Aug. 10, 1937. L. G. S. BROOKER 2,089,729

PHOTOGRAPHIC EMULSION

Filed Aug. 11, 1934 2 Sheets-Sheet 1

Fig. 1.

5-(P-DIETHYLAMINOBENZAL)-RHODANINE

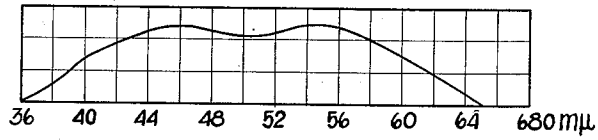
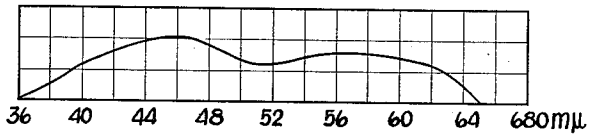


Fig. 2.

3-CARBETHOXYMETHYL-5-(P-DIETHYLAMINOBENZAL)-RHODANINE



DENSITY

Fig. 3.

5-(P-DIETHYLAMINOBENZAL)-3-ETHYLRHODANINE

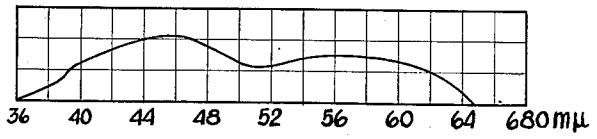
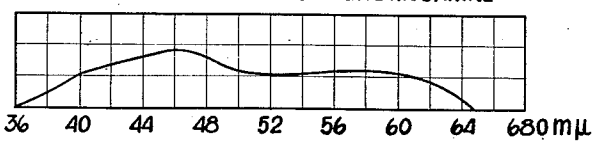


Fig. 4.

5-(P-DIETHYLAMINOBENZAL)-3-PHENYLRHODANINE



Leslie G.S. Brooker

INVENTOR

BY *N. M. Perrins*

Daniel J. Mayne

ATTORNEYS.

Aug. 10, 1937. L. G. S. BROOKER 2,089,729

PHOTOGRAPHIC EMULSION

Filed Aug. 11, 1934 2 Sheets-Sheet 2

Fig. 5.

5-(p-DIETHYLAMINOBENZAL)-2,4,6-TRIKETOHEXAHYDROPYRIMIDINE

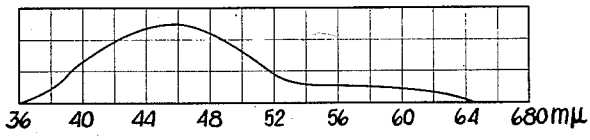
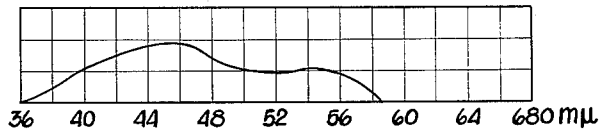


Fig. 6.

5-(p-DIETHYLAMINOBENZAL)-2-THIO-2,4,6-TRIKETOHEXAHYDROPYRIMIDINE



DENSITY

Fig. 7.

4-(p-DIMETHYLAMINOBENZAL)-3-METHYL-1-PHENYL-5-PYRAZOLONE

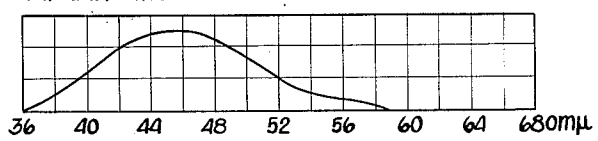
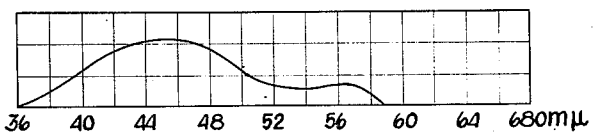


Fig. 8.

2-(p-DIMETHYLAMINOBENZAL)-4-INDOXYL



LesLie G.S. Brooker

INVENTOR

BY N. M. Perrins

Daniel J. Magne

ATTORNEYS.

Patented Aug. 10, 1937 2,089,729

UNITED STATES PATENT OFFICE

2,089,729

PHOTOGRAPHIC EMULSION

Leslie G. S. Brooker, Rochester, N. Y., assignor, by mesne assignments, to Eastman Kodak Company, Jersey City, N. J., a corporation of New Jersey

Application August 11, 1934, Serial No. 739,503

13 Claims. (Cl. 95—7)

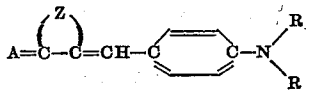
This invention relates to photographic emulsions containing p-dialkylaminobenzal derivatives of heterocyclic compounds containing a reactive methylene group, and more particularly to a photographic emulsion sensitized with such a dye.

It has been known for some time in the photographic art 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 pseudo-cyanines, sensitol red, thiocarbocyanine and others. Additional ones have been described in United States Patent No. 1,942,854 wherein emulsions containing thiazolino-carbocyanines are described, No. 1,962,123 wherein emulsions containing dibenzoxacarbocyanines are described and No. 1,962,124 wherein emulsions containing oxacarbocyanines are described.

Now I have found that p-dialkylaminobenzal derivatives of heterocyclic compounds containing a reactive methylene group are useful as photographic sensitizers. These dyes are particularly useful as sensitizers in the green and yellow regions of the spectrum.

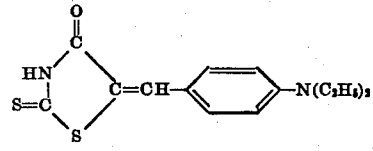
It is an object of the present invention to provide a photographic emulsion, such as a gelatino-silver-halide emulsion, which contains a p-dialkylaminobenzal derivative of a heterocyclic compound containing a reactive methylene group. A further object is to provide a photographic emulsion such as a gelatino-silver-halide emulsion, sensitized with a p-dialkylaminobenzal derivative of a heterocyclic compound containing a reactive methylene group. 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.

The p-dialkylaminobenzal derivatives which go to make up the emulsions of my invention can be represented by the following general formula:

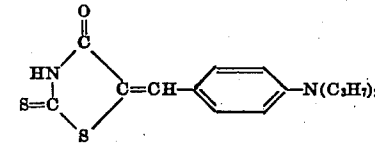


wherein A represents a divalent atom, such as oxygen or sulfur, R represents an alkyl group and Z represents the non-metallic atoms necessary to complete a five-membered or six-membered heterocyclic nucleus. As hereinafter illustrated, the five-membered or six-membered heterocyclic nuclei advantageously contain a nuclear nitrogen atom, a nuclear sulfur atom, or both a nuclear nitrogen and nuclear sulfur atom. The compounds containing both a nuclear nitrogen and a nuclear sulfur atom are particularly useful in practicing my invention. In each case the divalent atom (A) is connected to a trivalent alkylated nitrogen atom by means of a conjugated carbon chain.

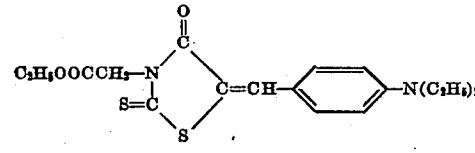
Examples of p-dialkylaminobenzal derivatives which I have found to possess photographic sensitizing properties are as follows:

1. 

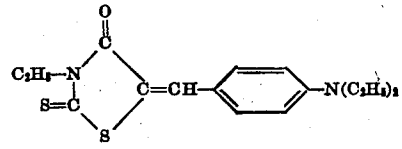
5-(p-diethylaminobenzal)-rhodanine

2. 

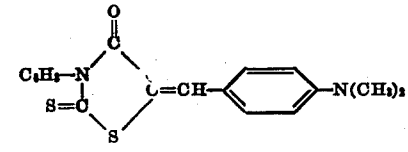
5-(p-di-n-propylaminobenzal)-rhodanine

3. 

3-carbethoxymethyl-5-(p-diethylaminobenzal)-rhodanine

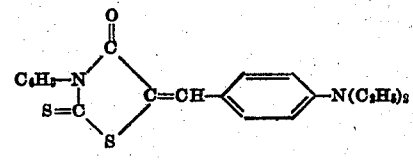
4. 

5-(p-diethylaminobenzal)-3-ethylrhodanine

5. 

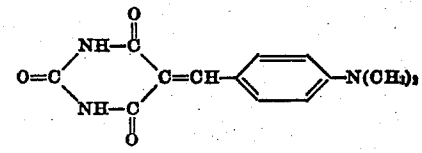
5-(p-dimethylaminobenzal)-3-phenylrhodanine

6.



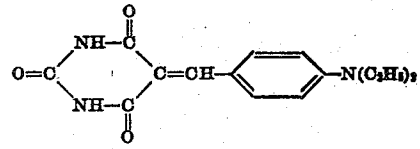
5-(p-diethylaminobenzal)-3-phenylrhodanine

7.



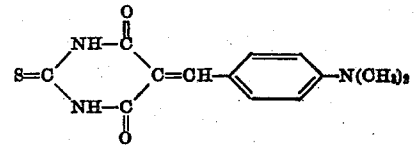
5-(p-dimethylaminobenzal)-2,4,6-triketo-hexahydro-pyrimidine

8.



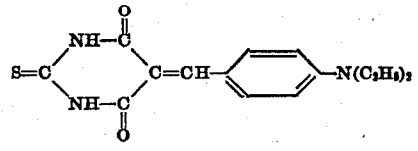
5-(p-diethylaminobenzal)-2,4,6-triketo-hyexahdropyrimidine

9.



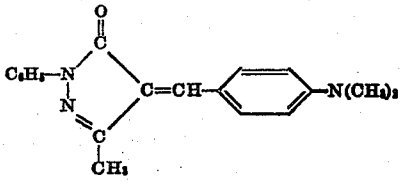
5-(p-dimethylaminobenzal)-2-thio-2,4,6-triketo-hexahydropyrimidine

10.



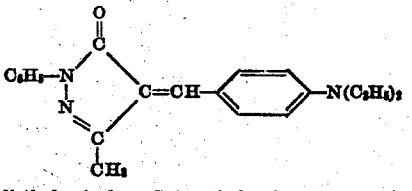
5-(p-diethylaminobenzal)-2-thio-2,4,6-triketohexahydropyrimidine

11.



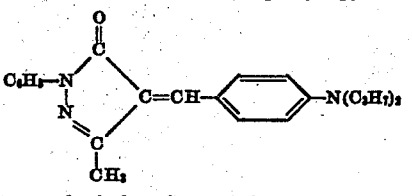
4-(p-dimethylaminobenzal)-3-methyl-1-phenyl-5-pyrazolone

12.



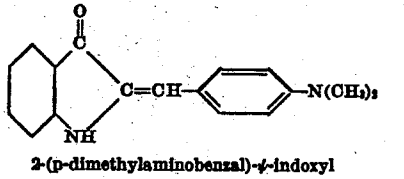
4-(p-diethylaminobenzal)-3-methyl-1-phenyl-5-pyrazolone

13.



4-(p-di-n-propylaminobenzal)-3-methyl-1-phenyl-5-pyrazolone

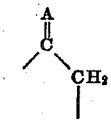
14.



2-(p-dimethylaminobenzal)-4-indoxyl

In each of the fourteen examples given above the dye is made up of a dialkylaminophenyl group linked through its para position by a methenyl group to a heterocyclic nucleus, the methenyl group being doubly bound to a nuclear carbon atom of the heterocyclic nucleus which is adjacent to an activating group, i. e., a carbonyl group.

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



The methylene group undoubtedly is activated on account of its position adjacent to the group



(carbonyl or thiocarbonyl). Such a group (carbonyl or thiocarbonyl) is herein referred to as an activating group.

The rhodanines described above may be prepared according to the method described by Holmberg, J. prakt. Chem. 81, 451 (1910). The other heterocyclic compounds given above may be prepared by methods given in the literature of chemistry and well known to the skilled organic chemist.

Condensation readily takes place between such heterocyclic compounds and p-dialkylaminobenzaldehydes to give the dyes described above. The condensation is usually carried out in glacial acetic acid with anhydrous sodium or potassium acetate. It may also be effected in a lower aliphatic alcohol, for instance, absolute ethyl alcohol, using an organic base such as piperidine as a catalyst.

When a dye containing the indoxyl nucleus is to be made, indoxylic acid may be used, since this acid readily loses carbon dioxide under the conditions of the experiment and hence functions as indoxyl.

Examples of the preparation of typical benzal derivatives are as follows:

Example 1.—5-(p-diethylaminobenzal)-rhodanine

5.32 parts of rhodanine and 7.1 parts of p-diethylaminobenzaldehyde were refluxed in 50 parts of glacial acetic acid for about two hours. The dye was filtered from the cooled solution and washed with acetic acid followed by water. It was recrystallized from benzene, giving red needles with a blue reflex which gave a yellow-orange methyl alcohol solution.

Example 2.—5-(p-dimethylaminobenzal)-3-phenylrhodanine

2.1 parts of 3-phenylrhodanine and 1.5 parts of p-dimethylaminobenzaldehyde were refluxed with 30 parts of absolute ethyl alcohol and a trace of piperidine for about two hours. The dye was filtered from the cooled solution and recrystallized from glacial acetic acid giving deep orange crystals.

Example 3.—2-(p-dimethylaminobenzal)-ψ-indoxyl

2.64 parts of indoxylic acid and 2.25 parts of p-dimethylaminobenzaldehyde were refluxed in 10 parts of glacial acetic acid for about fifteen minutes. The dye was precipitated by adding water. It was filtered off and recrystallized from methyl alcohol giving reddish-purple needles which gave a reddish-orange methyl alcohol solution.

Example 4.—4-(p-diethylaminobenzal)-3-methyl-1-phenyl-5-pyrazolone

1.74 parts of 3-methyl-1-phenyl-5-pyrazolone and 1.77 parts of p-diethylaminobenzaldehyde were refluxed in 10 parts of glacial acetic acid for about two hours. The dye was filtered from the cooled solution and was recrystallized from methyl alcohol giving lustrous scarlet crystals which gave an orange methyl alcohol solution.

Example 5.—5-(p-dimethylaminobenzal)-2,4,6-triketohexahydropyrimidine

1.64 parts of barbituric acid and 1.5 parts of p-dimethylaminobenzaldehyde were refluxed in 25 parts of glacial acetic acid for about twenty minutes. The dye separated from the hot solution. Upon cooling, the dye was filtered off and washed with water followed by acetone. It was recrystallized from acetic acid, giving brownish orange crystals which gave a yellow-orange solution.

Example 6.—5-(p-diethylaminobenzal)-2-thio-2,4,6-triketohexahydropyrimidine

2.9 parts of thiobarbituric acid and 3.5 parts of p-diethylaminobenzaldehyde were refluxed in 50 parts of glacial acetic acid for about fifteen minutes. The dye was filtered from the cooled solution. It was recrystallized from glacial acetic acid giving reddish-orange crystals.

The dyes described are useful as sensitizers for the visible spectrum, especially the green and yellow regions of the spectrum. The intensity and range of the sensitizing effect of these dyes on an ordinary gelatino-silver-bromide emulsion is indicated by the diagrammatic spectrograms in the accompanying drawings. The figures and the dyes, the sensitizing effect of which they illustrate, are as follows:

Fig. 1. 5-(p-diethylaminobenzal)-rhodanine.

Fig. 2. 3-carbethoxymethyl-5-(p-dimethylamino-benzal)-rhodanine.

Fig. 3. 5-(p-diethylaminobenzal)-3-ethyl-rhodanine.

Fig. 4. 5-(p-diethylaminobenzal)-3-phenyl-rhodanine.

Fig. 5. 5-(p-dimethylaminobenzal)-2,4,6-triketo-hexahydropyrimidine.

Fig. 6. 5-(p-diethylaminobenzal)-2-thio-2,4,6-triketohexahydropyrimidine.

Fig. 7. 4-(p-dimethylaminobenzal)-3-methyl-1-phenyl-5-pyrazolone.

Fig. 8. 2-(p-dimethylaminobenzal)-ψ-indoxyl.

The sensitizing effects of all the dyes of this class are comparable to those of the dyes indicated. In some cases, the dyes are more useful in chloride emulsions, owing to the fact that their sensitizing maxima lie within the region of normal sensitivity of the bromide emulsions but outside the region of normal sensitivity of the chloride emulsions. Such is true with some of the pyrimidine and pyrazolone dyes.

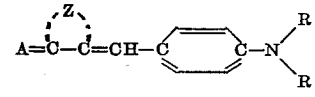
The preparation of gelatino-silver-halide emulsions is well known to those skilled in the art of photography. To sensitize such emulsions with the dyes herein described, a stock solution is prepared by dissolving the dye in a suitable solvent such as methyl alcohol, acetone or pyridine. Then into one 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.

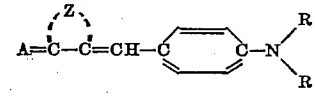
What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A photographic-silver-halide emulsion which contains a sensitizing dye selected from the group of dyes characterized by the following formula:



wherein A represents an atom selected from the group consisting of oxygen and sulfur, R represents an alkyl group, 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.

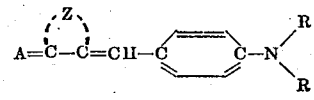
2. A gelatino-silver-halide emulsion which contains a sensitizing dye selected from the group of dyes characterized by the following formula:



wherein A represents an atom selected from the group consisting of oxygen and sulfur, R repre-

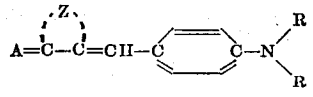
sents an alkyl group, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus, selected from the group consisting of five-membered and six-membered heterocyclic nuclei.

3. A gelatino-silver-halide emulsion which contains a sensitizing dye selected from the group of dyes characterized by the following formula:



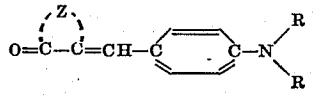
wherein A represents an atom selected from the group consisting of oxygen and sulfur, R represents an alkyl group, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing at least one nuclear nitrogen atom, selected from the group consisting of five-membered heterocyclic nuclei containing at least one nuclear nitrogen atom and six-membered heterocyclic nuclei containing at least one nuclear nitrogen atom.

4. A gelatino-silver-halide emulsion which contains a sensitizing dye selected from the group of dyes characterized by the following formula:



wherein A represents an atom selected from the group consisting of oxygen and sulfur, R represents an alkyl group, and Z represents the non-metallic atoms necessary to complete a five-membered heterocyclic nucleus containing a nuclear nitrogen atom and a nuclear sulfur atom.

5. A gelatino-silver-halide emulsion which contains a sensitizing dye selected from the group of dyes characterized by the following formula:



wherein R represents an alkyl group and Z represents the non-metallic atoms necessary to complete a rhodanine nucleus.

6. A gelatino-silver-halide emulsion which contains a 5-(p-dialkylaminobenzal)-rhodanine.

7. A gelatino-silver-halide emulsion which contains a 5-(p-diethylaminobenzal)-rhodanine.

8. A gelatino-silver-halide emulsion which contains a 5-(p-dialkylaminobenzal)-3-alkylrhodanine.

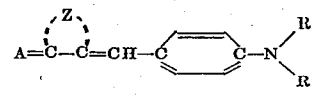
9. A gelatino-silver-halide emulsion which contains a 5-(p-dialkylaminobenzal)-3-ethylrhodanine.

10. A gelatino-silver-halide emulsion which contains 5-(p-diethylaminobenzal)-3-ethylrhodanine.

11. A gelatino-silver-halide emulsion which contains a 3-carbethoxymethyl-5-(p-dialkylaminobenzal)-rhodanine.

12. A gelatino-silver-halide emulsion which contains a 3-carbethoxymethyl-5-(p-diethylaminobenzal)-rhodanine.

13. As an article of manufacture, a support coated with a gelatino-silver-halide emulsion which contains a sensitizing dye selected from the group of dyes characterized by the following formula:



wherein A represents an atom selected from the group consisting of oxygen and sulfur, R represents an alkyl group, 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.

LESLIE G. S. BROOKER.