Oct. 31, 1950 H. R. SILBERSTEIN ET AL 2,527,583

MEROCYANINE FILTER AND BACKING DYES

Filed Feb. 7, 1946

FIG. 1.

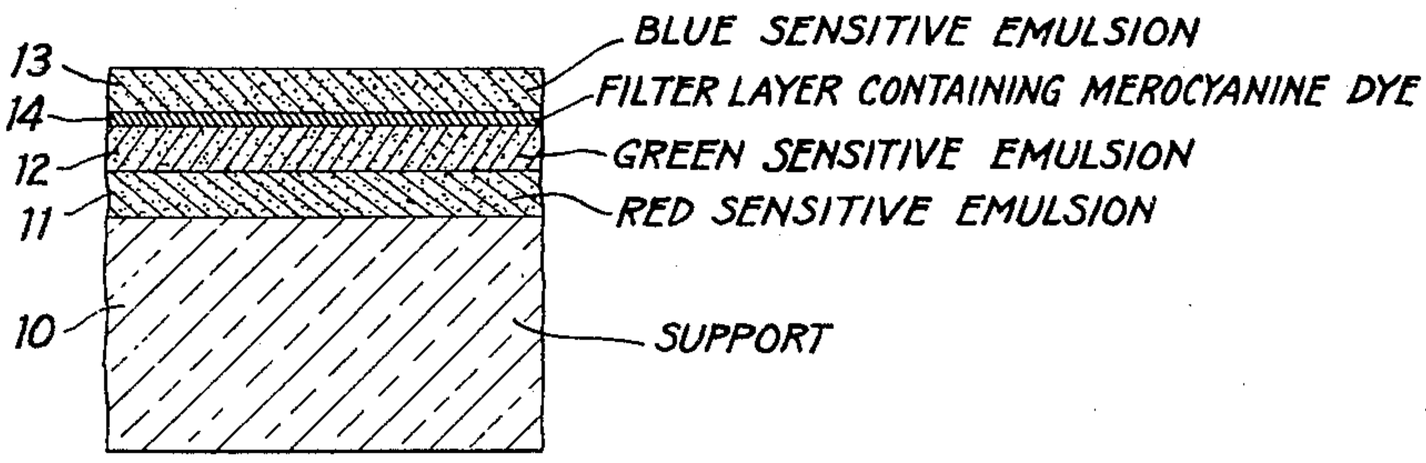
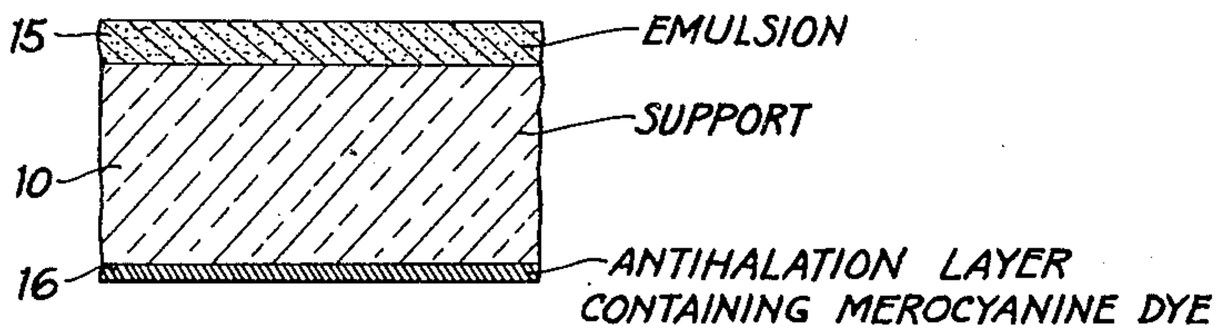


FIG. 2.



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MEROCYANINE FILTER AND BACKING DYES

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Application February 7, 1946, Serial No. 646,206

8 Claims. (Cl. 95—2)

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This invention relates to improvements in photographic elements and more particularly in photographic elements having light screening substances therein.

It is known that photographic elements require, for many purposes, to have light screening substances incorporated therein. Such a light screening substance may be in a layer overlying a light sensitive emulsion or overlying two or more light sensitive emulsions; or it may be in a light sensitive emulsion for the purpose of modifying a light record in such emulsion or of protecting an underlying light sensitive emulsion or emulsions from the action of light of wave length absorbed by such light screening substance; or it may be in a layer not containing a light sensitive substance but arranged between two light sensitive emulsions; or it may be in a layer serving as a backing on an element having one or more light sensitive emulsions (for example, to reduce halation).

In particular, light screening substances are often required in layers arranged between differentially colored senstized emulsions, e. g., to protect red and green sensitized emulsions from the action of blue light and in backings forming the so-called anti-halation layers on either side of a transparent support carrying the light-sensitive emulsion or emulsions.

In most cases, and especially when the element contains a color-sensitized emulsion or color-sensitized emulsions, it is particularly desirable to employ light-screening substances which do not affect the general sensitivity or the color sensitivity of light-sensitive emulsions with which they may come into contact.

It is also particularly desirable to employ light-screening substances which do not substantially diffuse from the layers or coatings in which they are incorporated, either during the manufacture of the element or on keeping it or in photographically processing it. Finally, it is generally necessary to employ light-screening substances which can readily be rendered ineffective, i.e. decolorized or destroyed and removed, prior to or 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, e. g. a photographic developing bath 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 screening substance

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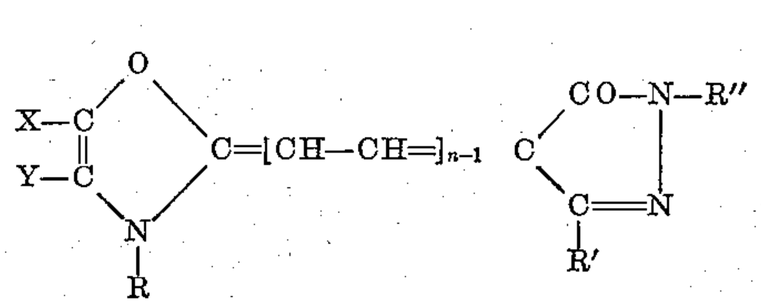
which is rendered ineffective by one of the processing baths. This is particularly the case when, in making color photographs, several differentially color-sensitized emulsions, constituted, for example, by silver halide, such as silver bromide dispersed in gelatin, collodion or other colloid, are coated on one or both sides of a support, for example in inseparably-superimposed layers. Such differentially color-sensitized emulsions have to be processed to different colors and to facilitate differential color-processing, methods involving selective exposure of light-sensitive images in the layers may be employed. Such selective re-exposure, e. g. of silver halide remaining undeveloped in development of the latent images formed in silver halide emulsion layers (residual silver halide) is often facilitated if the light-screening substance which was present during the original exposure is decolorized or removed in one of the processing baths. Any of the elements referred to above may be such that one or more of the emulsions contain coupling components, e. g. those described in U. S. Patent 2,306,410, granted August 16, 1938.

We have found a new type of filter dye which is bleached during photographic processing. These dyes form stable filter coatings and have the advantage of slight desensitizing properties combined with clean and apparently irreversible bleaching under a considerable range of conditions. Bleaching appears to be caused by sulfite.

The dyes which we propose to use for this purpose are merocyanines derived from 2-methyloxazoles or 2-methylbenzoxazoles, and pyrazolones containing an acid group. They have the following general formula:

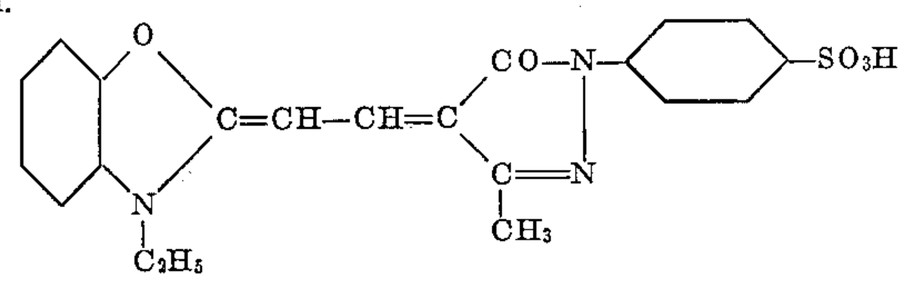


in which X and Y=hydrogen, phenyl or together represent the atoms necessary to complete an aryl ring of the benzene or naphthalene series, R=alkyl, R′=alkyl or carboxyl, R″=hydrogen or aryl containing an acid group, n=2 or 3.

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

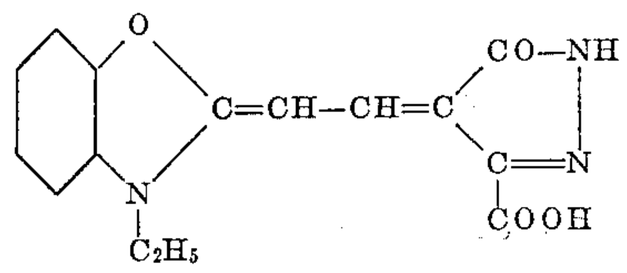
The following compounds illustrate dyes which may be used according to our invention.

1.



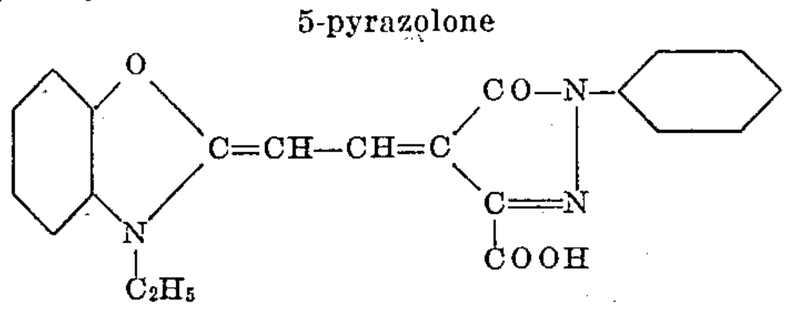
4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-methyl-1-(p-sulfophenyl)-5-pyrazolone

2.



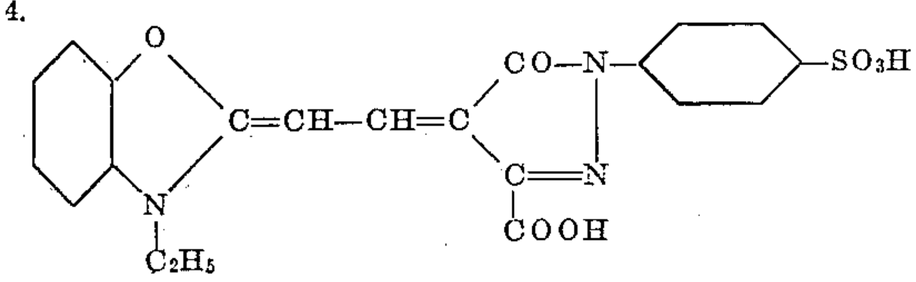
4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-carboxy-5-pyrazolone

3.



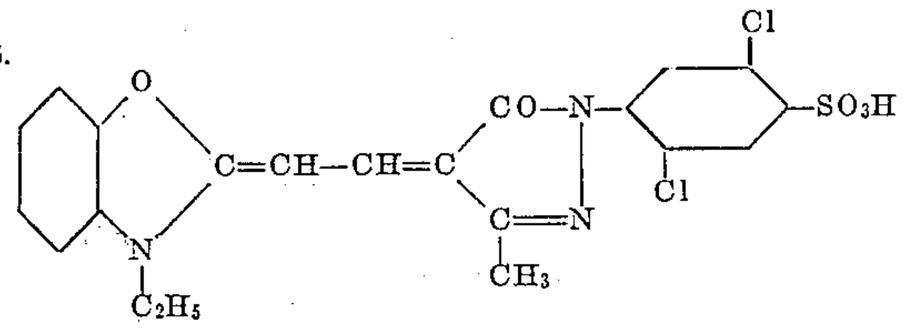
4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-carboxy-1-phenyl-5-pyrazolone

4.



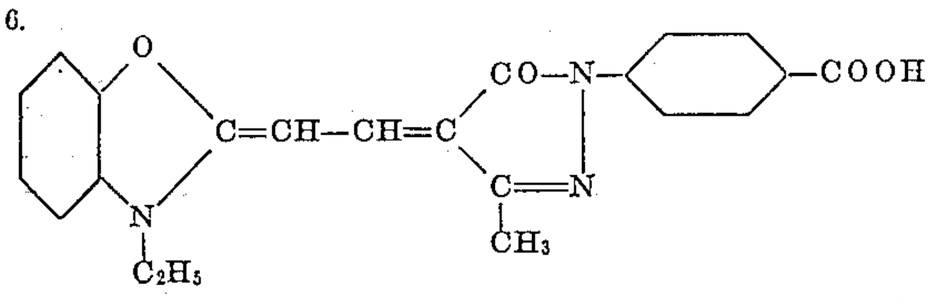
4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-carboxy-1-p-sulfophenyl-5-pyrazolone

5.



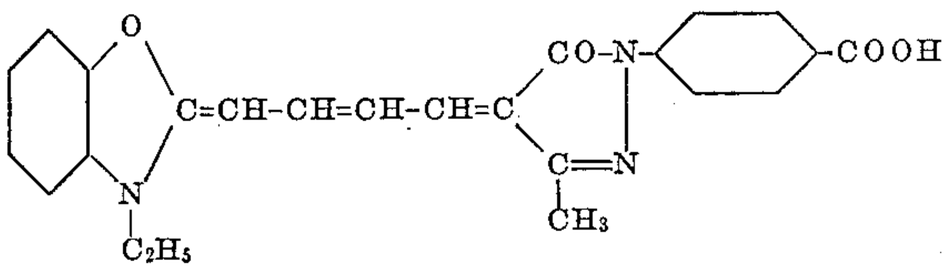
4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-methyl-1-(4-sulfo-2,5-dichlorophenyl)-4-pyrazolone

6.



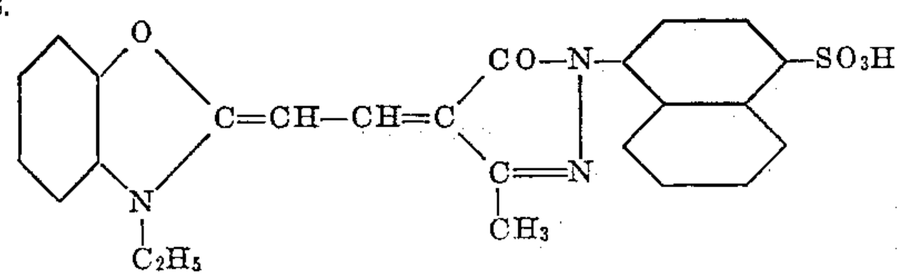
4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-ethyl-1-p-carboxyphenyl-5-pyrazolone

7.



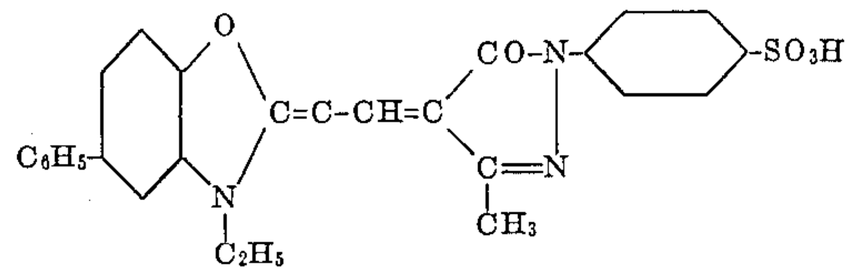
4-[(3-ethyl-2(3)-benzoxazolylidene)butylenilidene]-3-methyl-1-p-carboxy-phenyl-5-pyrazolone

8.



4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-methyl-1-(4'-sulfo-1-naphthyl)-5-pyrazolone

9.



4-[(3-ethyl-5-phenyl-2(3)-benzoxazolylidene)ethylidene]-3-methyl-1-(p-sulfophenyl)-5-pyrazolone

These dyes may be prepared according to the methods described in Brooker U. S. application, Ser. No. 605,472, filed July 16, 1945, now Patent No. 2,493,747 of January 10, 1950.

In the accompanying drawing, the various figures are enlarged sectional views of photographic elements having filter layers and anti-halation layers made according to our invention. As shown in Fig. 1, a support **10** of any suitable material such as cellulose nitrate, cellulose acetate, synthetic resin or paper is coated with sensitive emulsion layers **11**, **12** and **13** which record, respectively, the red, green and blue regions of the spectrum. Between the emulsion layers **12** and **13**, there is a filter layer **14**, containing a yellow merocyanine dye according to our invention. This filter layer serves the purpose well known in color photography of preventing exposure of the lower layers **11** and **12** with blue light which is recorded in layer **13**.

Fig. 2 illustrates a film having a anti-halation layer containing a merocyanine dye according to our invention. As shown therein, the support **10** contains an emulsion layer **15** on one side and an anti-halation layer **16** containing a merocyanine dye on the opposite side.

The following examples illustrate the use of merocyanine dyes according to our invention.

Example 1

For an anti-halation backing 1 gram of 4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]3-methyl-1-(p-sulfophenyl)-5-pyrazolone was dissolved in water and added to a solution of 50 grams of gelatin. This solution was spread on a film base at such concentration that the dried coating contains one pound of dried gelatin per 300 square feet of film surface. A sensitive emulsion layer was coated on the opposite side of the film support and upon exposures of this layer the dye was found to afford ample anti-halation protection for blue light and was bleached during normal photographic processing.

Example 2

For the preparation of a multi-layer photographic element the usual red-sensitive and green-sensitive silver halide emulsion layers were coated on a subbed film support. A solution was then prepared by dissolving one gram of 4-[(3-ethyl-2(3)-benzoxazolylidene)ethylidene]-3-methyl-1-(p-sulfophenyl)-5-pyrazolone in the form of its sodium salt in 100 cc. of water. Three grams of polyvinyl pyridine metho-p-toluene sulfonate were dissolved separately in 100 cc. of water and these two solutions were added successively with stirring to a solution of 18 grams of gelatin in 180 cc. of water. The resulting dispersion of a merocyanine dye was coated on the green-sensitive emulsion layer at such concentration that the dried coating contained 1 pound of gelatin per 700 sq. ft. of surface. The usual blue-sensitive silver halide emulsion layer was coated on the dried filter layer.

There was found to be no diffusion of the filter dye into the adjacent emulsion layers and consequently, there was no change in speed or other properties of the emulsions. Bleaching of the dye was found to be complete in most color processes using coupler development although in processes where the first developer was a color developer with low concentration of sulfite, it was found preferable first to treat the film with a 10% solution of sodium sulfite followed by washing before the first developer.

The polyvinyl pyridine metho-p-toluene sulfonate is described in Sprague and Brooker U. S. patent application Serial No. 719,624, filed December 31, 1946, now Patent No. 2,484,430. Other high molecular weight quaternary salts described in Carroll and Kenyon U. S. patent application Serial No. 87,578, filed April 14, 1949, may also be used.

Example 3

A dispersion was made as in Example 2, using 4 - [(3 - ethyl - 2(3) - benzoxazolylidene) ethylidene] - 3 - methyl - 1 - (4'sulfo - 1 - naphthyl) -5-pyrazolone in place of the dye of Example 2.

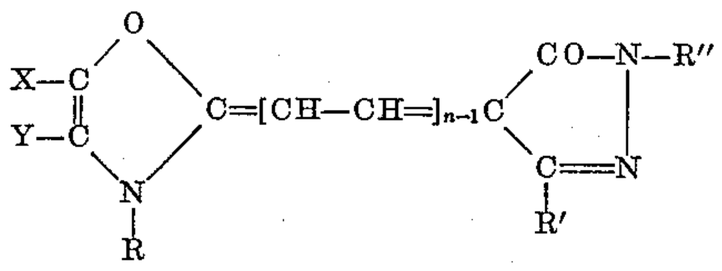
Example 4

A dispersion was made as in Example 2 using 4 - [(3 - ethyl - 5 - phenyl - 2(3) - benzoxazolylidene) ethylidene] - 3 - methyl - 1(p-sulfophenyl) -5-pyrazolone in place of the dye of Example 2.

Our invention is not limited to the examples and modifications included herein but includes all compounds falling within the scope of the appended claims. The dyes may be dispersed in gelatin, collodion, gum arabic, synthetic resins or other suitable colloids or they may be dispersed in gelatino silver halide emulsions and may be coated in any suitable manner.

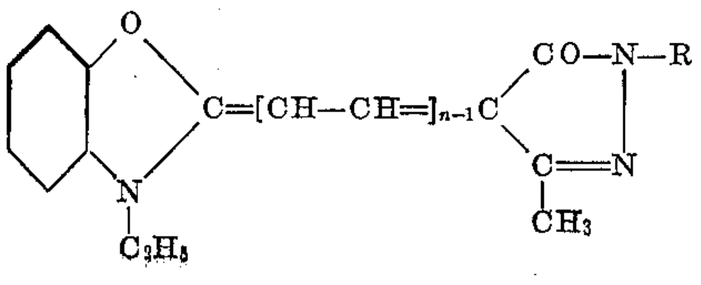
We claim:

1. A photographic element comprising a sensitive silver halide emulsion layer and a light-absorbing water-permeable colloid layer containing a dye having the following formula:



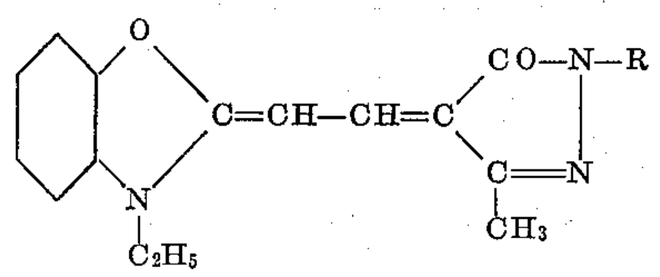
in which X and Y are selected from the class consisting of hydrogen, phenyl, and the atoms necessary to complete an aryl ring, R is alkyl, R′ is selected from the class consisting of alkyl and carboxyl, R″ is selected from the class consisting of hydrogen and aryl containing an acid group selected from the class consisting of sulfonic acid and carboxyl and *n* is a positive integer from 2 to 3, R′ always being carboxyl when R″ is hydrogen and R″ always being aryl containing an acid group selected from the class consisting of sulfonic acid and carboxyl when R′ is alkyl.

2. A photographic element comprising a sensitive silver halide emulsion layer and a light-absorbing water-permeable colloid layer containing a dye having the following formula:



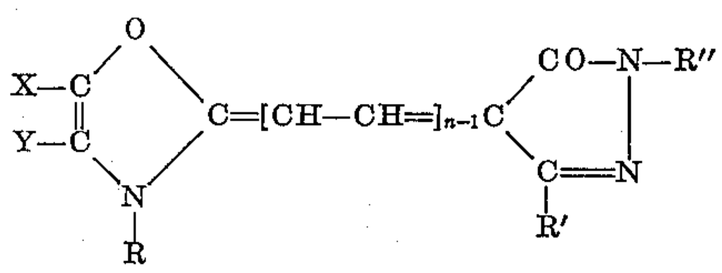
in which R represents a phenyl radical containing a carboxyl group in the p-position and *n* is a positive integer from 2 to 3.

3. A photographic element comprising a sensitive silver halide emulsion layer and a light-absorbing water-permeable colloid layer containing a dye having the following formula:



where R represents an aryl radical containing a sulfonic acid group in the para position.

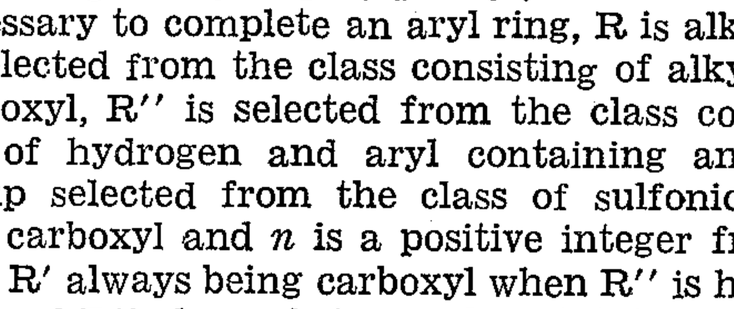
4. A sensitive photographic element comprising a support having a sensitive silver halide emulsion layer on one side thereof and on the opposite side thereof a water-permeable colloid anti-halation layer containing a dye having the following formula:



in which X and Y are selected from the class consisting of hydrogen, phenyl, and the atoms necessary to complete an aryl ring, R is alkyl, R′ is selected from the class consisting of alkyl and carboxyl, R″ is selected from the class consisting of hydrogen and aryl containing an acid group selected from the class of sulfonic acid and carboxyl and *n* is a positive integer from 2 to 3, R′ always being carboxyl when R″ is hydrogen and R″ always being aryl containing an acid group selected from the class consisting of sulfonic acid and carboxyl when R′ is alkyl.

5. A photographic element comprising a transparent support having a sensitive silver halide emulsion layer on one side thereof and a water-permeable colloid layer on the opposite side thereof having dispersed therein 4-[(3-ethyl - 2(3) - benzoxazolylidene) ethylidene] - 3 - methyl-1-(p-sulfophenyl) -5-pyrazolone.

6. A multi-layer photographic element comprising a support having thereon a plurality of differentially sensitive silver halide emulsion layers and between the emulsion layer farthest from said support and an inner emulsion layer, a water-permeable colloid layer containing a dye having the following formula:



in which X and Y are selected from the class consisting of hydrogen, phenyl, and the atoms necessary to complete an aryl ring, R is alkyl, R′ is selected from the class consisting of alkyl and carboxyl, R″ is selected from the class consisting of hydrogen and aryl containing an acid group selected from the class of sulfonic acid and carboxyl and *n* is a positive integer from 2 to 3, R′ always being carboxyl when R″ is hydrogen and R″ always being aryl containing an acid group selected from the class consisting of sulfonic acid and carboxyl when R′ is alkyl.

7. A multi-layer photographic element comprising a support having thereon a plurality of differentially sensitive silver halide emulsion layers and between the emulsion layer farthest from said support and an inner emulsion layer, a water-permeable colloid layer containing 4 - [(3 - ethyl - 2(3) - benzoxazolylidene) ethylidene] - 3 - methyl - 1 - (p-sulfophenyl) - 5 - pyrazolone.

8. A multi-layer photographic element comprising a support having thereon a plurality of differentially sensitive silver halide emulsion layers and between the emulsion layer farthest from said support and an inner emulsion layer, a water-permeable colloid layer containing 4 - [(3 - ethyl - 2(3) - benzoxazolylidene) ethylidene] - 3 - methyl - 1 - (4' - sulfo - 1 - naphthyl) -5-pyrazolone.

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BURT H. CARROLL.

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