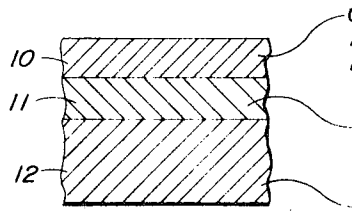
Sept. 23, 1969 J. BAILEY 3,468,883

OXONOL DYES FOR LIGHT FILTERING LAYERS IN PHOTOGRAPHIC ELEMENTS

Original Filed March 27, 1961

FIG. 1

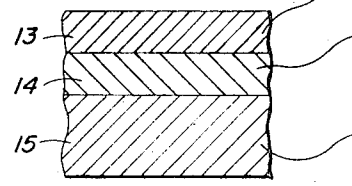


GELATIN CONTAINING BIS (1-CARBOXYMETHYL-HEXAHYDRO-3-n-OCTYL-2,4,6-TRIOXO-5-PYRIMIDINE) PENTAMETHINOXONOL

LIGHT SENSITIVE SILVER HALIDE EMULSION

SUPPORT

FIG. 2

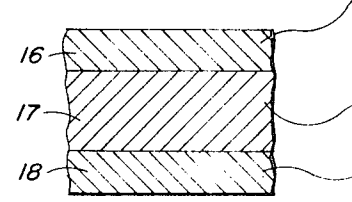


LIGHT SENSITIVE SILVER HALIDE EMULSION

GELATIN CONTAINING BIS (1-BUTYL-3-CARBOXYMETHYLHEXAHYDRO-2,4,6-TRIOXO-5-PYRIMIDINE) PENTAMETHINOXONOL

SUPPORT

FIG. 3



LIGHT SENSITIVE SILVER HALIDE EMULSION

SUPPORT

GELATIN CONTAINING BIS (1-BUTYL-3-CARBOXYMETHYLHEXAHYDRO-2,4,6-TRIOXO-5-PYRIMIDINE) PENTAMETHINONOXOL

JOSEPH BAILEY
INVENTOR.
BY
William E. Neely
ATTORNEYS

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3,468,883

OXONOL DYES FOR LIGHT FILTERING LAYERS IN PHOTOGRAPHIC ELEMENTS

Joseph Bailey, Harrow, England, assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Application June 25, 1965, Ser. No. 478,003, which is a division of application Ser. No. 98,709, Mar. 27, 1961, now Patent No. 3,247,127, dated Apr. 19, 1966. Divided and this application Aug. 25, 1966, Ser. No. 575,000
Int. Cl. C09b *23/12, 23/08;* G03c *1/14*
U.S. Cl. 260—240.2 9 Claims

ABSTRACT OF THE DISCLOSURE

Certain novel symmetrical oxonol dyes having a carboxyalkyl group have been found to possess desirable properties as light-screening materials for photographic elements and can be incorporated in light-screening layers, including light-sensitive emusion layers. The dyes, for example, absorb light of a wave-length desired to be absorbed and are readily removed. Bis(1-carboxymethylhexahydro - 3 - n - octyl - 2,4,6 - trioxo - 5 - pyrimidine)pentamethinoxonol and bis(1 - n - butyl - 3-carboxymethylhexahydro - 2,4,6 - trioxo - 5 - pyrimidine) pentamethinoxonol are illustrative of the new oxonol dyes.

This application is a division of copending U.S. patent application Ser. No. 478,003, filed June 25, 1965, which is a division of U.S. patent application Ser. No. 98,709, filed Mar. 27, 1961, now U.S. Patent 3,247,127, granted Apr. 19, 1966, and which was copending with application Serial No. 98,709.

This invention relates to new dyes and more particularly to photographic elements containing these dyes in light-screening layers.

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 for protecting an overlying light-sensitive emulsion or emulsions from the action of light of wavelengths 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., ultraviolet 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 sensitive 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 where the element contains a color sensitized emulsion or color sensitized emulsions, it is particularly desirable to employ light-screening susbtances 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 storing 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, such as a photographic developing bath or fixing bath. The decoloration or destruction of the light-screening dye will hereinafter be referred to as bleaching.

Numerous substances have been employed as light-screening materials for the purposes indicated above. Among the dyes used are the oxonol dyes. Oxonol dyes known in the past have not absorbed light of the wavelength desired. Previously known oxonol dye-mordant combinations, however, which are sufficiently nonwandering to use in layers in contact with emulsion layers, are bleached only with difficulty or not at all during normal processing of the film. Those known combinations which bleach more easily are not sufficiently nonwandering so the dye migrates to the emulsion layers with a consequent deleterious effect upon the sensitometric properties of the film. In some instances where the light-screening dye has been mordanted to make it sufficiently nonwandering, the dye does not bleach satisfactorily in the processing baths and it has been necessary to remove the light-screening layer itself from the photographic element to eliminate the unwanted residual dye.

It is therefore an object of my invention to provide a new class of symmetrical oxonol dyes which have their maximum absorption of light at the wavelength desired.

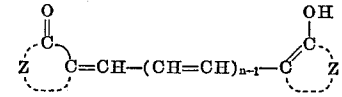
Another object is to provide new symmetrical acid oxonol dyes which are readily mordanted in light-screening layers so that they will not diffuse into adjacent emulsion layers and dyes which are readily bleached by conventional processing solutions without removing the light-screening layer containing them.

Another object is to provide a new class of light-screening filter layers which are valuable for use in photographic elements as interlayers between two sensitive silver halide emulsion layers, between the support and a sensitive silver halide emulsion layer, as a layer over a sensitive silver halide layer or as an antihalation layer behind the support.

Another object is to provide a method for preparing new symmetrical oxonol dyes.

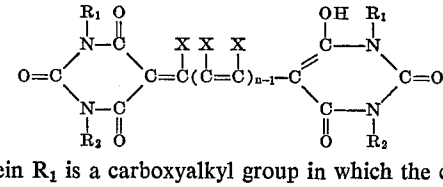
Still other objects will become apparent from the following specification and claims.

I have found that the above objects are accomplished by using symmetrical oxonol dyes represented by the following formula:



wherein Z represents the nommetallic atoms necessary to complete a 1-carboxyalkyl-3-hydrocarbon substituted hexahydro-2,4,6-trioxo-5-pyrimidine nucleus and *n* is an integer of from 1 to 3.

Particularly advantageous dyes of my invention may be represented by the following formula:



wherein R_1 is a carboxyalkyl group in which the carboxy

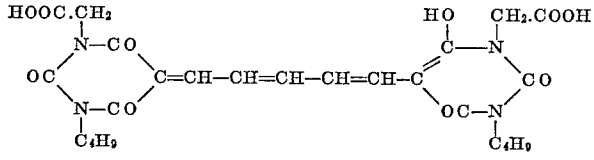
substituent is attached to an alkyl group having from 1 to 2 carbon atoms such as methyl and ethyl; R_2 is a member selected from the class consisting of an alkyl group having from 1 to 8 carbon atoms, such as methyl, benzyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, hexyl, octyl, cyclohexyl, etc., an aryl group, such as phenyl, 2-methylphenyl, 2-methoxyphenyl, 2,4-dimethylphenyl, etc.; *n* is an integer of from 1 to 3; X is a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms such as methyl, ethyl, propyl, butyl, etc., such that not more than one X is an alkyl group.

My dyes are valuable for use in photographic light-sensitive materials employing one or more sensitive silver halide layers. The dyes can be used to make light-screening layers including antihalation layers with or without dyes of other classes and can be incorporated readily in colloidal binders used for forming such layers. They are especially useful in gelatin layers lying adjacent to silver halide layers, since the dyes can be mordanted with organic polymeric substances to form excellent nonwandering characteristics in gelatin while the dyes can be readily bleached without the need for removing the layers containing them. Bleaching of the dyes occurs when the layer is treated with alkaline solutions containing sodium sulfite such as photographic developing solutions.

My dyes can be mordanted in layers coated in contact with light-sensitive silver halide emulsion layers since the dyes have very good stability at the pH of most sensitive silver halide emulsions (about 6.3) and have little or no undesirable effect on the silver halide. Consequently, the dyes may be used as light-screening dyes in layers coated directly on top of sensitive silver halide emulsion layers or between two sensitive silver halide emulsion layers or between the support and a sensitive silver halide emulsion layer or on the back of the support as an antihalation layer.

Representative dyes of my invention and their preparation are illustrated by the following examples which are not intended to limit my invention.

Example 1.—Bis(1-n-butyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol

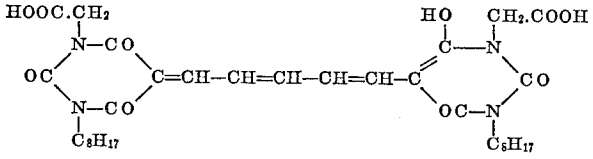


1-n-butyl-3-carboxymethylbarbituric acid (3.6 grams), glutaconic aldehyde dianilide hydrochloride (2.13 grams), ethanol (30 ccs.) and triethylamine (8.4 ccs.) were heated on the steam bath for 20 minutes. The dye solution was chilled and acidified with concentrated hydrochloric acid (12 ccs.) and the solution was poured into water (750 ccs.). The precipitated dye was collected, washed with water and dried. The product which weighed 3 grams (73%) melted at 88° C.

The dye in water had an absorption maximum at 590 mμ.

Analysis for $C_{25}H_{30}N_4O_{10}$.—Calc'd.: C, 55.0%; H, 5.5%; N, 10.2%. Found: C, 55.3%; H, 6.2%; N, 10.05%.

Example 2.—Bis(1-carboxymethylhexahydro-3-n-octyl-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol

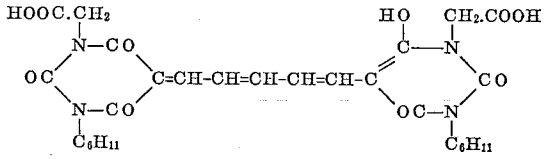


1-carboxymethyl-3-n-octylbarbituric acid (17.9 grams), glutaconic aldehyde dianilide hydrochloride (8.5 grams), ethanol (120 ccs.) and triethylamine (33.6 ccs.) were heated under reflux for twenty minutes. The reaction mixture was chilled and treated with concentrated hydrochloric acid (48 ccs.) and the solution was poured into water (3 liters). The dye was collected, washed with water and dried. It weighed 18 grams (91%) and melted at 131° C.

The dye in ethanol had an absorption maximum at 592 mμ.

Analysis for $C_{33}H_{46}N_4O_{10}$.—Calc'd.: C, 59.7%; H, 6.9%; N, 8.4%. Found: C, 59.8%; H, 7.1%; N, 8.7%.

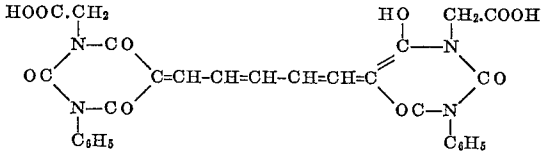
Example 3.—Bis(1-carboxymethyl-3-cyclohexylhexahydro-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol



Prepared similarly to Example 1 using a proportional amount of 1-carboxymethyl-3-cyclohexylbarbituric acid instead of 1-n-butyl-3-carboxymethylbarbituric acid. The dye was obtained in 80% yield, it melted at 120° and had an absorption maximum in ethanol at 592 mμ.

Analysis for $C_{29}H_{34}N_4O_{10}$.—Calc'd.: N, 9.4%. Found: N, 9.2%.

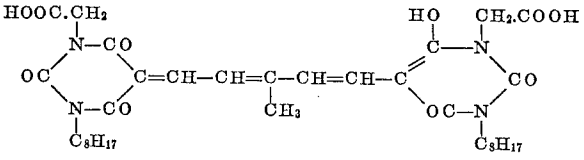
Example 4.—Bis(1-carboxymethylhexahydro-3-phenyl-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol



This dye was prepared similarly to Example 1 using a proportional amount of 1-carboxymethyl-3-phenylbarbituric acid instead of 1-n-butyl-3-carboxymethylbarbituric acid. The dye was obtained in 63% yield, it melted at 175° and had an absorption maximum in ethanol at 591 mμ.

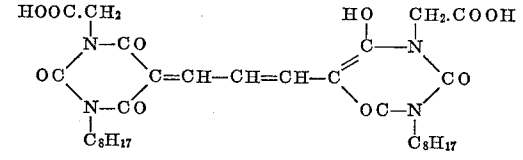
Analysis for $C_{29}H_{22}N_4O_{10}$.—Calcd.: C, 59.4%; H, 5.8%; N, 9.6%. Found: C, 59.0%; H, 5.5%; N, 9.45%.

Example 5.—Bis(1-carboxymethylhexahydro-3-n-octyl-2,4,6-trioxo-5-pyrimidine)-3-methylpentamethinoxonol



This dye was prepared similarly to Example 2 using 1-anilino-5-anilo-3-methyl-1,3-pentadiene HBr in place of glutaconicaldehyde dianilide HCl. The dye was obtained in 86% yield, it had an absorption maximum in ethanol at 614 mμ.

Example 6.—Bis(1-carboxymethylhexahydro-3-n-octyl-2,4,6-trioxo-5-pyrimidine)trimethinoxonol

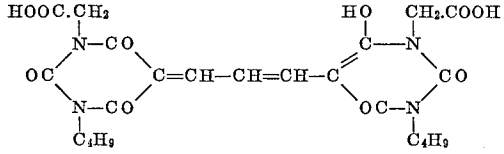


1-carboxymethyl-3-n-octylbarbituric acid (1.5 gram), β-ethoxyacroleinacetal (0.9 gram), pyridine (2.5 ccs.) and triethylamine (1.4 ccs.) were heated under reflux for 5 minutes. The reaction mixture was chilled, poured into water (100 ccs.) and acidified with concentrated HCl when the product separated as an oil which solidified on

chilling. The dye was collected by filtration and recrystallized from methanol. It weighed 0.8 gram (50%), melted at 219° and had an absorption maximum in methanol at 492 mμ.

Analysis for $C_{31}H_{44}N_4O_{10}$.—Calcd.: C, 58.9%; H, 7.0%; N, 8.9%. Found: C, 60.0%; H, 7.15%; N, 9.5%.

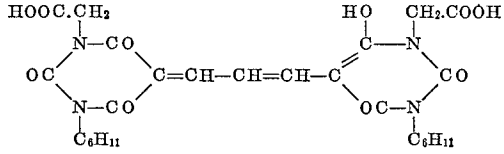
Example 7.—Bis(1-n-butyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)trimethinoxonol



Prepared similarly to Example 6 using a proportional amount of 1-n-butyl-3-carboxymethylbarbituric acid in place of 1-carboxymethyl-3-n-octylbarbituric acid. The dye was obtained in 60% yield melted at 66° and had an absorption maximum in ethanol at 493 mμ.

Analysis for $C_{23}H_{28}N_4O_{10}$, H_2O.—Calcd.: C, 51.3%; H, 5.6%; N, 10.4%. Found: C, 51.0%; H, 5.9%; N, 10.1%.

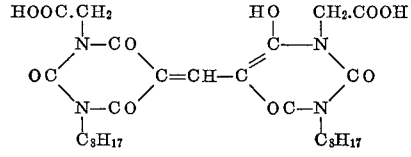
Example 8.—Bis(1-carboxymethyl-3-cyclohexylhexahydro-2,4,6-trioxo-5-pyrimidine)trimethinoxonol



Prepared similarly to Example 6 using a proportional amount of 1-carboxymethyl-3-cyclohexylbarbituric acid in place of 1-carboxymethyl-3-n-octylbarbituric acid. The dye was obtained in 63% yield, melted at 170° and had an absorption maximum in ethanol at 494 mμ.

Analysis for $C_{27}H_{32}N_4O_{10}$.—Calc'd.: N, 9.8%. Found: N, 9.9%.

Example 9.—Bis(1-carboxymethylhexahydro-3-n-octyl-2,4,6-trioxo-5-pyrimidine)methinoxonol



1-carboxymethyl-3-n-octylbarbituric acid (6 g.), ethyl orthoformate (3 ccs.), pyridine (15 ccs.) were heated under reflux for 30 minutes. The reaction mixture was cooled, diluted with water (100 ccs.), acidified with concentrated hydrochloric acid, cooled and the product collected by filtration. It was dried and recrystallized from ethyl acetate. The dye weighed 2.5 g. (41%), melted at 173° C. and had an absorption maximum in methanol at 415 mμ.

Analysis for $C_{29}H_{42}N_4O_{10}$.—Calcd.: C, 57.5%; H, 6.9%; N, 9.2%. Found: C, 58.0%; H, 7.3%; N, 9.4%.

The following are further examples of compounds according to the present invention.

Example 10.—Bis(1-tertiarybutyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol

Example 11.—Bis(1-carboxymethyl-3-n-hexylhexahydro-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol

Example 12.—Bis(1-benzyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol

Example 13.—Bis(1-carboxymethylhexahydro-3-o-methoxyphenyl-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol

Example 14.—Bis(1-tertiarybutyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)trimethinoxonol

Example 15.—Bis(1-carboxymethyl-3-n-hexylhexahydro-2,4,6-trioxo-5-pyrimidine)trimethinoxonol

Example 16.—Bis(1-benzyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)trimethinoxonol

Example 17.—Bis(1-carboxymethylhexahydro-3-o-methoxyphenyl-2,4,6-trioxo-5-pyrimidine)trimethinoxonol

Example 18.—Bis(1-n-butyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)methinoxonol

Example 19.—Bis(1-tertiarybutyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)methinoxonol

The intermediates used in preparing my dyes were synthesized according to the following procedures which are typical and will illustrate the methods used to prepare intermediates for other dyes of my invention.

N-ethoxycarbonylmethyl-N'-n-octylurea:

$$C_2H_5OOC.CH_2.NH.CO.NH.C_8H_{17}$$

Ethoxycarbonylmethyl isocyanate (Ann. 1948, 562, 76) (17.5 grams) in benzene (25 ccs.) was treated with n-octylamine (17.5 grams) in benzene (25 ccs.). There was a temperature rise on mixing and the solution was maintained at room temperature overnight. The solvent was distilled off and the product solidified on cooling. It weighed 33.5 grams (96%) M.P. 57° C.

Analysis for $C_{13}H_{26}N_2O_3$. — Calcd.: C, 60.4%; H, 10.1%; N, 10.8%. Found: C, 59.8%; H, 10.1%; N, 10.8%.

N-n-butyl-N'-ethoxycarbonylmethylurea:

$$C_2H_5OOC.CH_2.NH—CO.NH.C_4H_9$$

It was obtained in the same way as the above compound using a proportional amount of n-butylamine in place of n-octylamine. It (95% yield) was obtained as very low melting colourless needles.

Analysis for $C_9H_{18}N_2O_3$.—Calcd.: N, 13.9%. Found: N, 13.3%.

N-ethoxycarbonylmethyl-N'-phenylurea:

$$C_2H_5OOC.CH_2.NH.CO.NH.C_6H_5$$

It was obtained similarly to the above using a proportional amount of aniline in place of n-octylamine. It (72% yield) was obtained as colourless needles M.P. 108–109° C.

N-cyclohexyl-N'-ethoxycarbonylurea:

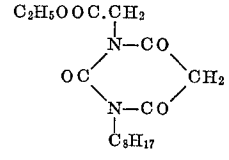
$$C_2H_5OOC.CH_2.NH.CO.NH.C_6H_{11}$$

It was obtained similarly to the above using a proportional amount of cyclohexylamine in place of n-octylamine. It (70% yield) was obtained as long colourless needles M.P. 121–122°.

Other intermediates according to the invention include:

N-tertiarybutyl-N'-ethoxycarbonylmethylurea
N-ethoxycarbonylmethyl-N'-n-hexylurea
N-benzyl-N'-ethoxycarbonylmethylurea
N-ethoxycarbonylmethyl-N'-o-methoxyphenylurea

1-ethoxycarbonylmethyl-3-n-octylbarbituric acid:

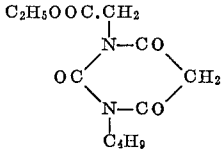


N-ethoxycarbonylmethyl-N'-n-octylurea (25.8 grams), malonic acid (11.5 grams), acetic anhydride (50 ccs.) and acetic acid (50 ccs.) were heated on a steam bath for three hours. The excess solvent was distilled off in vacuo and the residual oil was distilled in vacuo.

The product was obtained as a pale yellow viscous oil. It weighed 22.6 grams (69%) B.P. 204°–210°/0.08 mms.

Analysis for $C_{16}H_{26}O_5N_2$.—Calcd.: C, 58.9%, H, 8.0%, N, 8.6%. Found: 57.5%, H, 8.1%, N, 8.35%.

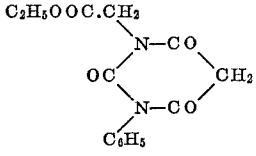
1-n-butyl-3-ethoxycarbonylmethylbarbituric acid:



Prepared similarly to the above intermediate. It was obtained in 52% yield as a colourless viscous oil B.P. 161°–163°/0.2 mms.

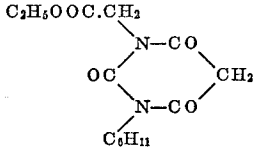
Analysis for $C_{12}H_{18}N_2O_5$.—Calcd.: C, 53.3%, H, 6.7%, N, 10.3%. Found: 55.1%, H, 7.1%, N, 10.2%.

1-ethoxycarbonylmethyl-3-phenylbarbituric acid:



Prepared similarly to the above intermediate. It was obtained in 63% yield as a pale yellow viscous oil B.P. 216–218°/0.5 mms.

1-cyclohexyl-3-ethoxycarbonylmethylbarbituric acid:

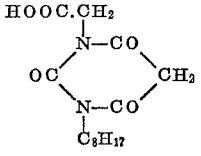


Prepared similarly to the above intermediate. It was obtained in 83% yield as a pale yellow viscous oil B.P. 178–180/0.2 mms.

Other intermediates according to the invention include:

1-tertiarybutyl-3-ethoxycarbonylmethylbarbituric acid
1-ethoxycarbonylmethyl-3-n-hexylbarbituric acid
1-benzyl-3-ethoxycarbonylmethylbarbituric acid
1-ethoxycarbonylmethyl-3-o-methoxyphenylbarbituric acid

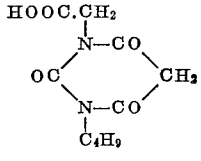
1-carboxymethyl-3-n-octylbarbituric acid:



1 - ethoxycarbonylmethyl - 3-octylbarbituric acid (16 grams) was treated with aqueous sodium hydroxide (10 ccs., 40%) in water (40 ccs.). The solution was heated on the steam bath for 4 hours. Then the reaction mixture was chilled and acidified with concentrated hydrochloric acid. The separated oil was extracted with benzene. The benzene solution was concentrated and solid product was obtained by warming the residual gum with petroleum ether (B.P. 40°–60°). The product was collected and recrystallized from petroleum ether (B.P. 80°–100° C.) as colourless shiny plates. The product weighed 9 grams (62%) and melted at 117.5°–118.5° C.

Analysis for $C_{14}H_{22}O_5N_2$.—Calcd.: C, 56.4%, H, 7.4%, N, 9.4%. Found: C, 56.3%, H, 7.6%, N, 9.2%.

1-n-butyl-3-carboxymethylbarbituric acid:



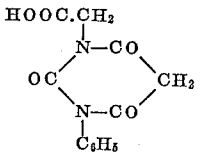
To a solution of potassium hydroxide (6.65 grams) in methanol (75 ccs.) was added 1-n-butyl-3-ethoxycarbonylmethylbarbituric acid (13.5 grams). The mixture was maintained overnight at room temperature when the solid potassium salt of the product precipitated. It was collected by filtration and washed with methanol. It was dissolved in water and the solution acidified with hydrochloric acid. The separated oil was extracted with benzene. The benzene solution was concentrated and the residual oil purified by dissolution in ethyl acetate and treating the solution by the dropwise addition of petroleum ether (B.P. 60°–80°) until the product began to precipitate. After chilling, the colourless crystals were collected. The product weighed 4 grams (33%) and melted at 73°–75° C.

Analysis for $C_{10}H_{14}O_5N_2$.—Calcd.: C, 49.6%; H, 5.8%; N, 11.6%. Found: C, 50.0%; H, 6.0%; N, 11.35%.

Note.—If the potassium salt did not separate from the reaction mixture the following procedure was adopted:

The methanol solution of the reactants after standing overnight was concentrated and the residual solid potassium salt was dissolved in water and the solution acidified with hydrochloric acid. The separated oil was extracted with benzene. The benzene extract was washed twice with small amounts of water, separated and filtered. The benzene was distilled off in vacuo leaving the product as a viscous gum. It may be used in the dye synthesis without further purification. The yield by this procedure was 87%.

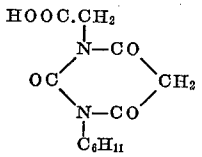
1-carboxymethyl-3-phenylbarbituric acid:



Prepared in a similar way to 1-n-butyl-3-carboxymethylbarbituric acid. It was obtained in 43% yield as colourless crystals M.P. 100°.

Analysis for $C_{12}H_{10}N_2O_5$.—Calcd.: C, 55.0%; H, 3.8%; N, 10.7%. Found: C, 54.3%; H, 4.5%; N, 10.6%.

1-carboxymethyl-3-cyclohexylbarbituric acid:



Hydrolysis was carried out in the same way as for 1-carboxymethyl-3-n-octylbarbituric acid. The product from acidification, however, was solid. It was collected by filtration and suspended in benzene, refiltered and washed with benzene and dried. It was obtained in 51% yield as colourless crystals M.P. 135°.

Analysis for $C_{12}H_{16}N_2O_5$.—Calcd.: C, 53.7%; H, 6.0%; N, 10.4%. Found: C, 53.6%; H, 5.85%; N, 10.7%.

Other intermediates according to the invention include:

1-tertiarybutyl-3-carboxymethylbarbituric acid
1-carboxymethyl-3-n-hexylbarbituric acid
1-benzyl-3-carboxymethylbarbituric acid
1-carboxymethyl-3-o-methoxyphenylbarbituric acid

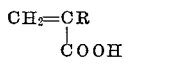
The light-screening layers of my invention are prepared by coating on the photographic element or on its support by methods well known in the art, a water solution of the dye, a hydrophilic colloid binder and a coating aid such as saponin. In addition to these materials it is advantageous to add a basic mordant to this solution to render the acid dye nonwandering. For most purposes it is desirable to add agents to harden the colloidal binder material so that the light-screening layer will remain intact in the photographic element during and follow-

ing the processing operation. The pH of the coating solution is adjusted when necessary to a level that is compatible with the light-sensitive emulsion layer by the usual methods.

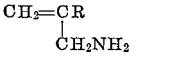
The proportions of dye, colloidal binder, mordant, hardener, coating aid used in making my light-screening layers may be varied over wide ranges and will depend upon the specific requirements of the photographic element being produced. The methods used to determine the optimum composition are well known in the art and need not be described here.

The light-sensitive layer or layers and the light-screening layer or layers of the photographic element may be coated on any suitable support material used in photography such as cellulose nitrate, cellulose acetate, synthetic resin, paper, etc.

Hydrophilic colloidal materials used as binders include collodion, gum arabic, cellulose ester derivatives such as alkyl esters of carboxylated cellulose, hydroxy ethyl cellulose, carboxy methyl hydroxy ethyl cellulose, synthetic resins, such as the amphoteric copolymers described by Clavier et al. in U.S. Patent 2,949,442, issued Aug. 16, 1960, polyvinyl alcohol, and others well known in the art. The above-mentioned amphoteric copolymers are made by polymerizing the monomer having the formula:



wherein R represents an atom of hydrogen or a methyl group, and a salt of a compound having the general formula:



wherein R has the above-mentioned meaning, such as an allylamine salt. These monomers can further be polymerized with a third unsaturated monomer in an amount of 0 to 20% of the total monomer used, such as an ethylene monomer that is copolymerizable with the two principal monomers. The third monomer may contain neither a basic group nor an acid group and may, for example, be vinyl acetate, vinyl chloride, acrylonitrile, methacrylonitrile, styrene, acrylates, methacrylates, acrylamide, methacrylamide, etc. Examples of these polymeric gelatin substitutes are copolymers of allylamine and methacrylic acid; copolymers of allylamine, acrylic acid and acrylamide; hydrolyzed copolymers of allylamine, methacrylic acid and vinyl acetate; copolymers of allylamine, acrylic acid and styrene; the copolymer of allylamine, methacrylic acid and acrylonitrile; etc.

My dyes are generally added to the water-permeable colloidal binder in water solution. In some instances it may be advantageous to form an alkali metal salt of the dye by dissolving the dye in a dilute aqueous alkali metal carbonate solution, for example. Usually a coating aid, such as saponin, is added to the dyed colloidal suspension before coating it as a layer on the photographic element. The dyes are advantageously mordanted with a suitable basic mordant added to the colloidal suspension before coating.

Basic mordants that may be used include the basic mordants described by Minsk in U.S. 2,882,156, issued Apr. 14, 1959, prepared by condensing a polyvinyl-oxo-compound such as polyacrolein, a poly-γ-methylacrolein, a polyvinyl alkyl ketone, such as polyvinyl methyl ketone, polyvinyl ethyl ketone, polyvinyl propyl ketone, polyvinyl butyl ketone, etc., or certain copolymers containing acrolein, methacrolein, or said vinyl alkyl ketone components, for example, 1 to 1 molar ratio copolymers of these components with styrene or alkyl methacrylates wherein the alkyl group contains from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, or butyl methacrylates in the proportions from about .25 to 5 parts by weight of the said polymeric oxo-compound with one part by weight of an aminoguanidine compound such as aminoguanidine bicarbonate, aminoguanidine acetate, aminoguanidine butyrate, etc.; the reaction products of polyvinyl-sulfonates with C-aminopyridines of Reynolds et al., U.S. 2,768,078, issued Oct. 23, 1956, prepared by reacting alkyl and aryl polyvinyl sulfonates prepared as described in our Patents U.S. 2,531,468 and U.S. 2,531,469 both dated Nov. 28, 1950, under controlled conditions with C-aminopyridines or alkyl group substituted C-aminopyridines such as 2-aminopyridine, 4-aminopyridine, the aminopicolines such as 2 - amino - 3 - methylpyridine, 2-amino - 4 - methylpyridine, 2 - amino - 5 - methylpyridine, 2 - amino - 6 - methylpyridine and corresponding 4-aminoethyl derivatives which react in this reaction in exactly the same way, 2 - amino - 6 - ethylpyridine, 2-amino - 6 - butylpyridine, 2 - amino - 6 - amylpyridine, etc., the various aminolutidines such as, for example, 4-amino-2,6-dimethylpyridine and the various aminocollidines such as, for example, 2-amino-3-ethyl-4-methylpyridine, etc.; the dialkylaminoalkyl esters or dialkylaminoalkylamino amides, e.g., such as those described by Carroll et al., U.S. Patent 2,675,316, issued Apr. 13, 1954, prepared by reacting addition polymers containing carboxyl groups with a basic dialkylamino compound, for example, N-dialkyl amine ethyl esters of polymers or copolymers containing carboxyl groups; the addition type polymers containing periodically occurring quaternary groups of Sprague et al., U.S. 2,548,564, issued Apr. 10, 1951, including quaternary ammonium salts of vinyl substituted azines such as vinylpyridine and its homologs such as vinylquinoline, vinylacridine, and vinyl derivatives of other six-membered heterocyclic ring compounds containing hydrogen atoms. These addition polymers include 2-vinylpyridine polymer metho - p - toluenesulfonate, 4-vinylpyridine polymer metho-p-toluenesulfonate.

Hardening materials that may be used to advantage include such hardening agents as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White, U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo (2,2,2)-7-octene-2,3,5,6-tetra-carboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll, U.S. Patents 2,725,294 and 2,725,295, both issued Nov. 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers, U.S. Patent 2,725,305, issued Nov. 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di(methanesulfonoxy)-ethane as described in Allen and Laakso, U.S. Patent 2,726,162, issued Dec. 6, 1955; 1,3-dihydroxymethyl-benzimidazol-2-one as described in July, Knott and Pollak, U.S. Patent 2,732,316, issued Jan. 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness, U.S. patent application Ser. No. 556,031, filed Dec. 29, 1955; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. Patent 2,950,197, issued Aug. 23, 1960; or 2,3-dihydroxydioxane as described in Jeffreys, U.S. Patent 2,870,013, issued Jan. 20, 1959.

The photographic element utilizing my light-screening layers have light-sensitive emulsion layers containing silver chloride, silver bromide, silver chlorobromide, silver iodide, silver bromoiodide, silver chlorobromoiodide, etc., as the light-sensitive material. Any light-sensitive silver halide emulsion layers may be used in these photographic elements. The silver halide emulsion may be sensitized by any of the sensitizers commonly used to produce the desired sensitometric characteristics.

My invention is further illustrated by the following examples describing the preparation of photographic elements containing my light-screening layers.

Example 20

An aqueous solution was made up which contained 4.54 g. of gelatin, .91 g. of poly(α-methyl allyl-N-guanidylketimine), .153 g. of saponin, and .302 g. of bis(1-butyl - 3 - carboxymethylhexahydro - 2,4,6 - trioxo - 5-pyridine) pentamethinoxonol to a total weight of 150 g. at a pH of 6.1. This solution was coated on clear cellulose acetate film support at 4.6 g. per sq. ft. The resulting coating was overcoated with a fine-grained silver chlorobromide emulsion with panchromatic sensitization at a silver coverage at 257 milligrams of silver per sq. ft. A control was coated on clear support. These film samples were exposed in an intensity scale sensitometer, then developed for 6 minutes in a developer having the composition:

	G.
p-Methylaminophenol sulfate	2.2
Sodium sulfite (desiccated)	72.0
Hydroquinone	8.8
Sodium carbonate (anhydrous)	48.0
Potassium bromide	4.0

Water to 1 liter.

fixed for 10 minutes in a fixing bath having the formula:

Sodium thiosulfate	g.	240.0
Sodium sulfite (desiccated)	g.	15.0
Acetic acid, 28%	cc.	48.0
Boric acid crystals	g.	7.5
Potassium alum	g.	150.0

Water to 1 liter.

washed and dried.

The following table gives the halation latitude determined for these film samples as the increase over normal required in log E exposure to give a halation density of 0.1 in the center of a 0.008 inch wide unexposed line.

	Halation Latitude			
	Clear	Blue	Green	Red
Control	.78	.51	.71	.53
Film sample provided with light-screening layer	1.67	.86	1.74	2.36

It can be seen that a very marked improvement resulted in the halation protection in the spectral region in which the dye absorbed light. For panchromatic halation protection a combination of my dye with another dye would be preferable to give the complete protection desired. On processing, no residual dye stain from the mordant-dye undercoat remained.

Example 21

0.5 gram of the dye of Example 2 was dissolved in 1% aqueous sodium carbonate and added to a 5% gelatin solution containing 0.5 gram polyvinylpyridinium metho-p-toluenesulfonate. The pH of the solution was adjusted to 6.5. This dyed gelatin solution was then coated on top of a sensitive silver halide emulsion of the kind used for X-ray photography at the rate of 25.5 mgs. of dye per square foot. Two such coated materials were made from exactly the same emulsion and dyed gelatin solution and measurements made on the products are shown below as A and B, along with the measurements on the same product but omitting the dye from the gelatin.

The three products were exposed, developed in the developer of Example 17 for 4 minutes and fixed in a hypo solution of Example 17 in the usual way and washed. The dyed layers were completely bleached by this treatment. In the following table, the column headed Safety Factor, are relative measurements of the inverse of the effective sensitivity of the material when exposed to the red component of light transmitted by a Wratten 6B Darkroom Safelight, which contains an amber coloured filter transmitting light in the range of 570 to 700 mμ with a maximum transmission at a wavelength of 595 mμ. The safety factor was calculated as the antilogarithm of the inverse of the logarithm of the speed measured as the exposure required to give a density of 0.2 above the fog density.

	Log Speed to blue light	Gamma	Fog	Safety Factor (6B Safelight)
Control [1]	2.93	4.15	0.07	8,500
Sample A [2]	2.91	4.15	0.09	17,000
Sample B [2]	2.90	4.30	0.08	16,600

[1] No dye in supercoat.
[2] Dye in supercoat.

Thus the safety factor to Wratten 6B Safelight for the photographic element protected with my light-screening layer was about twice as high as it was for the control.

The accompanying drawing containing FIGS. 1, 2, and 3 still further illustrates my invention. FIGS. 1, 2, and 3 represent greatly enlarged cross-sectional views of light-sensitive photographic elements containing my light-absorbing water-permeable colloid layers.

FIG. 1 shows light-screening layer **10** consisting of gelatin containing bis(1 - carboxymethylhexahydro-3-n-octyl - 2,4,6-trioxo-5-pyrimidine)pentamethinoxonol mordanted with polyvinyl-pyridinium metho-p-toluenesulfonate coated over light-sensitive silver halide emulsion layer **11** which is coated on support **12**.

FIG. 2 shows light-sensitive silver halide emulsion layer **13** coated over light-screening layer **14** consisting of gelatin containing bis(1-butyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)pentamethinoxonol mordanted with α-methyl allyl-N-guanidylketimine coated over support **15**.

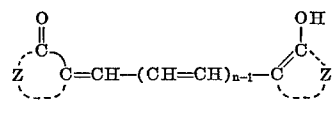
FIG. 3 shows light-sensitive silver halide emulsion layer **16** coated on support **17** bearing antihalation backing layer **18** consisting of gelatin containing bis(1-butyl-3 - carboxymethylhexahydro - 2,4,6-trioxo-5-pyrimidine) pentamethinoxonol mordanted with α-methyl allyl-N-guanidylketimine.

The symmetrical, acid oxonol dyes of my invention are valuable for preparing light-screening layers for making light-sensitive photographic elements containing silver halide emulsion layers. The light-screening layers containing my dyes are used to advantage either over the light-sensitive silver halide emulsion layers, between the light-sensitive silver halide emulsion layer and the support, between two different light-sensitive layers, or as an antihalation backing layer. My dyes are characterized by having maximum light absorption at desirable wavelengths. They are further characterized by being readily mordanted with basic mordants so that they will not wander into light-sensitive silver halide emulsion layers coated directly in contact with them and yet they are readily bleached in the light-screening layer by conventional processing solutions which contain sodium sulfite. Furthermore, my dyes are characterized by having very good stability at the pH of most sensitive silver halide emulsions (about 6.3) and have little or no undesirable effect on the sensitivity of the silver halide emulsion layer even when they are used in direct contact with them.

The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A novel light-absorbing dye having the formula:



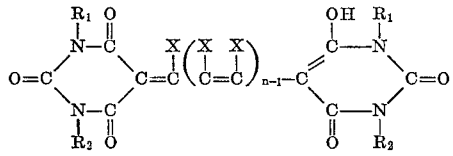
wherein Z represents the nonmetallic atoms necessary to complete a 1-(carboxymethyl or carboxyethyl)-3-(alkyl having 1 to 8 carbon atoms, benzyl, cyclohexyl, phenyl, methylphenyl or methoxyphenyl) hexahydro-2,4,6-trioxo-

5-pyrimidine nucleus and *n* is an integer of from 1 to 3.

2. A novel light-absorbing dye of claim 1 in which Z represents the nonmetallic atoms necessary to complete a 1-carboxymethyl-3-(alkyl having 1 to 8 carbon atoms) hexahydro-2,4,6-trioxo-5-pyrimidine nucleus and *n* is an integer of from 1 to 3.

3. A novel light-absorbing dye of claim 1 in which Z represents the nonmetallic atoms necessary to complete a 1-carboxymethyl-3-(phenyl, methylphenyl or methoxyphenyl)hexahydro-2,4,6-trioxo-5-pyrimidine nucleus and *n* is an integer of from 1 to 3.

4. A novel light-absorbing dye having the formula:



wherein R_1 is a carboxyalkyl group in which the alkyl group has from 1 to 2 carbon atoms; R_2 is a member selected from the class consisting of an alkyl group having from 1 to 8 carbon atoms, phenyl, methylphenyl and methoxyphenyl; *n* is an integer of from 1 to 3; X is a member selected from the class consisting of a hydrogen atom and an alkyl group having from 1 to 4 carbon atoms such that not more than one X is an alkyl group.

5. The novel light-absorbing dye bis(1-n-butyl-3-carboxymethylhexahydro - 2,4,6 - trioxo - 5 - pyrimidine) pentamethinoxonol.

6. The novel light-absorbing dye bis(1-carboxymethylhexahydro - 3 - n - octyl - 2,4,6 - trioxo - 5 - pyrimidine) pentamethinoxonol.

7. The novel light-absorbing dye bis(1-carboxymethylhexahydro - 3 - phenyl - 2,4,6 - trioxo - 5 - pyrimidine) pentamethinoxonol.

8. The novel light-absorbing dye bis(1-n-butyl-3-carboxymethylhexahydro - 2,4,6 - trioxo - 5 - pyrimidine) trimethinoxonol.

9. The novel light-absorbing dye bis(1-carboxymethyl-3 - cyclohexylhexahydro - 2,4,6 - trioxo - 5 - pyrimidine) trimethinoxonol.

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JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

96—84; 252—300; 260—257, 482