

Jan. 6, 1942.

L. G. S. BROOKER ET AL

2,268,798

PYRROLE METHINE AND TRI-METHINE CYANINE BACKING DYES

Filed Feb. 7, 1940

FIG. 1

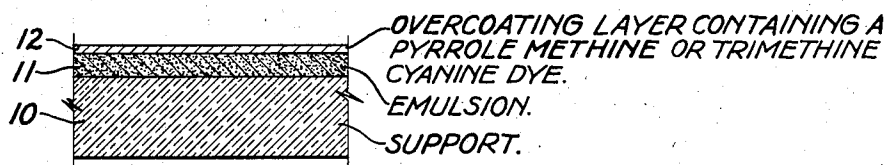
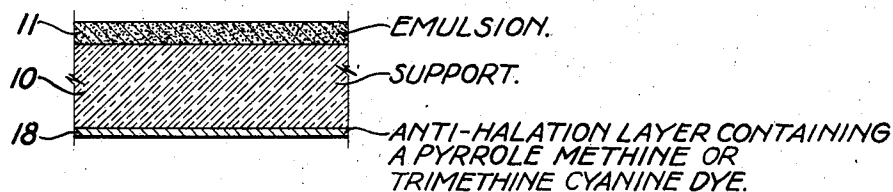


FIG. 2



LESLIE G. S. BROOKER
ROBERT H. SPRAGUE
INVENTORS

Walter M. Reider
BY *R. Frank Smith*
ATTORNEYS

UNITED STATES PATENT OFFICE

2,268,798

PYRROLE METHINE AND TRI-METHINE
CYANINE BACKING DYES

Leslie G. S. Brooker and Robert H. Sprague,
Rochester, N. Y., assignors to Eastman Kodak
Company, Rochester, N. Y., a corporation of
New Jersey

Application February 7, 1940, Serial No. 317,727
In Great Britain February 17, 1939

6 Claims. (Cl. 95—8)

This invention relates to improvements in photographic elements and more particularly to backing or anti-halation dyes for use in photographic elements.

The use of overcoating or backing layers containing light absorptive dyes for use in photographic films or plates is well known. These light screening substances are often required in overcoatings upon photographic elements to protect the light sensitive emulsion from the action of light which it is not desired to record or in backing layers forming so-called anti-halation layers on either side of a transparent support carrying the light-sensitive emulsion or emulsions.

In photographic elements it is generally necessary to employ light-screening substances which can readily be rendered ineffective, that is decolorized or destroyed and removed prior to, during, or after photographic processing. For many purposes it is particularly convenient to employ light-screening substances which are rendered ineffective by one of the photographic baths employed in processing the element after exposure, that is photographic developing or fixing bath or a silver oxidizing (including silver removing) bath. For example, in an element which is to be processed by reversal it is often convenient to employ a light-absorbing substance which is rendered ineffective by the developer employed to develop the latent image or images to silver, since exposure to light of the residual light-sensitive emulsion or emulsions may thereby be facilitated. This is particularly true in the case of color photography where several differentially sensitized emulsions composed, for example, of silver halide, such as silver bromide, dispersed in gelatin, collodion, or other colloid are coated on one or both sides of a support. It may be desirable in such cases to expose the photographic element from the rear side during processing, that is, from the side which contained an anti-halation backing during the original exposure.

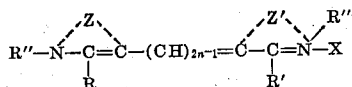
We have now found a class of dyes members of which fulfill to a very satisfactory extent the requirements of light screening substances for use in photographic elements. This class consists of methine and tri-methine cyanine dyes

derived from pyrrole or from its substituted derivatives.

Such dyes may have a pyrrole nucleus, substituted or unsubstituted, the nitrogen atom of which may also form a part of the pyridine nucleus, linked through an intermediate polymethine chain so that there is a chain of an odd number of carbon atoms having conjugated double linkages between the nitrogen atoms.

In the drawing the figures are enlarged sectional views of photographic elements showing overcoating or anti-halation layers according to our invention.

The compounds which we propose to use as screening dyes have the following general formula:



where

Z and Z' = the non-metallic atoms necessary to complete a pyrrole nucleus, and may be the same or different.

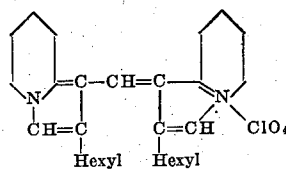
R and R' = hydrogen, alkyl, or a chemical bond in a pyridine ring.

R'' and R''' = hydrogen, alkyl, aryl, or a chemical bond of the same pyridine ring as R or R'.

n = a positive integer of from 1 to 2.

X = an acid radical.

Example 1

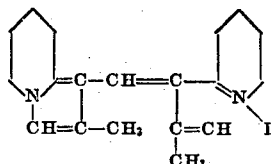


Bis - (2 - hexyl - 1 - pyrrocoline) methine - cyanine perchlorate.

3.0 g. (2 mols) 2-hexylpyrrocoline, 6.7 g. (1 mol+500%) ethylorthoformate and 25 cc. glacial acetic acid were stirred mechanically at room temperature for 5 minutes. Blue coloration at once. 2.3 g. (1 mol+100%) NaI added and stirring continued for 25 minutes. Diluted to 100 cc. with ether and chilled. No crystals separated. 1.8 g. (1 mol+100%) NaClO₄ in 25 cc.

acetone added and mixture again chilled. Dye filtered off, washed with water and a small amount of acetone and dried. Bronze crystals. Yield 2.0 g., 53%. After recrystallization from MeOH. (15 cc., 1 g.) the dye was obtained as bronze crystals melting with decomposition at 170-171°. Yield 1.6 g., 42%. MeOH solution blue.

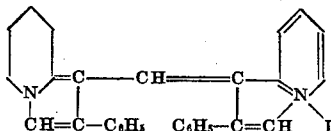
Example 2



Bis-(2-methyl-1-pyrrocoline)methine-cyanine iodide.

2.6 g. (2 mols) 2-methyl pyrrocoline, 3.0 g. (1 mol+100%) ethyl orthoformate and 20 cc. glacial acetic acid were stirred mechanically with heating on steam pot for 1 minute. Blue coloration at once. Steam shut off and stirring continued 5 minutes. 3.0 g. (1 mol+100%) sodium iodide added and mixture stirred 2 minutes longer. Chilled, filtered, washed with acetone and water and dried. Yield of blue-green crystals. 3.55 g., 89%. After recrystallization from MeOH (35 cc., 1 g.), the product was obtained as green crystals melting with decomposition at 232-233°. Yield 1.5 g., 37%. MeOH solution blue.

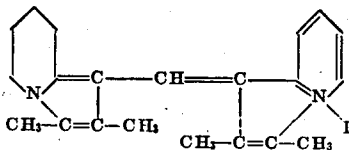
Example 3



Bis-(2-phenyl-1-pyrrocoline)methine-cyanine iodide.

3.86 g. (2 mols) 2-phenylpyrrocoline, 3.0 g. (1 mol+100%) ethylorthoformate and 25 cc. glacial acetic acid were stirred mechanically with heating on steam pot for 1 minute. Blue coloration at once. Steam shut off and stirring continued 5 minutes. 3.0 g. (1 mol+100%) sodium iodide added and mixture stirred 2 minutes longer. Green crystals separated from the hot solution; chilled, filtered, washed with acetone and water and dried. Yield of violet crystals 4.0 g., 76%. After recrystallization from MeOH, (33 cc., 1 g.) the dye was obtained as bronze crystals melting with decomposition at 165-166°. Yield 2.2 g., 42%. MeOH solution blue.

Example 4

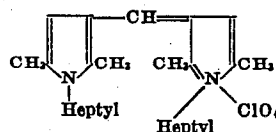


Bis-(2,3-dimethyl-1-pyrrocoline)-methine-cyanine iodide.

2.9 g. (2 mols) 2,3-dimethylpyrrocoline, 9.0 g. (1 mol+500%) ethylorthoformate and 30 cc. glacial acetic acid were stirred mechanically at room temperature for 5 minutes. 3.0 g. (1 mol+100%) NaI were added and the mixture stirred 10 minutes longer. Green crystals separated. Chilled, filtered, washed with acetone and water and dried. Yield 3.6 g., 84%. After recrystallization from MeOH, (27 cc., 1 g.) the dye was obtained

as green crystals with bright green reflex melting with decomposition at 269-271°. Yield 3.1 g., 72%. Solution blue in MeOH.

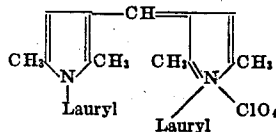
Example 5



Bis-(1-heptyl-2,5-dimethyl-3-pyrrole)methine-cyanine perchlorate.

2.2 g. (1 mol) 1-heptyl-2,5-dimethyl-3-pyrrole-aldehyde, 1.9 g. (1 mol) 1-heptyl-2,5-dimethylpyrrole, 1.1 g. (1 mol) 35% hydrochloric acid and 15 cc. absolute C₂H₅OH were refluxed 30 minutes. Orange coloration. A solution of 2.4 g. (1 mol+100%) sodium perchlorate in 15 cc. CH₃OH was added and the mixture cooled. Diluted to 200 cc. with ether and chilled. Filtered, washed with ether and water and dried. Yield of orange crystals 2.2 g., 44%. After recrystallization from absolute C₂H₅OH, (11 cc., 1 g.) the dye was obtained as bright orange flakes melting with decomposition at 150-151°. Yield 1.8 g., 36%. MeOH solution yellow.

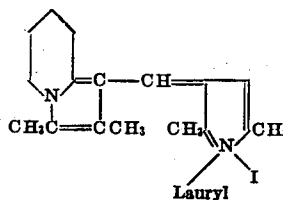
Example 6



Bis-(1-lauryl-2,5-dimethyl-3-pyrrole)-methine-cyanine perchlorate.

2.9 g. (1 mol) 1-lauryl-2,5-dimethyl-3-pyrrole-aldehyde, 2.6 g. (1 mol) 1-lauryl-2,5-dimethylpyrrole, 1.1 g. (1 mol) 35% hydrochloric acid and 15 cc. absolute C₂H₅OH were refluxed 30 minutes. Orange coloration. A solution of 2.4 g. (1 mol+100%) NaClO₄ in 15 cc. CH₃OH was added and the mixture cooled. Diluted to 200 cc. with ether and chilled. Filtered, washed with ether and water and dried. Yield of orange crystals 3.8 g., 59%. After recrystallization from absolute C₂H₅OH, (8 cc., 1 g.) the dye was obtained as bright orange crystals melting with decomposition at 158-160°. Yield 3.6 g., 56%. MeOH solution yellow.

Example 7

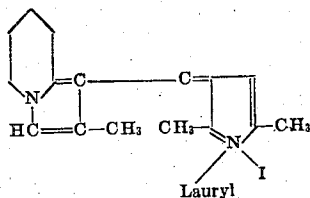


(1-Lauryl-2,5-dimethyl-3-pyrrole)-(2,3-dimethyl-1-pyrrocoline)methine-cyanine iodide.

2.0 g. (1 mol) 2,3-dimethylpyrrocoline, 4.0 g. (1 mol) 1-lauryl-2,5-dimethyl-3-pyrrolealdehyde, 1.5 g. (1 mol) 35% hydrochloric acid and 15 cc. absolute C₂H₅OH were refluxed 5 minutes. Reddish orange coloration. A solution of 5 g. (1 mol+150%) NaI in 15 cc. CH₃OH was added and the mixture boiled 1 minute with stirring. Cooled, diluted to 700 cc. with ether and chilled. Dye filtered off, washed with ether and water and dried. Yield of red crystals 5.4 g., 72%. After recrystallization from absolute C₂H₅OH, (11 cc., 1 g.) the dye was obtained as red crystals

melting at 144-145° with decomposition. Yield 4.5 g., 60%. MeOH solution pinkish orange.

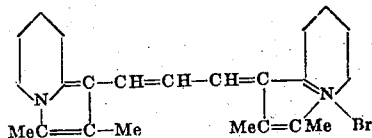
Example 8



(1 - Lauryl - 2,5 - dimethyl - 3 - pyrrole)-(2-methyl-1-pyrrocoline) methine-cyanine iodide.

2.6 g. (1 mol.) 2-methylpyrrocoline, 5.8 grams (1 mol.) 1-lauryl-2,5-dimethyl-3-pyrrolealdehyde, 6.0 g. (1 mol.+100%) sodium iodide, 2.2 g. (1 mol.) 35% hydrochloric acid and 25 cc. absolute C₂H₅OH were refluxed 5 minutes. The red mixture was chilled, the dye which separated was filtered off, washed with water and acetone and dried. Yield of red crystals, 7.9 g., 75%. After recrystallization from CH₃OH, (10 cc. 1 g.) the product was obtained as felted red crystals melting with decomposition at 146-148°. Yield 4.9 g., 46%. Solution pink in CH₃OH. Bleached by developer. No sensitizing action. No diffusion when coated in multi-layer gelatine coating.

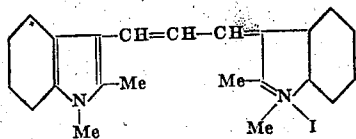
Example 9



Bis-(2,3-dimethyl-1-pyrrocoline) trimethinecyanine bromide.

2.9 g. (2 mols.) 2,3-dimethylpyrrocoline, 2.6 g. (1 mol.) β-anilinoacrolein anil hydrochloride, 2.0 g. (1 mol.+100%) sodium bromide and 25 cc. acetic anhydride were refluxed 5 minutes. The blue reaction mixture was diluted with 100 cc. acetone and chilled to 0° C. The dye was filtered off, washed with acetone and water and dried. Yield of green solid 2.4 g., 83%. After crystallization from MeOH (165 cc/g.) the product was obtained as bright blue-green crystals melting with decomposition at 273-274°. Yield 2.7 g., 66%. MeOH solution blue.

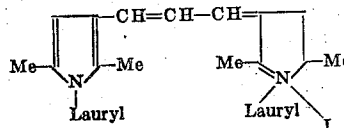
Example 10



Bis-(1,2-dimethyl-3-indole) trimethinecyanine iodide.

2.9 g. (2 mols.) 1,2-dimethylindole, 2.6 g. (1 mol.) β-anilinoacrolein anil hydrochloride, 3.0 g. (1 mol.+100%) sodium iodide and 15 cc. acetic anhydride were refluxed 5 minutes. The purple solution was chilled to 0° C., the dye filtered off, washed with acetone and water and dried. Yield of dull blue crystals 2.1 g., 46%. After crystallization from MeOH, (1075 cc./g.) the dye was obtained as shiny blue crystals melting with decomposition at 237-239°. Yield 1.3 g., 29%. Solution bluish red in MeOH.

Example 11



Bis-(1-lauryl-2,5-dimethyl-3-pyrrole) trimethine cyanine iodide.

5.26 g. (2 mols.) 1-lauryl-2,5-dimethylpyrrole, 2.6 g. (1 mol.) β-anilinoacrolein anil hydrochloride, 3.0 g. (1 mol.+100%) sodium iodide, 25 cc. acetic anhydride and 5 cc. glacial acetic acid were refluxed 1 minute. The purple mixture was chilled to 0° C., the dye filtered off, washed with acetone and water and dried. Yield of green crystals 1.5 grams, 22%. After crystallization from absolute ethyl alcohol the product was obtained as green crystals with a golden reflex melting with decomposition at 165-166°. Yield 1.2 grams, 17%. MeOH solution bluish-red.

For the preparation of overcoating layers, filter layers and anti-halation layers according to our invention, from 50 mg. to 150 mg. of dye are dissolved in from 2 to 5 cc. of a water miscible solvent. Methanol and acetone are suitable for this purpose but pyridine and Cellosolve may also be used. The solution is then added to about 25 cc. of a 5% gelatin solution at 40° C. and the mixture coated on a support. If the dye is too insoluble as the iodide salt, it may conveniently be converted into the chloride using cresol as a solvent for the conversion.

In the accompanying drawing the various figures are enlarged sectional views of photographic elements having overcoating layers and anti-halation layers made according to our invention. As shown in Fig. 1, a support of 10 of any suitable material such as cellulose nitrate or cellulose acetate, resinous material, or opaque material such as paper is coated with an emulsion layer 11 and an overcoating layer 12 containing a bis-methine cyanine dye containing a pyrrole nucleus according to our invention.

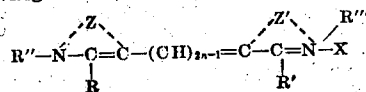
Fig. 2 represents a film having an anti-halation layer containing a bis-methine cyanine pyrrole dye according to our invention. As shown therein, the support 10 contains an emulsion layer 11 on one side and an anti-halation layer 13 containing the bis-methine cyanine dye on the opposite side.

Our invention is not limited to the examples included in the present specification but any compounds coming within the scope of the invention may be used. The dye may be dispersed in gelatin, collodion, gum arabic, synthetic resins or other suitable colloid or they may be dispersed in photographic emulsions such as gelatino-silver halide emulsions and may be coated in any suitable manner.

It is to be understood that our invention is limited only by the scope of the appended claims.

We claim:

1. A photographic element comprising a sensitive layer and a light-absorbing layer containing a dye having the following formula:



in which Z and Z' = the non-metallic atoms necessary to complete a pyrrole nucleus, and may be the same or different; R and R' = hydrogen, alkyl, or a chemical bond in a pyridine ring;

R'' and R'''=hydrogen, alkyl, aryl, or a chemical bond of the same pyridine ring as R or R'; n=a positive integer of from 1 to 2; and X=an acid radical.

2. A sensitive photographic element comprising a filter layer containing a dye having the general formula expressed in claim 1.

3. A sensitive photographic element comprising a filter layer containing a bis- (1-pyrrocoline) methine cyanine salt.

4. A sensitive photographic element compris-

ing a filter layer containing bis- (2-hexyl-1-pyrrocoline) methine cyanine perchlorate.

5. A sensitive photographic element comprising a filter layer containing bis- (2-methyl-1-pyrrocoline) methine cyanine iodide.

6. A sensitive photographic element comprising a filter layer containing bis- (2-phenyl-1-pyrrocoline) methine cyanine iodide.

LESLIE G. S. BROOKER.
ROBERT H. SPRAGUE.