRAZOLONE.

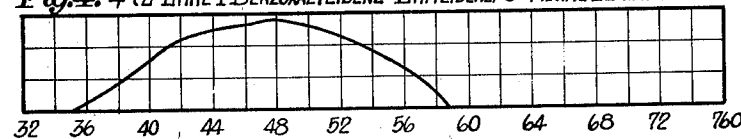


Fig. 5. 2-ETHYL-1-(THIOINDOGEN-ETHYLIDENE)-BENZOTHAZOLINE.

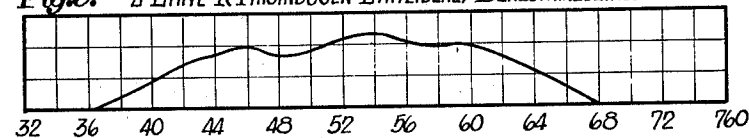
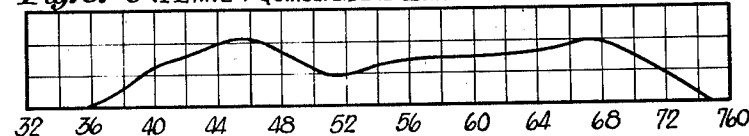


Fig. 6. 5-(1-ETHYL-4-QUINOLYLIDENE-ETHYLIDENE)-3-PHENYLRHODANINE.



Density

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UNITED STATES PATENT OFFICE

2,078,233

PHOTOGRAPHIC EMULSION

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Application November 8, 1934, Serial No. 752,036
In Great Britain September 14, 1934

21 Claims. (Cl. 95—7)

This invention relates to photographic emulsions and more particularly to photographic emulsions which contain sensitizing dyes of a new class, namely such dyes as N-alkyl-heterocyclidene derivatives, N-alkyl-heterocyclidene-ethylidene derivatives and N-alkyl-heterocyclidene-butenylidene derivatives of heterocyclic compounds containing a reactive methylene group.

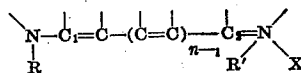
It has been known for some time in the art of photography that in order to render photographic emulsions, such as gelatino-silver-halide emulsions, sensitive to substantially all of the visible spectrum, it has been necessary to treat the emulsions, either by overcoating or by admixture with the emulsions themselves, with a compound which extends or enhances the sensitivity of the emulsions to light beyond their natural sensitivity. Many dyes suitable for this purpose have been described in the literature, such for instance as pseudocyanine, pinacyanol, thiocarbocyanine and others. Additional ones have been described in United States Patent No. 1,942,854, wherein emulsions containing thiazolinocarbocyanine dyes are described, No. 1,962,123 wherein emulsions containing dibenzoxacarbocyanine dyes are described and No. 1,962,124 wherein emulsions containing oxacarbocyanine dyes are described.

It is an object of the present invention to provide a photographic emulsion, such as a gelatino-silver-halide emulsion, which contains dyes of a new class, namely, such dyes as N-alkyl-heterocyclidene derivatives, N-alkyl-heterocyclidene-ethylidene derivatives and N-alkyl-heterocyclidene-butenylidene derivatives of heterocyclic compounds containing a reactive methylene group. A further object is to provide a photographic emulsion, such as a gelatino-silver-halide emulsion, which is sensitized with such dyes. A still further object is to provide a photographic element consisting of a transparent support coated with such an emulsion. Other objects will appear hereinafter.

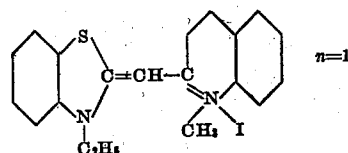
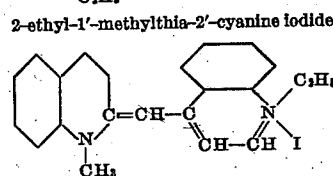
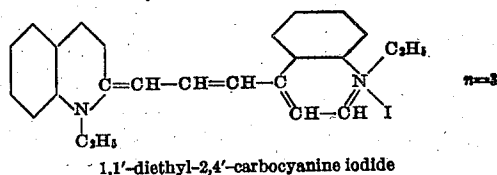
Dyes of this new class are described both as to chemical nature and as to methods of preparation in my copending application Serial No. 739,502, filed August 11, 1934. The sensitizing properties of related dyes are described in my copending application Serial No. 739,503, filed August 11, 1934, of which the present application is a continuation-in-part.

It is interesting and instructive to compare the dyes of this new class with those of the well known cyanine class. While these new dyes are distinctly different from the cyanines, a comparison of the two classes serves to make clear the nature of this new discovery.

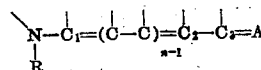
The cyanine dyes have in common the following grouping:



wherein R and R' represent alkyl groups, X represents an acid radical, the carbon atom C₁ and the tervalent nitrogen atom are situated in a heterocyclic ring system and the carbon atom C₂ and the quinquivalent nitrogen atom are situated in another heterocyclic ring system and n represents a positive integer. The two nitrogen atoms are always linked together by means of a conjugated carbon chain. The following formulae of some typical cyanine dyes serve to illustrate the application of this general formulae:



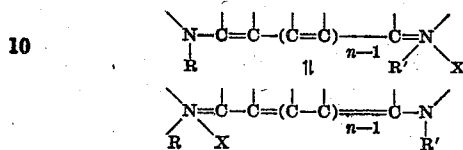
Now it has been found that dyes having in common the following grouping are valuable photographic sensitizers:



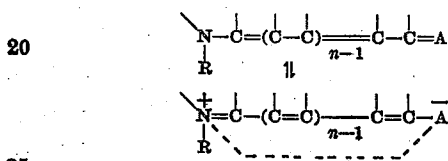
In this general formula, R represents an alkyl group, A represents an atom such as oxygen or sulfur, the carbon atom C₁ and the nitrogen atom are situated in a heterocyclic ring system, the carbon atoms C₂ and C₃ are situated in another heterocyclic ring system and n represents a positive integer. The atom A (oxygen or sulfur) is

linked to the nitrogen atom by means of a conjugated carbon chain.

In the case of the cyanine dyes, there is considerable evidence (cf. Mills and Braunholtz, J. Chem. Soc. 121, 1489 (1922) and Hamer, *ibid.* (1928) 206 in favor of the existence of the virtual tautomerism represented by:



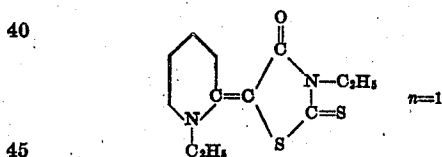
In the case of the new dyes, there quite possibly exists a similar equilibrium as:



The sensitizing properties of the cyanine dyes may be associated with the first type of equilibrium shown above, although this has not been proved. Likewise, the sensitizing properties of the new dyes may be associated with the second type of tautomeric equilibrium shown. In any event, the new class of dyes appears to offer as wide a field for photographic sensitizers as the well known cyanine class.

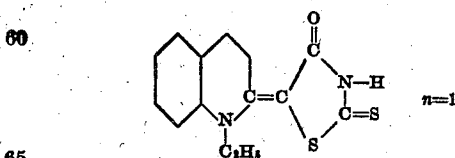
Examples of typical dyes of this new class are:

Example 1.—5-(1-ethyl-2-pyridylidene)-3-phenylrhodanine



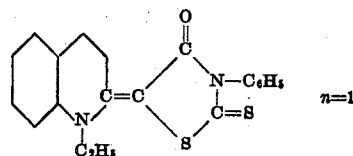
This dye can be prepared as follows: 2.1 parts of 3-phenylrhodanine and 3.6 parts of 2-iodopyridine ethiodide were refluxed with 2.12 parts of triethylamine and 30 parts of absolute ethyl alcohol for about fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from methyl alcohol, giving reddish-brown plates which gave a yellow-orange solution in methyl alcohol.

Example 2.—5-(1-ethyl-2-quinolyldiene)-rhodanine



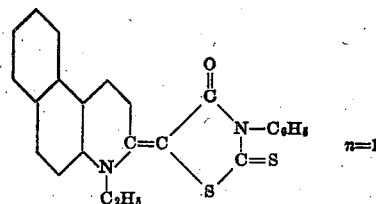
This dye can be prepared as follows: 2.66 parts of rhodanine, 8.2 parts of 2-iodoquinoline ethiodide and 4.24 parts of triethylamine were refluxed in 25 parts of absolute ethyl alcohol for about 15 minutes. The dye separated from the hot solution. It was filtered off and recrystallized from glacial acetic acid, giving brownish red needles with a green reflex. The methyl alcohol solution was orange in color.

Example 3.—5-(1-ethyl-2-quinolyldiene)-3-phenylrhodanine



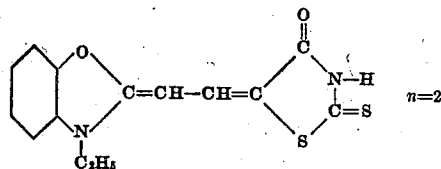
This dye can be prepared as follows: 2.1 parts of 3-phenylrhodanine and 4.1 parts of 2-iodoquinoline ethiodide were refluxed with 55 parts of absolute ethyl alcohol and 2.1 parts of triethylamine for about fifteen minutes. The dye separated from the cooled solution. It was filtered off and recrystallized from glacial acetic acid, yielding red crystals with a green reflex.

Example 4.—5-(1-ethyl-2-β-naphthoquinolyldiene)-3-phenylrhodanine



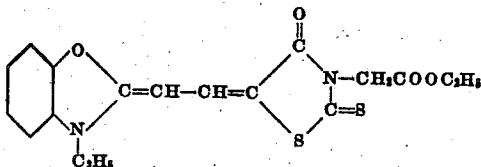
This dye can be prepared as follows: 0.3 part of 3-phenylrhodanine and 0.66 part of 2-iodo-β-naphthoquinoline ethiodide were refluxed with 0.3 part of triethylamine and 15 parts of absolute ethyl alcohol for fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid, giving brick red crystals which gave a red solution in methyl alcohol.

Example 5.—5-(2-ethyl-1-benzoxazylidene-ethylidene)-rhodanine



This dye can be prepared as follows: 1.33 parts of rhodanine, 4.34 parts of 1-(β-acetanilidovinyl)-benzoxazole ethiodide and 0.9 part of anhydrous sodium acetate were refluxed in 50 parts of glacial acetic acid for about fifteen minutes. The dye separated from the hot solution. It was filtered off and recrystallized from glacial acetic acid, yielding brownish crystals with a bright blue reflex which gave a brownish-yellow solution in methyl alcohol.

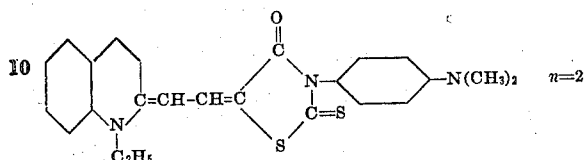
Example 6.—3-carbethoxymethyl-5-(2-ethyl-1-benzoxazylidene-ethylidene)-rhodanine



This dye can be prepared as follows: 1.1 parts of 3-carbethoxymethylrhodanine and 2.2 parts of 1-(β-acetanilidovinyl)-benzoxazole ethiodide were refluxed with 20 parts of absolute ethyl alcohol and 0.53 part of triethylamine for about fifteen

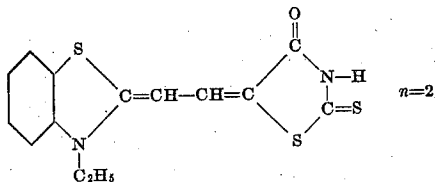
minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid, yielding reddish-orange crystals which gave an orange colored methyl alcohol solution.

5 **Example 7.** — 3-(*p*-dimethylaminophenyl)-5-(1-ethyl-2-quinolydene-ethylidene)-rhodanine



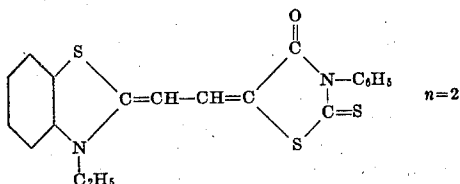
15 This dye can be prepared as follows: 1.25 parts of 3-(*p*-dimethylaminophenyl)-rhodanine and 2.2 parts of 2-(β -acetanilidovinyl)-quinoline ethiodide were refluxed with 25 parts of acetic anhydride and 0.45 part of anhydrous sodium acetate for about five minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid, yielding minute greenish crystals which gave a bluish-red solution in methyl alcohol.

Example 8. — 5-(2-ethyl-1-benzothiazylidene-ethylidene)-rhodanine



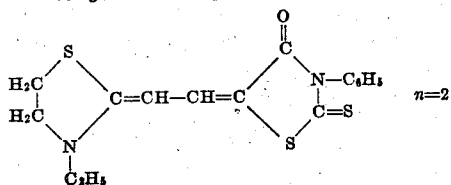
This dye can be prepared as follows: 1.33 parts of rhodanine, 4.5 parts of 1-(β -acetanilidovinyl)-benzothiazole ethiodide and 0.9 part of anhydrous sodium acetate were refluxed in 50 parts of glacial acetic acid for about fifteen minutes. The dye separated from the hot solution. It was filtered off and recrystallized from glacial acetic acid, yielding crystals resembling iron filings which gave a reddish-orange solution in methyl alcohol.

Example 9. — 5-(2-ethyl-1-benzothiazylidene-ethylidene)-3-phenylrhodanine



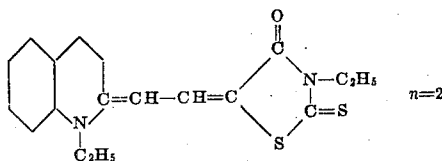
This dye can be prepared as follows: 2.1 parts of 3-phenylrhodanine and 4.5 parts of 1-(β -acetanilidovinyl)-benzothiazole ethiodide were refluxed with 55 parts of absolute ethyl alcohol and 1.06 parts of triethylamine for about twenty minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid, yielding small dark crystals with a glittering green reflex which gave a pinkish methyl alcohol solution.

Example 10. — 5-(3-methyl-2-thiazolinyldene-ethylidene)-3-phenylrhodanine



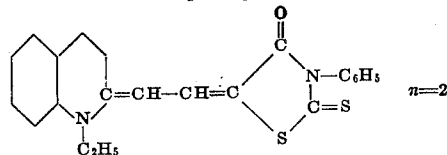
This dye can be prepared as follows: 2.1 parts of 3-phenylrhodanine and 3.9 parts of 2-(β -acetanilidovinyl)-thiazoline methiodide were refluxed with 50 parts of acetic anhydride and 0.9 part of anhydrous sodium acetate for fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid, yielding brown needles with a blue reflex which gave a yellow methyl alcohol solution.

Example 11. — 3-ethyl-5-(1-ethyl-2-quinolydene-ethylidene)-rhodanine



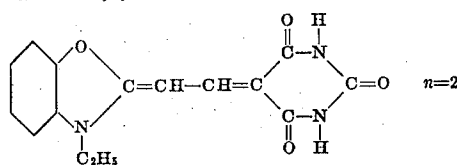
This dye can be prepared as follows: 0.8 part of 3-ethylrhodanine and 2.2 parts of 2-(β -acetanilidovinyl)-quinoline ethiodide were refluxed with 25 parts of acetic anhydride and 0.5 part of anhydrous sodium acetate for about five minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid, yielding dark bluish-gray crystals which gave a bluish-red methyl alcohol solution.

Example 12. — 5-(1-ethyl-2-quinolydene-ethylidene)-3-phenylrhodanine



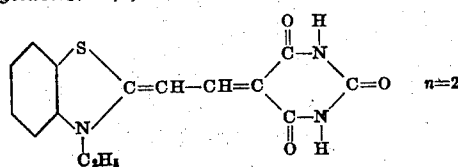
This dye can be prepared as follows: 2.1 parts of 3-phenylrhodanine and 4.4 parts of 2-(β -acetanilidovinyl)-quinoline ethiodide were refluxed with 50 parts of acetic anhydride and 0.9 part of anhydrous sodium acetate for about fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid and yielded brown needles with a green reflex which gave a pinkish-brown methyl alcohol solution.

Example 13. — 5-2-ethyl-1-benzoxazylidene-ethylidene)-2,4,6-triketohexahydropyrimidine



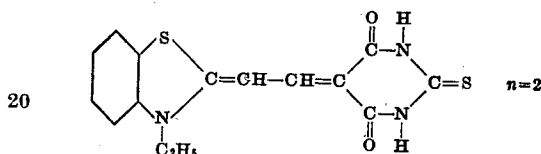
This dye can be prepared as follows: 1.3 parts of barbituric acid and 4.3 parts of 1-(β -acetanilidovinyl)-benzoxazole ethiodide were refluxed with 35 parts of absolute ethyl alcohol and 1.06 parts of triethylamine for about twenty minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid and yielded bright yellow crystals which gave a yellow methyl alcohol solution.

Example 14. — 5-2-ethyl-1-benzothiazylidene-ethylidene)-2,4,6-triketohexahydropyrimidine



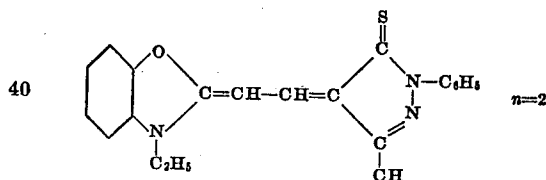
This dye can be prepared as follows: 2.6 parts of barbituric acid, 9 parts of 1-(β -acetanilidovinyl)-benzothiazole ethiodide and 1.8 parts of anhydrous sodium acetate were suspended in 50 parts of acetic anhydride. This mixture was heated just under the boiling point for about one minute. The dye separated from the cooled solution and was filtered off. It was recrystallized from dilute acetic acid, yielding minute crystals with a blue reflex which gave a yellow-orange methyl alcohol solution.

Example 15.—5-(2-ethyl-1-benzothiazylidene-ethylidene)-2-thio-2,4,6-triketohexahydropyrimidine



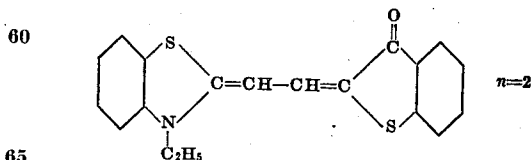
This dye can be prepared as follows: 1.4 parts of thiobarbituric acid and 4.5 parts of 1-(β -acetanilidovinyl)-benzothiazole ethiodide were refluxed with 30 parts of absolute ethyl alcohol and 1.06 parts of triethylamine for about fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from pyridine and gave dull red crystals which gave a reddish-orange methyl alcohol solution.

Example 16.—4-(2-ethyl-1-benzoxazylidene-ethylidene)-3-methyl-1-phenyl-5-thiopyrazolone



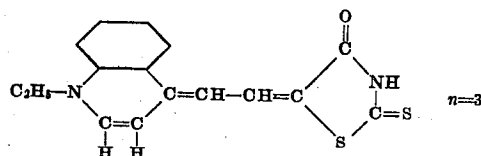
This dye can be prepared as follows: 0.95 part of 3-methyl-1-phenyl-5-thiopyrazolone and 2.2 parts of 1-(β -acetanilidovinyl)-benzoxazole ethiodide were refluxed with 25 parts of absolute ethyl alcohol and 0.53 part of triethylamine for about fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from methyl alcohol, yielding brownish crystals with a green reflex which gave a reddish-orange methyl alcohol solution.

Example 17.—(2-ethyl-1-benzothiazylidene-ethylidene)-thioxindogenide



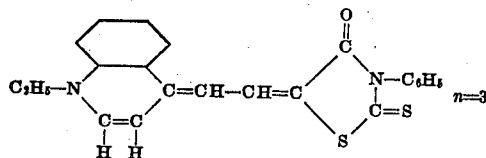
This dye can be prepared as follows: 0.97 part of thioindoxyllic acid, 2.25 parts of 1-(β -acetanilidovinyl)-benzothiazole ethiodide and 0.5 part of triethylamine were refluxed in 15 parts of absolute ethyl alcohol for about fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from methyl alcohol giving purplish needles and a crimson methyl alcohol solution.

Example 18.—5-(1-ethyl-4-quinolyldiene-ethylidene)-rhodanine



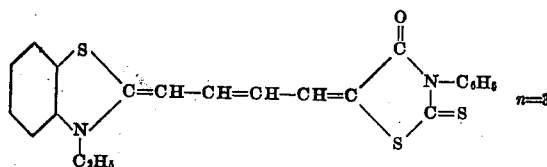
This dye can be prepared as follows: 0.34 part of rhodanine, 1.1 parts of 4-(β -acetanilidovinyl)-quinoline ethiodide and 0.22 part of anhydrous sodium acetate were suspended in 12 parts of acetic anhydride. The mixture was heated for about two minutes just under the boiling point. The dye was filtered from the cooled solution. It was recrystallized from ethyl alcohol, yielding reddish-blue crystals which gave a blue methyl alcohol solution.

Example 19.—5-(1-ethyl-4-quinolyldiene-ethylidene)-3-phenylrhodanine



This dye can be prepared as follows: 1.05 parts of 3-phenylrhodanine and 2.2 parts of 4-(β -acetanilidovinyl)-quinoline ethiodide were refluxed with 25 parts of acetic anhydride and 0.45 part of sodium acetate for about five minutes. The dye was filtered from the cooled solution and was recrystallized from glacial acetic acid yielding dark blue crystals which gave a blue methyl alcohol solution.

Example 20.—5-(2-ethyl-1-benzothiazylidene-butenylidene)-3-phenylrhodanine



This dye can be prepared as in Example 9, using the condensation product of 1-methylbenzothiazole ethiodide and β -anilinoacrolein anil hydrochloride, instead of the condensation product of 1-methylbenzothiazole ethiodide and diphenylformamide. The diphenylformamide condensation products are prepared in known manner according to the process of British Patent No. 344,409 and the β -anilinoacrolein anil condensation products are prepared in known similar manner.

The above dyes are all prepared from heterocyclic compounds such as rhodanine, 3-carboethoxymethylrhodanine, 3-(p-dimethylaminophenyl)-rhodanine, 3-ethylrhodanine, 3-phenylrhodanine, barbituric acid (2,4,6-triketohexahydropyrimidine), thiobarbituric acid (2-thio-2,4,6-triketohexahydropyrimidine), 3-methyl-1-phenyl-5-thio-pyrazolone and thioindoxyl. These compounds have the common property of containing a reactive methylene group as shown below:



wherein A represents an atom such as oxygen or sulfur. The methylene group undoubtedly is activated on account of its position adjacent to the group

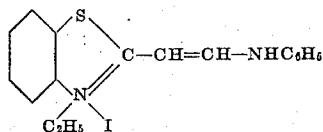


(carbonyl or thiocarbonyl). Hereinafter such a group (carbonyl or thiocarbonyl) is referred to as an activating group.

The heterocyclic compound containing the reactive methylene group may be condensed with a 2-iodopyridine alkiodide, with a 2-iodoquinoline alkiodide or with a 2-iodo- β -naphthoquinoline alkiodide. Dyes No. 1-4 inclusive are examples of such condensation products. Such dyes are called N-alkyl-heterocyclidene derivatives of heterocyclic compounds containing a reactive methylene group.

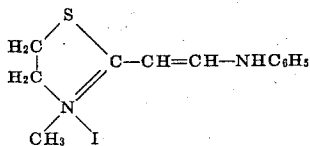
Condensation also takes place readily between such heterocyclic compounds and intermediate compounds formed by the condensation of an alkyl quaternary salt of a heterocyclic base containing a reactive methyl group with a diarylformamidine. The following three compounds are examples of such intermediates.

1.



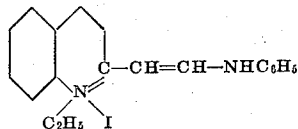
1-(β -anilino vinyl)-benzothiazole ethiodide

2.



2-(β -anilino vinyl)-thiazoline methiodide

3.



2-(β -anilino vinyl)-quinoline ethiodide

The acetyl derivatives of these compounds may also be used.

When such intermediates are condensed with heterocyclic compounds containing a reactive methylene group, dyes of which Nos. 5-19 inclusive are examples, are produced.

The heterocyclic compounds containing reactive methylene groups may also be condensed with intermediate compounds formed by the condensation of alkyl quaternary salts of heterocyclic bases containing a reactive methyl group with compounds such as β -anilinoacrolein anil hydrochloride. In the resultant dyes, the two heterocyclic nuclei are linked together by a chain of four carbon atoms, which may also be called a tetramethenyl chain. Dye No. 20 is an example of such a condensation product.

The dyes described above are useful as photographic sensitizers over a wide range of the spectrum. This is illustrated in the accompanying diagrammatic spectrograms which give the intensity and range of the sensitizing properties of six of the dyes. Unless otherwise indicated the

sensitivity measurements have been made using a silver bromide emulsion.

Fig. 1, 5-(2-ethyl-1-benzoazacylidene-ethylidene)-rhodanine (dye No. 5).

Fig. 2, 5-(2-ethyl-1-benzothiazylidene-ethylidene)-3-phenylrhodanine (dye No. 9.)

Fig. 3, 5-(1-ethyl-2-quinolyldiene-ethylidene)-3-phenylrhodanine (dye No. 12).

Fig. 4, 4-(2-ethyl-1-benzoazacylidene-ethylidene)-3-methyl-1-phenyl-5-thiopyrazolone (dye No. 16).

Fig. 5, (2-ethyl-1-benzothiazylidene-ethylidene)-thioindogenide or 2-ethyl-1-(thioindogen-ethylidene)-benzothiazoline (dye No. 17).

Fig. 6, 5-(1-ethyl-4-quinolyldiene-ethylidene)-3-phenylrhodanine (dye No. 19).

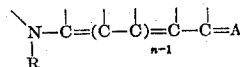
Of the other dyes described herein, the following sensitize in the blue-green and green portions of the spectrum: dye No. 1 with a maximum at 490 millimicrons and a range extending to 585 millimicrons, dye No. 2 with a broad maximum at 530 millimicrons and a range extending to 580 millimicrons, dye No. 3 with a broad maximum at 525 millimicrons and a range extending to 580 millimicrons, dye No. 4 with a maximum at 540 millimicrons and a range extending to 595 millimicrons, dye No. 6 with a maximum at 550 millimicrons and a range extending to 600 millimicrons, dye No. 7 with a maximum at 555 millimicrons and a range extending to 605 millimicrons, dye No. 10 with a maximum at 540 millimicrons and a range extending to 600 millimicrons, dye No. 15 with a maximum at 525 millimicrons and a range extending to 560 millimicrons. Dyes Nos. 13 and 14 sensitize less strongly than the above described dyes in a silver bromide emulsion. However, they are of use particularly in a silver chloride emulsion. For instance, dye No. 14 shows a maximum at 495 millimicrons and a range extending to 530 millimicrons when tested in a silver chloride emulsion.

Dye No. 8 sensitizes farther toward the red than the above dyes, having a broad maximum at 580 millimicrons and the range extending to 660 millimicrons.

Dye No. 11 is a panchromatic sensitizer with two maxima, the first at 560 millimicrons and the second at 625 millimicrons, the range extending to 720 millimicrons.

Dyes Nos. 18 and 20 are sensitizers for the red and deep red regions. The former has a maximum at 665 millimicrons and a range extending to 705 millimicrons with a gap between the regions of ordinary and extraordinary sensitivity. The latter has a maximum at 705 millimicrons and a range extending to 745 millimicrons with a gap between the regions of ordinary and extraordinary sensitivity.

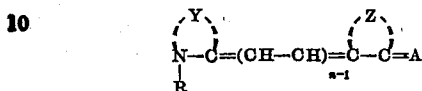
While I have described herein specifically the sensitizing effect of only those dyes containing the following grouping:



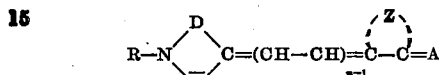
wherein n represents one, two or three, it will be obvious from the breadth of this description that dyes wherein n represents the integer four or even a larger integer, may be prepared in a similar manner by choosing suitable starting materials. Further it is obvious by analogy with the dyes of the cyanine class that such higher molecular weight dyes may possess photographic

sensitizing powers. In other words, the preparation of the remaining dyes in this entire new class of dyes as well as their possibilities as photographic sensitizers will be apparent to those skilled in the art from the teachings set forth above.

The new dyes of my new emulsions can be formulated as follows:



and



wherein A represents a divalent atom, such as oxygen or sulfur, D represents a phenylene group, R represents an alkyl group, n represents a positive integer not greater than three, Y represents the non-metallic atoms necessary to complete a five-membered heterocyclic nucleus, for example, a five-membered heterocyclic nucleus containing two nuclear non-metallic atoms other than carbon, one of which non-metallic atoms is trivalent nitrogen and the other of which is divalent, such as benzothiazole, thiazoline and benzoxazole, Y also represents the non-metallic atoms necessary to complete a six-membered heterocyclic nucleus, for example, a six-membered heterocyclic nucleus containing but one nuclear non-metallic atom other than carbon, such as pyridine, quinoline and naphthoquinoline, and Z represents the non-metallic atoms necessary to complete a five-membered heterocyclic nucleus, for example, a five-membered heterocyclic nucleus containing two nuclear non-metallic atoms other than carbon, at least one of which is trivalent nitrogen and the other of which is divalent when other than nitrogen, such as rhodanines, Z also represents the non-metallic atoms necessary to complete a six-membered heterocyclic nucleus, for example, a six-membered heterocyclic nucleus containing two nuclear trivalent nitrogen atoms and four nuclear carbon atoms, such as barbituric acids. It has recently been proposed to call the dyes of this new and very large class, merocyanine dyes. In the above formulas, when n represents 1, the dyes are conveniently referred to as simple merocyanine dyes, when n represents 2, as merocarbocyanine dyes, and when n represents 3, as merodicarbocyanine dyes.

The preparation of gelatin-silver-halide emulsions is well known to those skilled in the art of photography. To sensitize such emulsions with the dyes herein described, a stock solution is prepared by dissolving the dye in a suitable solvent such as methyl alcohol, acetone or pyridine. Then into one liter of a flowable photographic gelatino-silver-halide emulsion, an amount of the above stock solution, diluted somewhat if desired, containing about 0.010 g. of the desired dye is thoroughly incorporated. This sensitized emulsion may then be coated upon a suitable support, such as glass, cellulose derivative, paper or the like, to a suitable thickness and allowed to dry, details of these processes being well known to photographic experts.

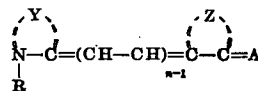
Photographic elements so sensitized have properties different from the ones heretofore produced with other sensitizing dyes and hence are of special utility.

The amount of dye which is actually incorporated in a given quantity of emulsion will, of course, vary from dye to dye and emulsion to emulsion and the regulation and adoption of the most economical and useful preparation will be apparent to those skilled in the art upon observing the sensitizing power of the particular dye for the particular emulsion in question. The above proportions are, therefore, to be regarded only as illustrative and not to be understood as limiting the invention in any sense. Furthermore, it will be apparent that these dyes may be incorporated in the emulsion by other methods practiced in the art as, for instance, by bathing the plate or film upon which the emulsion has been coated, in a solution of the dye in an appropriate solvent, although this method of incorporating the dye in the emulsion is not to be preferred over the first described. Obviously the claims are intended to cover any combination of these dyes with a photographic emulsion whereby the dye exerts a sensitizing effect upon the emulsion.

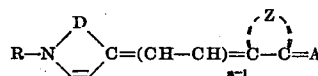
Under the class of gelatino-silver-halide emulsions, of course, are included all of the silver halides customarily employed in the art, but more particularly the silver chloride and silver bromide emulsions.

What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A gelatino-silver-halide emulsion which contains a 5-(1-alkyl-2-quinolyldiene)-3-phenylrhodanine.
2. A gelatino-silver-halide emulsion which contains a 5-(1-ethyl-2-quinolyldiene)-3-phenylrhodanine.
3. A gelatino-silver-halide emulsion which contains a 5-(1-alkyl-2-quinolyldiene-ethylidene)-3-phenylrhodanine.
4. A gelatino-silver-halide emulsion, which contains a 5-(1-ethyl-2-quinolyldiene-ethylidene)-3-phenylrhodanine.
5. A gelatino-silver-halide emulsion which contains a 5-(2-alkyl-1-benzothiazylidene-butenyldiene)-3-phenylrhodanine.
6. A gelatino-silver-halide emulsion which contains a 5-(2-ethyl-1-benzothiazylidene-butenyldiene)-3-phenylrhodanine.
7. A photographic-silver-halide emulsion containing a photographic sensitizing dye selected from the group consisting of dyes characterized by the following formula:



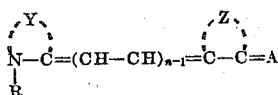
and dyes characterized by the following formula:



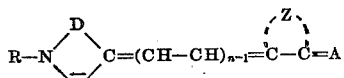
wherein A represents an atom selected from the group consisting of oxygen and sulfur, D represents a phenylene group, R represents an alkyl group, n represents a positive integer not greater than three and Y and Z represent the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei.

8. A gelatino-silver halide emulsion containing a photographic sensitizing dye selected from the

group consisting of dyes characterized by the following formula:

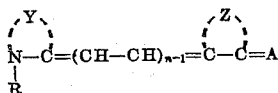


and dyes characterized by the following formula:

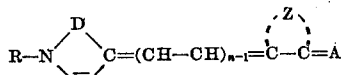


wherein A represents an atom selected from the group consisting of oxygen and sulfur, D represents a phenylene group, R represents an alkyl group, n represents a positive integer not greater than three and Y and Z represent the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei.

9. A photographic-silver-halide emulsion containing a photographic sensitizing dye selected from the group consisting of dyes characterized by the following formula:

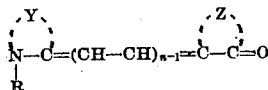


and dyes characterized by the following formula:

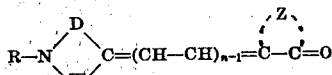


wherein A represents an atom selected from the group consisting of oxygen and sulfur atoms, D represents a phenylene group, R represents an alkyl group, n represents a positive integer not greater than three, Y represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, the five-membered heterocyclic nuclei containing two nuclear non-metallic atoms other than carbon one of which non-metallic atoms is trivalent nitrogen and the other of which is divalent, and the six-membered heterocyclic nuclei containing but one nuclear nonmetallic atom other than carbon, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, the five-membered nuclei containing two nuclear non-metallic atoms other than carbon, at least one of which nuclear atoms is trivalent nitrogen and the other of which is divalent when other than nitrogen, and the six-membered nuclei containing two nuclear trivalent nitrogen atoms and four nuclear carbon atoms.

10. A gelatino-silver-halide emulsion containing a photographic sensitizing dye selected from the group consisting of dyes characterized by the following formula:



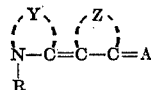
and dyes characterized by the following formula:



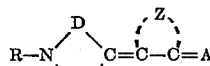
wherein A represents an atom selected from the

group consisting of oxygen and sulfur, D represents a phenylene group, R represents an alkyl group, n represents a positive integer not greater than three and Y represents the non-metallic atoms necessary to complete a nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, the five-membered heterocyclic nuclei containing two nuclear non-metallic atoms other than carbon one of which non-metallic atoms is trivalent nitrogen and the other of which is divalent, and the six-membered heterocyclic nuclei containing but one nuclear non-metallic atom other than carbon, and Z represents the non-metallic atoms necessary to complete a rhodanine nucleus.

11. A gelatino-silver halide emulsion containing a photographic sensitizing dye selected from the group consisting of dyes characterized by the following formula:

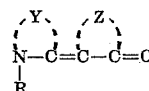


and dyes characterized by the following formula:



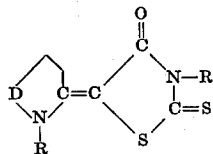
wherein A represents an atom selected from the group consisting of oxygen and sulfur, D represents a phenylene group, R represents an alkyl group, and Y and Z represent the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei.

12. A gelatino-silver-halide emulsion containing a photographic sensitizing dye selected from the group of dyes characterized by the following formula:



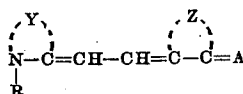
wherein R represents an alkyl group, Y represents the non-metallic atoms necessary to complete a six-membered heterocyclic nucleus, the six-membered heterocyclic nucleus containing but one nuclear non-metallic atom other than carbon, and Z represents the non-metallic atoms necessary to complete a rhodanine nucleus.

13. A gelatino-silver-halide emulsion containing a photographic sensitizing dye selected from the group of dyes characterized by the following formula:

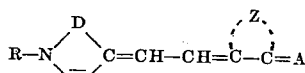


wherein D represents an arylene group of the benzene series, R represents an alkyl group and R' represents an aryl group of the benzene series.

14. A gelatino-silver halide emulsion containing a photographic sensitizing dye selected from the group consisting of dyes characterized by the following formula:

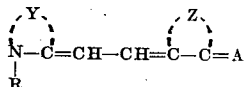


and dyes characterized by the following formula:

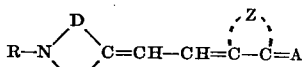


wherein A represents an atom selected from the group consisting of oxygen and sulfur, D represents a phenylene group, R represents an alkyl group, and Y and Z represent the non-metallic atoms necessary to complete a heterocyclic nuclei selected from the group consisting of five-membered and six-membered heterocyclic nuclei.

15. A photographic-silver-halide emulsion containing a photographic sensitizing dye selected from the group consisting of dyes characterized by the following formula:

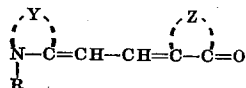


and dyes characterized by the following formula:



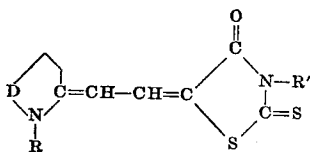
wherein A represents an atom selected from the group consisting of oxygen and sulfur atoms, D represents a phenylene group, R represents an alkyl group, Y represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, the five-membered heterocyclic nuclei containing two nuclear non-metallic atoms other than carbon one of which non-metallic atoms is trivalent nitrogen and the other of which is divalent, and the six-membered heterocyclic nuclei containing but one nuclear non-metallic atom other than carbon, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei, the five-membered nuclei containing two nuclear non-metallic atoms other than carbon, at least one of which nuclear atoms is trivalent nitrogen, and the other of which is divalent when other than nitrogen, and the six-membered nuclei containing two nuclear trivalent nitrogen atoms and four nuclear carbon atoms.

16. A gelatino-silver-halide emulsion containing a photographic sensitizing dye selected from the group of dyes characterized by the following formula:



wherein R represents an alkyl group, Y represents the non-metallic atoms necessary to complete a six-membered heterocyclic nucleus, the six-membered heterocyclic nucleus containing but one nuclear non-metallic atom other than carbon and Z represents the non-metallic atoms necessary to complete a rhodanine nucleus.

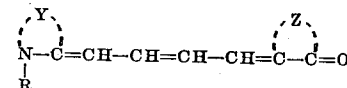
17. A gelatino-silver-halide emulsion containing a photographic sensitizing dye selected from the group of dyes characterized by the following formula:



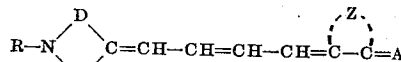
wherein D represents an arylene group of the

benzene series, R represents an alkyl group and R' represents an aryl group of the benzene series.

18. A gelatino-silver halide emulsion containing a photographic sensitizing dye selected from the group consisting of dyes characterized by the following formula:

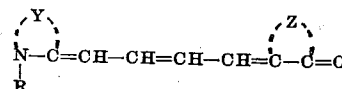


and dyes characterized by the following formula:



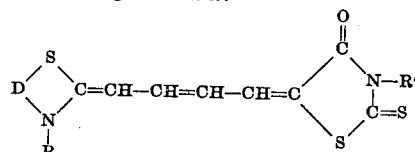
wherein A represents an atom selected from the group consisting of oxygen and sulfur, D represents a phenylene group, R represents an alkyl group, and Y and Z represent the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei.

19. A gelatino-silver-halide emulsion containing a photographic sensitizing dye selected from the group of dyes characterized by the following formula:



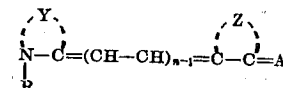
wherein R represents an alkyl group, Y represents the non-metallic atoms necessary to complete a five-membered heterocyclic nucleus, the five-membered heterocyclic nucleus containing two nuclear non-metallic atoms other than carbon, one of which non-metallic atoms is trivalent nitrogen and the other of which is divalent, and Z represents the non-metallic atoms necessary to complete a rhodanine nucleus.

20. A gelatino-silver-halide emulsion containing a photographic sensitizing dye characterized by the following formula:

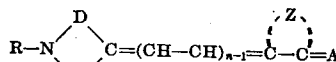


wherein D represents an arylene group of the benzene series, R' represents an aryl group of the benzene series and R represents an alkyl group.

21. As an article of manufacture, a photographic element comprising a transparent support coated with a photographic-silver-halide emulsion which contains a dye selected from the group consisting of dyes characterized by the following formula:



and dyes characterized by the following formula:



wherein A represents an atom selected from the group consisting of oxygen and sulfur, D represents a phenylene group, R represents an alkyl group, n represents a positive integer not greater than three and Y and Z represent the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of five-membered and six-membered heterocyclic nuclei.

LESLIE G. S. BROOKER.