Sept. 23, 1952 G. H. KEYES ET AL 2,611,696

PHOTOGRAPHIC ELEMENT CONTAINING UNSYMMETRICAL OXONOL FILTER AND ANTIHALATION DYES

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Fig. 1

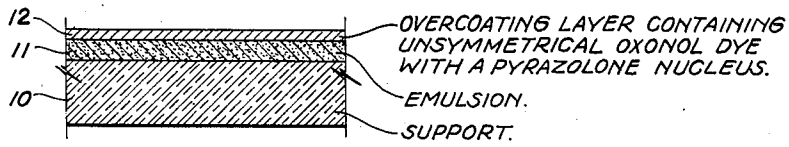


Fig. 2

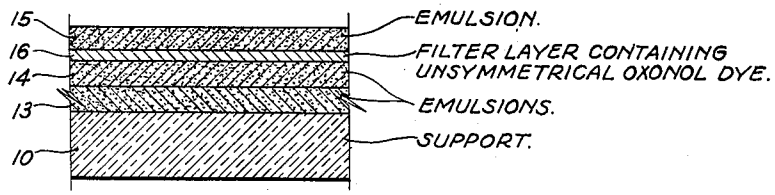
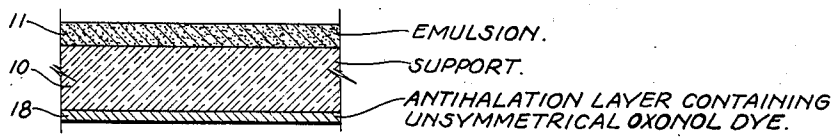


Fig. 3



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PHOTOGRAPHIC ELEMENT CONTAINING UNSYMMETRICAL OXONOL FILTER AND ANTIHALATION DYES

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Application January 17, 1947, Serial No. 722,739

4 Claims. (Cl. 95—8)

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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 (*a*) in overcoatings upon photographic elements to protect the light sensitive emulsion or emulsions from the action of light which it is not desired to record, e. g. ultra-violet light in the case of still or moving pictures, especially color pictures, (*b*) in layers arranged between differentially color-sensitized emulsions, e. g. to protect red- and green-sensitized emulsions from the action of blue light and (*c*) in backings, forming the so-called antihalation 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. decolorised 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 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 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 the 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 the developing bath employed to develop the latent images to silver. 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 French Patent 834,371, granted August 16, 1938.

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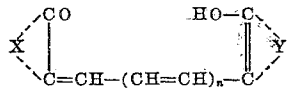
Numerous substances have been employed as light-screening substances for the purposes indicated above. Many of these are known yellow dyes but it has proved extremely difficult to find dyes having the combination of qualities desired. Many are not resistant to diffusion and wander rather freely from the layer in which it is intended that they should remain; many adversely affect the sensitivity of light sensitive emulsions with which they come into contact (a number of these reduce the general sensitivity or some specific color sensitivity thereof, but others of them may even impart an additional and unwanted specific color sensitivity thereto).

We have now found a class of dyes which satisfactorily fulfill the requirements of filter and antihalation dyes for use in photographic elements. This class consists of certain unsymmetrical methineoxonol and polymethineoxonol dyes. These dyes are characterized by the fact that they contain the oxochromic atoms O= and —OH connected by a conjugated chain of carbon atoms.

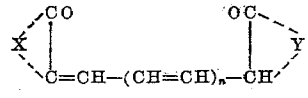
We propose to use dyes in which the nucleus at one end of the carbon chain is a barbituric acid, thiobarbituric acid, isoxazolone or indandione nucleus, and the nucleus at the other end of the carbon chain is a pyrazolone nucleus.

In the drawing, the figures are enlarged sectional views of photographic elements showing overcoating, filter and antihalation layers according to our invention.

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



or

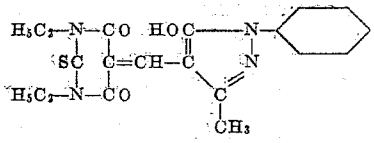


where X represents the atoms necessary to complete a barbituric acid, thiobarbituric acid, isoxazolone or indandione nucleus, Y represents the atoms necessary to complete a pyrazolone nucleus, and n is 0, 1 or 2.

The general formula indicates that our compounds may be depicted in two electromeric forms.

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

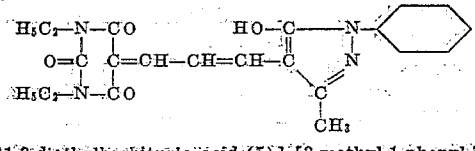
Example 1



[1,3-diethyl-2-thiobarbituric acid-(5)]-[3-methyl-1-phenyl-5-pyrazolone-(4)]-methineoxonol

3.2 g. (1 mol.) of 4-acetanilidomethylene-3-methyl-1-phenyl-5-pyrazolone, 2 g. (1 mol.) of 1,3-diethyl-2-thiobarbituric acid, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were heated under reflux for 5 minutes. The reaction mixture was then chilled, diluted with about 50 cc. of water, and the mixture made acid to Congo red by addition of concentrated hydrochloric acid. The solid which separated was collected on a filter, washed well with methyl alcohol and dried. It was purified by dissolving in methyl alcohol as the triethylamine salt, filtering hot and acidifying and chilling. Two such treatments gave a yellow powder, M. P. 188–191° C., with decomposition. The orange yellow solution of the triethylamine salt was bleached by developer. The 4-acetanilidomethylene-3-methyl-5-pyrazolone employed was made by acetylation of 4-anilidomethylene-3-methyl-5-pyrazolone which has been described by Daines et al.; see for example J. Chem. Soc. 31, 1148 (1909); 2310 (1922) and Kansas Univ. Science Bull. 15, 265 (1924); 19, 215 (1930). See also Rodd and Watts, British Patent 366,964.

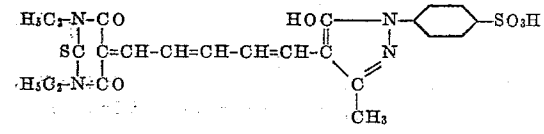
Example 2



[1,3-diethylbarbituric acid-(5)]-[3-methyl-1-phenyl-5-pyrazolone-(4)]-trimethineoxonol

3.45 g. (1 mol.) of 4-(3-acetanilidoallylidene)-3-methyl-1-phenyl-5-pyrazolone, 1.85 g. (1 mol.) of 1,3-diethylbarbituric acid, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were refluxed for 15 minutes. The cooled reaction mixture was diluted with about 100 cc. of water, made acidic with hydrochloric acid and chilled. A sticky mass was precipitated. After decanting the liquors, the residue was stirred up with methyl alcohol and it became crystalline. It was collected on filter and washed with methyl alcohol. It was purified by dissolving in methyl alcohol as the triethylamine salt, filtering hot, acidifying and chilling. Two such treatments gave red crystals with a bluish reflex, M. P. 248–250° C., with decomposition. The bluish red solution of the triethylamine salt was bleached by developer.

Example 3

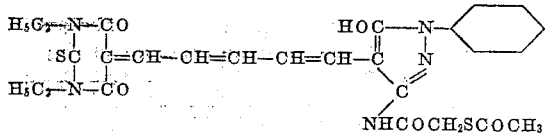


[1,3-diethyl-2-thiobarbituric acid-(5)]-[3-methyl-1-p-sulfophenyl-5-pyrazolone-(4)]-pentamethineoxonol

2 g. (1 mol.) of 5-(5-acetanilido-2,4-pentadienylidene)-1,3-diethyl-2-thiobarbituric acid, 1.3 g. (1 mol.) of 3-methyl-1-p-sulfophenyl-5-pyrazolone, 20 cc. of pyridine and 1 g. (2 mol.) of triethylamine were mixed together in a flash and allowed to stand at room temperature for 15 minutes a deep blue color developed. The reaction mixture was diluted with about 50 cc. of water and made acidic with hydrochloric acid and chilled. The solid which separated was collected on filter, washed with water and dried. It was purified by dissolving in methyl alcohol as the triethylamine salt and precipitating on making acidic. Two such treatments gave the dye as blackish crystals, M. P. 196–198° C., with decomposition. The blue solution of the triethylamine salt was bleached by developer. The 5-(5-acetanilido-2,4-pentadienylidene)-1,3-diethyl-2-thiobarbituric acid was made as follows:

4 g. (1 mol.) of 1,3-diethyl-2-thiobarbituric acid, 5.5 g. (1 mol.) of glutaconicaldehyde dianilide hydrochloride, 30 cc. of acetic anhydride and 1.65 g. (1 mol.) of fused sodium acetate were mixed together and refluxed for 2 to 3 minutes. The product was separated from the cooled reaction mixture. It was obtained in purity sufficient for use as dye intermediate by washing with water and methyl alcohol. The 1,3-diethyl-2-thiobarbituric acid used in the above was made in a manner similar to that used by Whitely, J. C. S. 91, 1338 (1907) in preparing 1,3-diphenyl-barbituric acid. The 1,3-diethyl-2-thiobarbituric acid was obtained as colorless crystals of M. P. 101–103° C.

Example 4

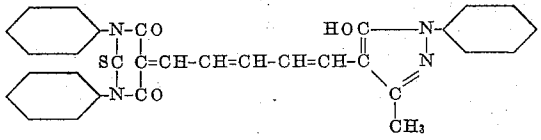


[3-acetylthioglycolylamino-1-phenyl-5-pyrazolone-(4)]-[1,3-diethyl-2-thiobarbituric acid-(5)]-pentamethine oxonol

4 g. (1 mol.) of 5-(5-acetanilido-2,4-pentadienylidene)-1,3-diethyl-2-thiobarbituric acid, 2.9 g. (1 mol.) of 3-acetylthioglycolylamino-1-phenyl-5-pyrazolone, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were heated for 10 minutes at temperature of the steam bath. Dye

separated on chilling and acidification with dilute hydrochloric acid. The crude, washed dye was purified by dissolving as the triethylamine salt, filtering hot and precipitating on addition of acid to the filtrate. Two such treatments gave the dye as dark green crystals. M. P. 219–221° C. with decomposition. The blue solution of the triethylamine salt was readily bleached by developer. The 3 - acetylthioglycollylamino - 1 - phenyl-5-pyrazolone used in the above preparation was made according to the method of Weissberger and Porter, J. A. C. S. 64, 2133 (1942). It was obtained as colorless crystals of M. P. 195° C.

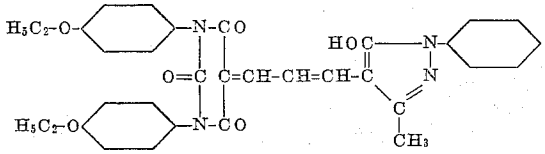
Example 5



[1,3-diphenyl-2-thiobarbituric acid-(5)]-[3-methyl-1-phenyl-5-pyrazolone-(4)] pentamethineoxonol

3.7 g. (1 mol.) of 4-(5-acetanilido-2,4-pentadienylidine-3-methyl-1-phenyl-5-pyrazolone, 3 g. (1 mol.) of 1,3-diphenyl-2-thiobarbituric acid, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were heated for 10 minutes at steam bath temperature. Dye separated on acidification of the chilled reaction mixture. The crude washed dye was purified by dissolving as the triethylamine salt, filtering hot and precipitating on addition of hydrochloric acid to the filtrate. Two such treatments gave the dye as dull greenish black powder, M. P. 225–227° C., with decomposition. The blue solution of the triethylamine salt was readily bleached by developer. The 4-(5-acetanilido - 2,4 - pentadienylidene) - 3 - methyl-1-phenyl-5-pyrazolone employed above was prepared by allowing a mixture of 7 g. (1 mol.) of 3-methyl-1-phenyl-5-pyrazolone, 11 g. (1 mol.) of glutaconic aldehyde dianilide hydrochloride, 100 cc. of absolute ethyl alcohol and 4 g. (1 mol.) of triethylamine to stand at about 0° C. for 1½ hours. This mixture was then poured into about 600 cc. of cold water. The solid which separated was collected and washed on filter. It was then treated with 50 cc. of acetic anhydride and 4 g. of triethylamine and heated 10 minutes at steam bath temperature. The acetylated product separated on pouring this mixture into 400 cc. of cold water. It was collected on filter, washed with methyl alcohol and used without further purification.

Example 6

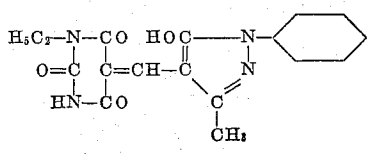


[1,3-di-p-phenetylbarbituric acid-(5)]-[3-methyl-1-phenyl-5-pyrazolone-(4)]-trimethine oxonol

3.45 g. (1 mol.) of 4-(3-acetanilidoallylidene)-3-methyl-1-phenyl-5-pyrazoline, 3.7 g. (1 mol.) of 1,3-di-p-phenetyl barbituric acid, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were refluxed for 15 minutes. Dye separated on acidification of the chilled reaction mixture. The crude washed dye was purified by dissolving as the triethylamine salt, filtering hot and precipitating on addition of acid to the filtrate. Two such treatments gave the dye as orange brown crystalline powder, M. P. 194–196° C., with decomposition. The reddish orange solution of the triethylamine salt was readily bleached by developer.

4-(3-acetanilidoallylidine)-3-methyl-1-phenyl-5-pyrazolone is described in Example 11 of Keyes U. S. Patent 2,216,441 and also Example 11 of Keyes U. S. Patent 2,186,608.

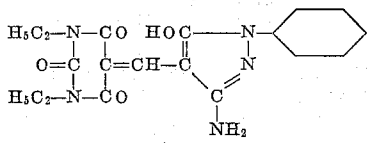
Example 7



[1-ethylbarbituric acid-(5)]-[3-methyl-1-phenyl-5-pyrazolone-(4)]-methineoxonol

3.2 g. (1 mol.) of 4-acetanilidomethylene-3-methyl-1-phenyl-5-pyrazolene, 1.6 g. (1 mol.) of 1-ethylbarbituric acid, 25 cc. of absolute ethyl alcohol and 2 g. (2 mol.) of triethylamine were refluxed together for 45 minutes. Dye separated on acidification of the chilled reaction mixture. Crude, washed dye was purified by dissolving as the triethylamine salt, filtering hot and precipitating on acidification of the chilled filtrate. Two such treatments gave the dye as yellow crystals, M. P. 234–236° C. with decomposition. The yellow solution of the triethylamine salt was readily bleached by developer.

Example 8

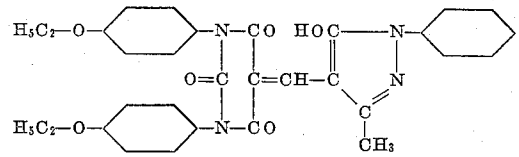


[3-amino-1-phenyl-5-pyrazolone-(4)]-[1,3-diethylbarbituric acid-(5)]-methineoxonol

3.3 g. (1 mol.) of 5-acetanilidomethylene-1,3-diethylbarbituric acid, 1.75 g. (1 mol.) of 3-amino-1-phenyl-5-pyrazolone, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were refluxed together for ten minutes. Dye separated on acidification of the chilled reaction mixture. The crude, washed dye was purified by dissolving in alcohol as the triethylamine salt, filtering hot and precipitating on acidification of the chilled filtrate. Two such treatments gave the dye as a yellowish buff powder, M. P. 165–168° C. with decomposition. The 5-acetanilidomethylene-1,3-diethylbarbituric acid used in the above example was prepared by heating under reflux for about 5 minutes 23.2 g. (1 mol.) of 5-anilinomethylene-1,3-diethylbarbituric acid, 40 cc. of acetic anhydride and 8.1 g. (1 mol.) of triethylamine. The crude product was twice recrystallized from methyl alcohol and obtained as colorless needles melting at 121–123° C.

The 5-anilinomethylene-1,3-diethylbarbituric acid was prepared according to the method of Dains, Kansas Univ. Science Bull. 15, 265 (1924), by heating together equimolecular portions of 1,3-diethylbarbituric acid and diphenylformamidine in kerosene at about 130–140° C. for a 2-hour period. The reaction product separated and was washed with methyl alcohol.

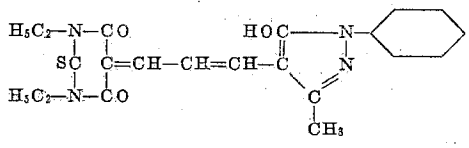
Example 9



[1,3-di-p-phenetylbarbituric acid-(5)]-[3-methyl-1-phenyl-5-pyrazolone-(4)]-methineoxonol

3.2 g. (1 mol.) of 4-acetanilidomethylene-3-methyl-1-phenyl-5-pyrazolone, 3.7 g. (1 mol.) of 1,3-di-p-phenetylbarbituric acid, 20 cc. of absolute ethyl alcohol and 1 g. (1 mol.) of triethylamine were refluxed together for 45 minutes. Dye separated on acidification of the chilled reaction mixture. The crude, washed dye was purified by dissolving in alcohol as the triethylamine salt, filtering hot and precipitating on acidification of the chilled filtrate. Two such treatments gave the dye as yellow crystals, M. P. 255–257° C. with decomposition.

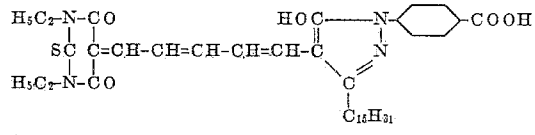
Example 10



[1,3-diethyl-2-thiobarbituric acid-(5)]-[3-methyl-1-phenyl-5-pyrazolone-(4)]-trimethineoxonol

3.45 g. (1 mol.) of 4-(3-acetanilidoallylidene)-3-methyl-1-phenyl-5-pyrazolone, 2 g. (1 mol.) of 1,3-diethyl-2-thiobarbituric acid, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were heated together under reflux for 15 minutes. Dye separated from the chilled reaction mixture on treatment with dilute hydrochloric acid. Crude washed dye was purified by dissolving as the triethylamine salt in alcohol, filtering hot and precipitating from the chilled filtrate on acidification. Two such treatments gave the dye as dull brownish powder, M. P. 165–167° C., with decomposition.

Example 11

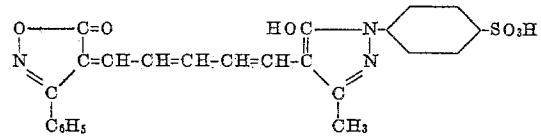


[1-p-carboxyphenyl-3-pentadecyl-5-pyrazolone-(4)]-[1,3-diethyl-2-thiobarbituric acid (5)]-pentamethineoxonol

4 g. (1 mol.) of 5-(5-acetanilido-2,4-pentadienylidene)-1,3-diethyl-2-thiobarbituric acid, 4.1 g. (1 mol.) of 1-p-carboxyphenyl-3-pentadecyl-5-pyrazolone, 20 cc. of pyridine and 2 g. (2 mol.) of triethylamine heated together at steam bath temperature for a period of about ten minutes. Dye separated from the reaction mixture on treatment with excess of dilute hydrochloric acid and chilling. The crude washed dye was dissolved in alcohol as the triethylamine salt and precipitated from the chilled filtrate on acidification. Two such treatments gave the dye as dark crystals, M. P. 184–187° C., with decomposition.

The 1-p-carboxyphenyl-3-pentadecyl-5-pyrazolone employed above was made as follows: 44 g. (1 mol.) of ethyl palmityl acetate, 20 g. (1 mol.) of p-hydrazinobenzoic acid and 200 cc. of glacial acetic acid were refluxed together for 90 minutes. The product separated on chilling and was collected, washed or filtered and dried. It was obtained as cream colored crystals, M. P. 165–169° C.

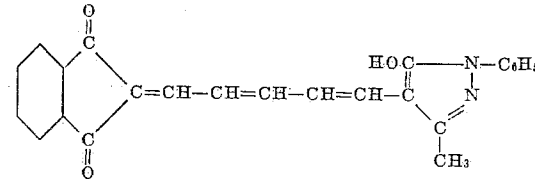
Example 12



[3-methyl-1-p-sulfophenyl-5-pyrazolone-(4)]-[3-phenyl-5(4)-isoxazolone (4)] pentamethineoxonol

3.6 g. (1 mol.) of 4-(5-acetanilido-2,4-pentadienylidine)-3-phenyl-5(4)isoxazolone, 2.55 g. (1 mol.) of 3-methyl-1-p-sulfophenyl-5-pyrazolone, 30 cc. of pyridine and 2 g. (2 mol.) of triethylamine were mixed together and heated at steam bath temperature for 15 minutes. Dye separated from the reaction mixture on chilling and acidification with dilute hydrochloric acid. The crude washed dye was purified in the usual manner and obtained as lustrous greenish crystals, M. P. 188–190° C. with decomposition. The 4-(5-acetanilido-2,4-pentadienylidene)-3-phenyl-5(4)-isoxazolone employed was made by refluxing together for about 3 minutes a mixture of 8 g. (1 mol.) of 3-phenyl-5(4)-isoxazolone, 14.2 g. (1 mol.) of glutaconic aldehyde dianilide hydrochloric, 4.1 g. (1 mol.) of fused sodium acetate and 30 cc. of acetic anhydride. The product separated on chilling the reaction mixture. It was obtained in purity sufficient for use as a dye intermediate by washing with water and methyl alcohol.

Example 13



[1,3-indanedione-(2)] [3-methyl-1-phenyl-5-pyrazolone-(4)] pentamethineoxonol

3.4 g. (1 mol.) of 2-(5-acetanilido-2,4-pentadienylidine)-1,3-indandione, 1.75 g. (1 mol.) of 3-methyl-1-phenyl-5-pyrazolone, 20 cc. of pyridine and 1 g. (1 mol.) of triethylamine were heated together at steam bath temperature for 15 minutes. Dye separated from the chilled reaction mixture on treatment with excess of dilute hydrochloric acid. The crude washed dye was purified in the usual manner and obtained as dull coppery crystals, M. P. 169–171° C. with decomposition.

The 2-(5-acetanilido-2,4-pentadienylidine)-1,3-indandione employed was prepared by refluxing a mixture of 7.15 g. (1 mol.) of 1,3-indandione, 14.2 g. (1 mol.) of glutaconic aldehyde dianilide hydrochloride, 4.1 g. (1 mol.) of fluxed sodium acetate and 50 cc. of acetic anhydride for a period of 3 minutes. The product separated from the chilled reaction mixture. It was obtained in purity sufficient for use as dye intermediate by washing with water and methyl alcohol.

For the preparation of filter layers from 5 milligrams to 25 milligrams of dye are wet with 2 cc. of triethylamine or pyridine and dissolved in 10 to 20 cc. of methanol, acetone or other water-miscible solvent. The solution is added to 100 cc. of 3% to 6% aqueous gelatin solution at 40° C. After adjusting the pH to its optimum value, the dye-gel solution is coated on the support which may already have other photographic layers.

The preparation of filter layers may be illustrated by the following examples.

1. A 22 mg. portion of [1,3-diethyl-2-thiobarbituric acid-(5)] [3-methyl-1-p-sulphophenyl-5-pyrazolone-(4)] pentamethineoxonol is wet with 1 cc. of pyridine and dissolved in 10 cc. of methanol. This dye solution is added to 50 cc. of 10% aqueous gel containing 30 mg. of polyvinylpyridine paratoluene sulfonate. The volume is brought to 100 cc. (=5% gel). The pH is adjusted to 5.5. It is then ready for coating on the support.

2. A 30 mg. sample of [1,3-diethyl-2-thiobarbituric acid-(5)] [3-methyl-1-phenyl-5-pyrazolone-(4)] trimethineoxonol is wet with 1 cc. of pyridine and dissolved in 20 cc. of methanol. The dye solution is added to 50 cc. of 10% aqueous gel. The volume is brought to 100 cc. and the pH is adjusted to 5.5. It is then ready for coating on the support.

In the accompanying drawing, the various figures are enlarged sectional views of photographic elements having filter layers or 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 resinous material or opaque material such as paper is coated with an emulsion layer 11 and an overcoating layer 12 containing an unsymmetrical methine or polymethine oxonol dye according to our invention.

Fig. 2 illustrates a multi-layer photographic element for color photography in which the support 10 is coated with sensitive layers 13, 14 and 15 which record, respectively, the red, green and blue regions of the spectrum. Between the emulsion layers 14 and 15 there is a filter layer 16 containing a yellow methine or polymethine oxonol dye. This filter layer serves a purpose well known in color photography of preventing exposure of a lower layer of the element by light which the filter layer absorbs. The dye may also absorb light in other regions such as the ultraviolet region of the spectrum.

Fig. 3 represents a film having an anti-halation layer containing an oxonol dye according to our invention. As shown therein, the support 10 carries an emulsion layer 11 on one side and an anti-halation layer 18 containing an oxonol dye on the opposite side.

As stated above, the oxonol dyes are found to be useful in filter or anti-halation layers. The dyes in general are dissolved in water as the sodium, pyridinium or triethylamine salt, or in organic solvents such as alcohol or acetone and then dispersed in gelatin or other protein or synthetic vehicle such as polyvinyl alcohol.

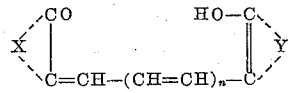
The dyes used according to our invention have a number of advantages. They may contain acidic groups such as carboxylic acid or sulfonic acid groups and may therefore be mordanted by addition of equivalent amounts of cations such as Pb^{++}, Ca^{++}, Ba^{++}, etc., or organic agents such as polyvinyl pyridine metho-p-toluene sulfonate and other high molecular weight quaternary salts. Since the dyes are unsymmetrical, they may contain only a single acid group and are frequently easier to mordant than dyes containing two or more acid groups.

A further advantage of the unsymmetrical dyes is that they permit the choice of a wider range of spectral absorptions and thus give a better chance of meeting specific requirements of absorption maxima and distribution of absorption properties. The dyes are bleached in the usual photographic processing solutions such as developing and fixing solutions.

It will be understood that the examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

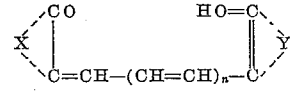
What we claim is:

1. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer and a light absorbing layer containing a dye having the formula:



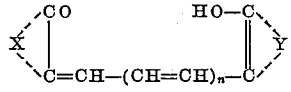
where X represents the atoms necessary to complete a nucleus of the class consisting of 1-ethylbarbituric acid, 1,3-diethyl-barbituric acid, 1,3-di-p-phenetyl-barbituric acid, 1,3-diethyl-2-thiobarbituric acid, 1,3-diphenyl-2-thiobarbituric acid, isoxazolone and indandione, Y represents the atoms necessary to complete a pyrazolone nucleus and n is a digit from 0 to 1.

2. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer and a light absorbing layer containinga dye having the formula:



where X represents the atoms necessary to complete a 1,3-diethyl-barbituric acid ring, Y represents the atoms necessary to complete a pyrazolone ring, and n is a digit from 0 to 1.

3. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer and a light absorbing layer containing a dye having the formula:



where X represents the atoms necessary to complete a 1,3-diethyl-2-thiobarbituric acid ring, Y represents the atoms necessary to complete a pyrazolone ring, and n is a digit from 0 to 1.

4. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer and a light-absorbing layer containing [1,3-diethyl-2-thiobarbituric acid-(5)] [3-methyl-1-phenyl-5-pyrazolone(4)] trimethineoxonol.

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