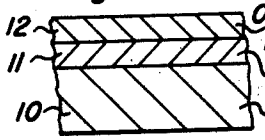
March 17, 1964 D. W. HESELTINE ETAL 3,125,448

PHOTOGRAPHIC SILVER HALIDE EMULSIONS CONTAINING CATIONIC MEROCYANINE DYES

Filed March 10, 1960

Fig. 1

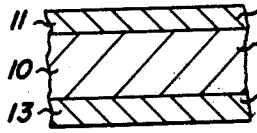


OVERCOATING LAYER CONTAINING A CATIONIC MEROCYANINE DYE

EMULSION

SUPPORT

Fig. 2

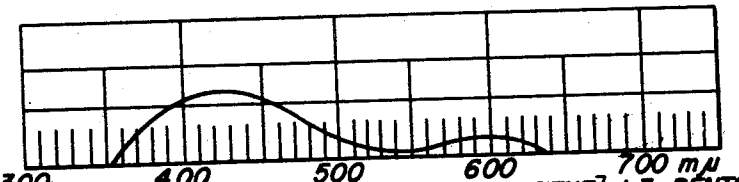


EMULSION

SUPPORT

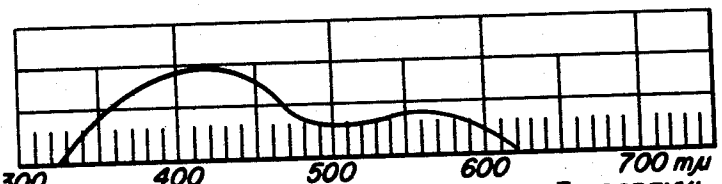
ANTIHALATION LAYER CONTAINING A CATIONIC MEROCYANINE DYE

Fig. 3



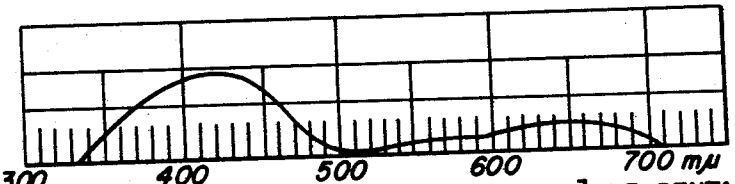
1-BENZOYL-5-[3-ETHYL-2(3H)-BENZOTHIAZOLYLIDENE]-1,3-PENTADIENYL-PYRIDINIUM IODIDE

Fig. 4



1-CYANO-3-[3-ETHYL-2(3H)-BENZOTHIAZOLYLIDENE] PROPENYL-PYRIDINIUM IODIDE

Fig. 5



1-CYANO-5-[3-ETHYL-2 (3H)-BENZOTHIAZOLYLIDENE]-1,3-PENTADIENYL-PYRIDINIUM IODIDE

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3,125,448

PHOTOGRAPHIC SILVER HALIDE EMULSIONS CONTAINING CATIONIC MEROCYANINE DYES

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Filed Mar. 10, 1960, Ser. No. 14,101
9 Claims. (Cl. 96—105)

This invention relates to a novel class of dyes, and more particularly to cationic merocyanine dyes useful as bleachable antihalation and filter dyes, and as optical sensitizers in photographic silver halide elements.

It is known that photographic elements require, for many purposes, 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 of such an emulsion or protecting an overlying light sensitive emulsion or emulsions from the action of light of wavelength 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 a 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 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.

Numerous substances have been employed as light screening materials for the purposes indicated above. Many of these, however, are not resistant to diffusion and wander from the layer in which it is intended that they should remain. Some of them are not as water soluble as is desired and therefore present problems in their incorporation in the filter layers. Some dyes are not readily bleachable or destroyed in the photographic processing and present stain problems in the processed photographic element.

It is therefore an object of the invention to provide a novel class of dyes which are valuable for use in making light sensitive photographic elements.

Another object is to provide a novel class of cationic merocyanine dyes for making light absorbing filter layers and antihalation layers in photographic elements which not only have valuable light absorbing characteristics but are more water soluble than prior art merocyanine dyes and are thus more easily incorporated in the filter layer.

Another object is to provide a novel class of dyes which are useful as photographic sensitizers.

Another object is to provide a novel class of cationic merocyanine dyes for light absorbing filter layers which not only have the desired light absorbing properties and solubility properties but which are further characterized by being less subject to diffusion from the filter layer than are the prior art dyes.

Another object is to provide a novel class of dyes which not only have the above desired characteristics but also are bleachable by the developer solution during the processing of the photographic element.

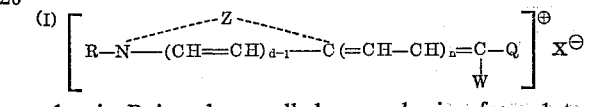
Another object is to provide a photographic element having at least one sensitive silver halide emulsion layer and a light absorbing filter layer containing a dye selected from the novel class of dyes of our invention.

Still another object is to provide a photographic element having at least one sensitive silver halide emulsion layer containing a sensitizing amount of a dye selected from the novel class of dyes of our invention.

Still other objects will become apparent from the following specification.

We have discovered that the above objects can be accomplished by the use of the novel dyes of our invention. Our dyes have a characteristic structure which distinguishes them from the prior art dyes. This structure has a methine chain with one terminal carbon atom substituted with a pyridinium group and with a phenacyl group, a cyano group or a benzothiazolyl group, and the other terminal carbon atom forms a part of a heterocyclic nucleus such as a benzothiazole nucleus, a benzoxazole nucleus or a 4-quinoline nucleus.

The novel dyes of our invention can advantageously be expressed by the formula:

(I) 

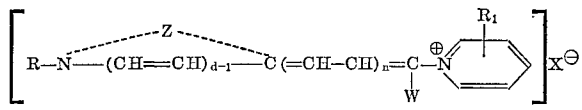
wherein R is a lower alkyl group having from 1 to 6 carbon atoms such as methyl, ethyl, propyl, butyl, isobutyl, amyl, isoamyl, hexyl, β-methoxy ethyl, β-ethoxy ethyl, allyl (i.e. vinylmethyl), benzyl (phenylmethyl), β-phenylethyl, carboxymethyl, etc.; Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus, containing from 5 to 6 atoms in the heterocyclic ring, such as those selected from the group consisting of those of the thiazole series (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), those of the benzothiazole series (e.g.,

benzothiazole,
4-chlorobenzothiazole,
5-chlorobenzothiazole,
6-chlorobenzothiazole,
7-chlorobenzothiazole,
4-methylbenzothiazole,
5-methylbenzothiazole,
6-methylbenzothiazole,
5-bromobenzothiazole,
6-bromobenzothiazole,
4-phenylbenzothiazole,
5-phenylbenzothiazole,
4-methoxybenzothiazole,
5-methoxybenzothiazole,
6-methoxybenzothiazole,
5-iodobenzothiazole,
6-iodobenzothiazole,
4-ethoxybenzothiazole,
5-ethoxybenzothiazole,
tetrahydrobenzothiazole,
5,6-dimethoxybenzothiazole,
5,6-dioxymethylenebenzothiazole,
5-hydroxybenzothiazole,
6-hydroxybenzothiazole, etc.),
those of the naphthothiazole series (e.g.,
naphtho[1,2]thiazole,
naphtho[2,1]thiazole,
5-methoxynaphtho[2,1]thiazole,
5-ethoxynaphtho[2,1]thiazole,
8-methoxynaphtho[1,2]thiazole,
7-methoxynaphtho[1,2]thiazole, etc.),
those of the thianaphtheno-7′,6′,4,5-thiazole series (e.g.,
4′-methoxythianaphtheno-7′,6′,4,5-thiazole, etc.),
those of the oxazole series (e.g.
4-methyloxazole,

5-methyloxazole,
4-phenyloxazole,
4,5-diphenyloxazole,
4-ethyloxazole,
4,5-dimethyloxazole,
5-phenyloxazole, etc.),
those of the benzoxazole series (e.g.,
benzoxazole,
5-chlorobenzoxazole,
5-methylbenzoxazole,
5-phenylbenzoxazole,
6-methylbenzoxazole,
5,6-dimethylbenzoxazole,
4,6-dimethylbenzoxazole,
5-methoxybenzoxazole,
5-ethoxybenzoxazole,
5-chlorobenzoxazole,
6-methoxybenzoxazole,
5-hydroxybenzoxazole,
6-hydroxybenzoxazole, etc.).
those of the naphthoxazole series (e.g.,
naphtho[1,2]oxazole,
naphtho[2,1]oxazole, etc.),
those of the selenazole series (e.g.,
4-methylselenazole,
4-phenylselenazole, etc.),
those of the benzoselenazole series (e.g.,
benzoselenazole,
5-chlorobenzoselenazole,
5-methoxybenzoselenazole,
5-hydroxybenzoselenazole,
tetrahydrobenzoselenazole, etc.),
those of the naphthoselenazole series (e.g.,
naphtho[1,2]selenazole,
naphtho[2,1]selenazole, etc.),
those of the thiazoline series, e.g.,
thiazoline,
4-methylthiazoline, etc.),
those of the 2-quinoline series (e.g.,
quinoline,
3-methylquinoline,
5-methylquinoline,
7-methylquinoline,
8-methylquinoline,
6-chloroquinoline,
8-chloroquinoline,
6-methoxyquinoline,
6-ethoxyquinoline,
6-hydroxyquinoline,
8-hydroxyquinoline, etc.),
those of the benzimidazole series (e.g.,
1,3-diethylbenzimidazole,
1-ethyl-3-phenylbenzimidazole etc.),
those of the 3,3-dialkylindolenine series (e.g.,
3,3-dimethylindolenine,
3,3,5-trimethylindolenine,
3,3,7-trimethylindolenine, etc.),
those of the 2-pyridine series (e.g., pyridine, 5-methylpyridine, etc.), those of the 4-pyridine series (e.g., pyridine, etc.), etc.; *d* is a positive integer of from 1 to 2; *n* is a positive integer 1, 2, or 3; W is a benzoyl group, a cyano group, or a benzothiazolyl group; Q is a heterocyclic nucleus such as a pyridinium group, a substituted pyridinium group, a quinolinium group, a substituted quinolinium group and etc.; X is an acid anion such as iodide, chloride, bromide, perchlorate, etc.

The preferred dyes of our invention can be expressed by the formula:

(II)

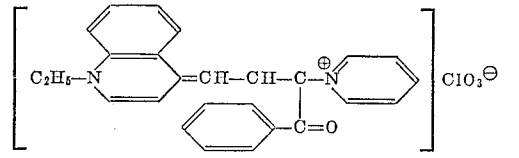


wherein R, Z, *d*, *n*, W and X are as defined above, and

R_1 is a hydrogen atom, a bromine atom, a methyl group, or a phenyl group, provided that when R_1 is a methyl group or a bromine atom this group is substituted on the carbon meta to the nitrogen atom of the pyridine ring.

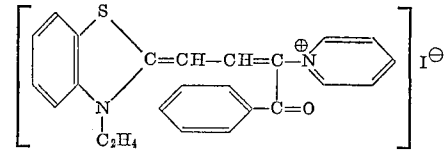
Among the dyes selected from those represented by Formula I which can be used in practicing our invention are those represented by the formulas below. It is to be understood, however, that these illustrative dyes are in no way to limit the scope of our invention.

DYE 1



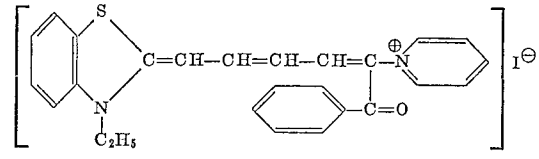
1-benzoyl-3-[1-ethyl-4-(1H)quinolylidene]propenylpyridinium perchlorate

DYE 2



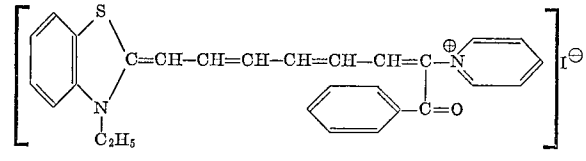
1-benzoyl-3-[3-ethyl-2(3H)-benzothiazolylidene]-propenylpyridinium iodide

DYE 3



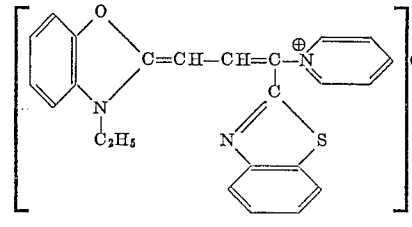
1-benzoyl-5-[3-ethyl-2(3H)-benzothiazolylidene]-1,3-pentadienylpyridinium iodide

DYE 4



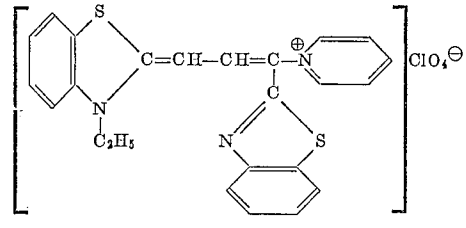
6-[3-ethyl-2(3H)-benzothiazolylidene]-2,4-hexadienylidenephenacyl pyridinium iodide

DYE 5



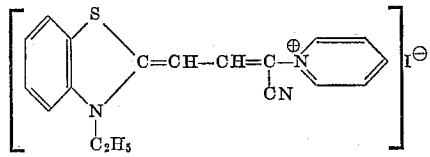
2-[3-(3-ethyl-2(3H)benzoxazolylidene)1-(1-pyridinium perchlorate)propenyl]benzothiazole

DYE 6



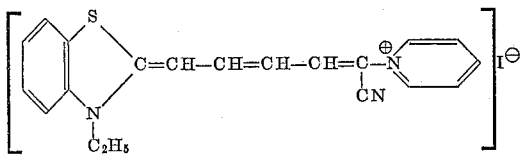
2-[3-(3-ethyl-2(3H)benzothiazolylidene)-1-(1-pyridinium perchlorate)propenyl]benzothiazole

DYE 7



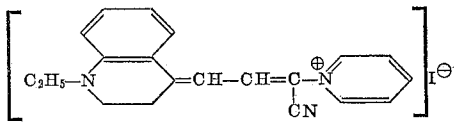
1-cyano-3-[3-ethyl-2(3H)-benzothiazolylidene]-propenyl-pyridinium iodide

DYE 8



1-cyano-5-[3-ethyl-2(3H)-benzothiazolylidene]-1,3-pentadienylpyridinium iodide

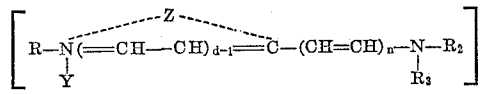
DYE 9



1-cyano-3-[1-ethyl-4-4(1H)-quinolylidene]propenylpyridinium iodide

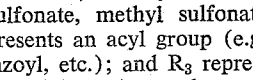
The merocyanine dyes represented by Formula I above can advantageously be prepared by condensing a compound selected from those represented by the following formula:

(III)



wherein R, Z, *d* and *n* are each as defined above; Y represents an acid radical such as chloride, bromide, iodide, perchlorate, thiocyanate, benzene sulfonate, p-toluene sulfonate, methyl sulfonate, ethyl sulfonate, etc.; R_2 represents an acyl group (e.g. acetyl, propionyl, butyryl, benzoyl, etc.); and R_3 represents an aryl group (e.g. phenyl, tolyl, etc.) together with a salt having a cation with an active methylene group in it which can be represented by the formula:

(IV)



wherein Q, W and X are as defined above.

The condensations of the cycloammonium quaternary salts of Formula III with compounds of Formula IV can be accelerated by basic condensing agents such as the trialkyl amines, (e.g., triethylamine, tri-N-propylamine, triisopropylamine, tri-N-butylamine, etc.), N,N-dialkylanilines (e.g., N,N-dimethylaniline, N,N-diethylaniline, etc.), N-alkylpiperidines (e.g., N-methylpiperidine, N-ethylpiperidine, etc.), etc. The condensations are usually carried out in the presence of basic solvents such as pyridine, quinoline, etc., (i.e. heterocyclic tertiary amines). The condensations are accelerated by heat and are normally carried out at the reflux temperature of the reaction mixture.

Among the preferred salts of Formula IV used for making our dyes are those having the cation 1-phenacylpyridinium, 1-cyanomethylpyridinium, and benzothiazolylmethylpyridinium.

The preparation of salts having a cation with an active methylene group such as are used in making our dyes is illustrated by the preparations below.

1-PHENACYLPYRIDINIUM BROMIDE

Dry pyridine (2 mols., 31.6 g.) and α-bromoacetophenone (1 mol., 39.8 g.,) were mixed and allowed to stand at room temperature for fifteen minutes. At this point the reaction mixture turned darker in color with the evolution of heat. The reaction mixture was then allowed to stand at room temperature overnight. The product was thrown out of solution by adding an excess of ether with stirring, the ether decanted from the residue, and the product obtained as a solid by refluxing with acetone. The salt was filtered off, washed with acetone and dried. After one recrystallization from ethyl alcohol the yield of pure quaternary salt was 44.5 g. (80%), M.P. 197–198° C.

1-CYANOMETHYLPYRIDINIUM CHLORIDE

Dry pyridine (1 mol., 15.8 g.) and chloroacetonitrile (1 mol., 15 g.) were mixed and allowed to stand at room temperature for fifteen minutes. At this point the reaction mixture evolved heat yielding a light tan solid. The solid cake was then heated on a steam bath for thirty minutes, cooled, ground under acetone, filtered off and dried. Aften one recrystallization from ethyl alcohol the yield of pure quaternary salt was 25 g. (80%), M.P. 178–179° C. decomposition.

1-(2-BENZOTHIAZOLYLMETHYL)PYRIDINIUM PERCHLORATE

Prepared as described by Walter Ried and Heinz Bender, Chemische Berichte 89, p. 1893–1896 (1956).

The preparation of our dyes is further illustrated by the following examples.

Example I

DYE 1

1-phenacylpyridinium bromide (1 mol., 2.78 g.), 4-β-acetanilidovinyl-1-ethylquinolinium iodide (1 mol., 4.44 g.) and triethylamine (2 mols., 2.8 ml.) were dissolved in dry pyridine (30 ml.) and heated under reflux for ten minutes. The reaction mixture was then chilled overnight and the crude dye precipitated from solution as a sticky mass by adding an excess of ether with stirring. The ether solution was decanted, the residue dissolved in water and the dye precipitated as the perchlorate salt by adding sodium perchlorate. The crude dye was filtered off, washed with water and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 1.8 g. (40%), M.P. 195– 196° C., decomposition.

Example II

DYE 2

1-phenacylpyridinium bromide (1 mol., 2.78 g.), 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide (1 mol., 4.5 g.) and triethylamine (2 mols., 2.8 ml.) were dissolved in dry pyridine (30 ml.) and heated under reflux for ten minutes. The reaction mixture was then chilled overnight and the crude dye precipitated from solution by adding an excess of ether with stirring. The crude dye was filtered off, washed with water and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 2.2 g. (43%), M.P. 275–276° C., decomposition.

Example III

DYE 3

1-phenacylpyridinium bromide (1 mol., 2.78 g.), 2-(4-acetanilido - 1,3 - butadienyl) - 3 - ethylbenzothiazolium iodide (1 mol., 4.76 g.) and triethylamine (2 mols., 2.8 ml.) were dissolved in dry pyridine (30 ml.) and heated under reflux for ten minutes. The reaction mixture was then chilled overnight and crude dye precipitated from solution by adding an excess of ether with stirring. The crude dye was filtered off, washed with water and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 1.5 g. (30%), M.P. 222°–223° C., decomposition.

Example IV

DYE 4

3 - ethyl - 2 - methylbenzothiazolium p - toluenesulfonate (1 mol., 34.9 g.) and glutaconicaldehyde dianilide hydrochloride (1 mol., 28.4 g.) were mixed in acetic anhydride (100 ml.) and refluxed for ten minutes. The

brown solution was chilled and the product precipitated from solution as an oily mass by adding ether (400 ml.) with stirring. The residue was obtained crystalline by stirring with acetone (100 ml.), solid filtered off, washed with more acetone and dried. The yield of 2-(6-acetanilido - 1,3,5 - hexatrienyl - 3 - ethylbenzothiazolium) p-toluenesulfonate was 29 g. (53%), M.P. 175°–176° C.

1-phenacylpyridinium bromide (1 mol., 1.39 g.), 2-(6-acetanilido - 1,3,5 - hexatrienyl-3-ethylbenzothiazolium) p-toluene-sulfonate (1 mol., 2.67 g.) and triethylamine (1 mol., 7 ml.) were dissolved in dry pyridine and heated under reflux ten minutes. The reaction mixture was then chilled overnight and the crude dye precipitated from solution as a sticky mass by adding an excess of ether with stirring. The ether solution was decanted and the residue dissolved in water, and the dye precipitated as the iodide salt by adding sodium iodide. The crude dye was filtered off, washed with water and dried. After two recrystallizations from aqueous methyl alcohol, the yield of pure dye was 0.8 g. (30%), M.P. 161–162° C.

Example V

DYE 5

1-(2-benzothiazolylmethyl)pyridinium perchlorate (1 mol., 3.27 g.), 2-β-acetanilidovinyl-3-ethylbenzoxazolium iodide (1 mol., 4.34 g.) and triethylamine (1 mol., 1.4 ml.) were dissolved in dry pyridine (20 ml.) and heated under reflux for twenty minutes. The reaction mixture was then chilled overnight and the crude dye precipitated from solution by adding an excess of ether with stirring. The crude dye was filtered off, washed with water and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 1 g. (20%), M.P. 227–228° C., decomposition.

Example VI

DYE 6

1-(2-benzothiazolylmethyl)pyridinium perchlorate (1 mol., 3.27 g.), 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide (1 mol., 4.5 g.) and triethylamine (1 mol., 1.4 ml.) were dissolved in dry pyridine (20 ml.) and heated under reflux for twenty minutes. The reaction mixture was then chilled overnight and the crude dye precipitated from solution by adding an excess of ether with stirring. The crude dye was filtered off, washed with water and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 1.2 g. (24%), M.P. 234–235° C., decomposition.

Example VII

DYE 7

1-cyanomethylpyridinium chloride (1 mol., 1.55 g.), 2 - β-acetanilidovinyl-3-ethylbenzothiazolium iodide (1 mol., 4.5 g.) and triethylamine (1 mol., 1.4 ml.) were dissolved in dry pyridine and heated under reflux for five minutes. The reaction mixture was then chilled overnight and the crude dye filtered off, washed sparingly with methyl alcohol and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 1.9 g. (44%), M.P. 233–234° C., decomposition.

Example VIII

DYE 8

1-cyanomethylpyridinium chloride (1 mol., 1.55 g.), 2 - (4-acetanilido-1,3-butadienyl)-3-ethylbenzothiazolium iodide (1 mol., 4.76 g.) and triethylamine (1 mol., 1.4 ml.) were dissolved in dry pyridine (30 ml.) and heated under reflux for five minutes. The reaction mixture was then chilled overnight and the crude dye filtered off, washed with acetone and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 1.8 g. (40%), M.P. 205–206° C., decomposition.

Example IX

DYE 9

1-cyanomethylpyridinium chloride (1 mol., 1.55 g.), 4-β-acetanilidovinyl-1-ethylquinolinium iodide (1 mol., 4.4 g.) and triethylamine (1 mol., 1.4 ml.) were dissolved in dry pyridine (30 ml.) and heated under reflux for five minutes. The reaction mixture was then chilled overnight and the crude dye filtered off, washed sparingly with methyl alcohol and dried. After two recrystallizations from methyl alcohol, the yield of pure dye was 3 g. (70%), M.P. 221–222° C., decomposition.

Our dyes have light absorbing characteristics that make them valuable for use in light absorbing and antihalation layers of photographic elements. These characteristics are illustrated by Table I below.

TABLE I

Dye Number	Maximum light absorption by dye occurs at a wavelength in mμ of—
1	538
2	458
4	662
8	595
9	590

Our dyes are readily soluble in water because of their ionic nature and are thus readily incorporated in hydrophilic colloids such as gelatin, polyvinyl alcohols, albumin, casein which are usually used for such layers. A stock solution may advantageously be made of the dye to be used and this can simply be added as desired to the hydrophilic colloid before it is to be coated.

The concentration of the dye used in the hydrophilic colloid may vary considerably depending upon the product in which the filter layer or the antihalation layer is to be used. The method of determining the proper amount of dye to be used for a given product is well known in the art.

In the accompanying drawing, FIGURES 1 and 2 are enlarged sectional views of photographic elements having filter layers or antihalation layers made according to our invention. As shown in FIGURE 1, a support **10** of any suitable material such as cellulose acetate, cellulose nitrate, synthetic resin materials or opaque materials such as paper, is coated with an emulsion layer **11** and an overcoating layer **12** containing a cationic merocyanine dye of our invention.

FIGURE 2 represents a film having an antihalation layer containing a cationic merocyanine dye according to our invention. As shown therein, the support **10** carries an emulsion layer **11** and an antihalation layer **13** containing a cationic merocyanine dye on the opposite sides.

The following examples will illustrate more fully how our dyes may be used in preparing light absorbing filter layers.

Example X

1.5 gram of dye No. 1 was dissolved in 37½ ccs. of water and this solution was added to 4.5 liters of 5% aqueous gelatin. This mixture was then coated as an antihalation backing on the reverse side of a support which had been coated with a photographic silver halide emulsion layer.

After exposure of the photographic element in the usual manner, development of the exposed material in a developer having the following composition:

	Grams
N-methyl-p-aminophenol sulfate	2
Sodium sulfite (desiccated)	90
Hydroquinone	8
Sodium carbonate monohydrate	52.2
Potassium bromide	5
Water to make 1 liter.	

resulted in complete removal of the dye from the photographic element.

Example XI

A photographic element made as in Example X was exposed and treated in a conventional sodium thiosulfate fixing bath. The dye was completely bleached by this treatment.

Example XII

A photographic element made as in Example X but using dye 4 in place of dye 1, was exposed. No dye was left in this element after development with a developer such as was used in Example X.

Example XIII

A mixture of dye No. 1 and aqueous gelatin solution as prepared in Example X was coated over a light sensitive silver halide emulsion layer on a conventional support.

After exposure of the photographic element in the usual manner, development of the exposed material in the developer of Example X resulted in a complete removal of the dye from the light filtering layer over the developed image.

Example XIV

Similarly, the other dyes of our invention can be used in light filtering layers as in Example No. XIII.

Although the above examples show the use of our dyes in antihalation layers and in layers overcoating the light sensitive silver halide emulsion layer, they can also be coated between light sensitive silver halide layers in multilayer photographic elements.

Some of our dyes are useful as sensitizers for optically sensitizing silver halide (e.g., silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, etc.) emulsion layers in photographic elements. The following table illustrates the wavelengths of light to which a silver bromoiodide emulsion layer is sensitized by some of our dyes.

TABLE II

Dye No.	Wavelength, in mμ, of light to which emulsion has highest sensitivity	Range of wavelengths, in mμ, to which emulsion is sensitized
1	565	565–590
3	600	600–630
4	700	600–720
5	490	490–520
6	530	530–575
7	550	550–615
8	660	600–700
9	640	600–670

The sensitizing effect is further illustrated by FIGURES 3, 4 and 5 of the attached drawings which show wedge spectrograms for three dyes of our invention.

FIGURE 3 shows the sensitizing effect produced in a silver halide emulsion by our cationic dye 1-benzoyl-5-[3-ethyl-2-(3H)-benzothiazolylidene]-1,3-pentadienylpyridinium iodide.

FIGURE 4 shows the sensitizing effect produced in a silver halide emulsion by our cationic dye 1-cyano-3-[3-ethyl-2-(3H)-benzothiazolylidene]propenylpyridinium iodide.

FIGURE 5 shows the sensitizing effect produced in a silver halide emulsion by our cationic dye 1-cyano-5-[3-ethyl-2-(3H)-benzothiazolylidene]-1,3-pentadienylpyridinium iodide.

The solubility characteristics of our dyes, as well as the good bleaching characteristics that they show in photographic developers and other processing solutions combined with the sensitizing characteristics shown by some of our dyes makes them useful as sensitizers for photographic elements.

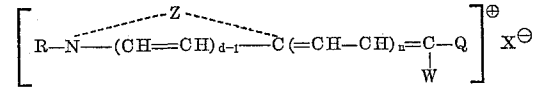
The concentration at which our dyes are used in emulsions as optical sensitizers may vary considerably depending upon the particular photographic product in which they are to be used and the effects desired. The sensitizing amounts of a particular dye needed for a particular silver halide emulsion is determined by techniques well known in the art.

The novel cationic merocyanine dyes of our invention are characterized by being readily water soluble and readily bleachable by ordinary photographic developers and processing solutions. These properties make our dyes valuable for use in making light sensitive photographic elements. Some of our dyes are particularly valuable in light absorbing filter layers either overcoating the silver halide emulsion layers or coatings between the light sensitive silver halide layers or coatings on the support of the photographic element over which the light sensitive silver halide emulsion layers are coated. Some of our dyes are also characterized by having useful optical sensitizing effects on photographic silver halide emulsions.

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.

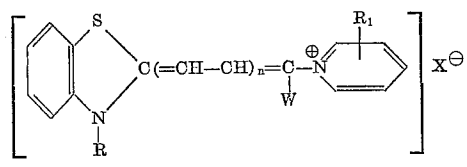
We claim:

1. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing a dye having the formula:



wherein R is a lower alkyl group having from 1 to 6 carbon atoms, Z represents the non-metallic atoms needed to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, *d* represents a positive integer of from 1 to 2, *n* represents a positive integer of from 1 to 3, Q represents a member selected from the class consisting of a pyridinium group and a quinolinium group such that the nitrogen atom in said Q group is attached to the terminal carbon atom in the conjugated chain, W represents a member selected from the class consisting of the cyano group, a benzoyl group, and a benzothiazolyl group, and X represents an acid anion.

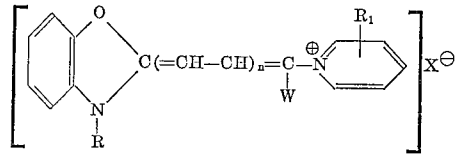
2. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing a dye having the formula:



wherein R is a lower alkyl having from 1 to 6 carbon atoms, *n* is a positive integer of from 1 to 3, W is a member selected from the group consisting of a cyano group, benzoyl groups, and benzothiazolyl groups, R_1 is a member selected from the class consisting of a hydrogen atom, a bromine atom, a methyl group, and a phenyl group, provided that when R_1 is selected from the class consisting of a methyl group and a bromine atom, said R_1 group is substituted on the carbon atom meta to the nitrogen atom of the pyridine ring, and X is an acid anion.

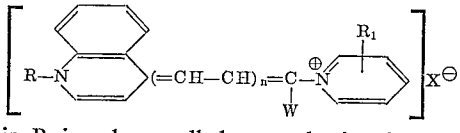
3. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer,

at least one layer of said photographic element containing a dye having the formula:



wherein R is a lower alkyl group having from 1 to 6 carbon atoms, *n* is a positive integer of from 1 to 3, W is a member selected from the class consisting of a cyano group, benzoyl groups and benzothiazolyl groups, R_1 is a member selected from the class consisting of a hydrogen atom, a bromine atom, a methyl group and a phenyl group, provided that when R_1 is selected from the class consisting of a methyl group and a bromine atom, said R_1 group is substituted on the carbon atom meta to the nitrogen atom of the pyridine ring, and X is an acid anion.

4. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing a dye having the formula:



wherein R is a lower alkyl group having from 1 to 6 carbon atoms, *n* is a positive integer of from 1 to 3, W is a member selected from the class consisting of a cyano group, benzoyl groups and benzothiazolyl groups, R_1 is a member selected from the class consisting of a hydrogen atom, a bromine atom, a methyl group and a phenyl group, provided that when R_1 is selected from the class consisting of a methyl group and a bromine atom, said

R_1 group is substituted on the carbon atom meta to the nitrogen atom of the pyridine ring, and X is an acid anion.

5. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing the dye 1-cyano-5-[3-ethyl-2-(3H)-benzothiazolylidene]-1,3-pentadienylpyridinium iodide.

6. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing the dye 6-[3-ethyl-2(3H)-benzothiazolylidene]-2,4-hexadienylidenephenacylpyridinium iodide.

7. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing the dye 1-benzoyl-3-[1-ethyl-4(1H)-quinolylidene]-propenylpyridinium perchlorate.

8. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing the dye 1-cyano-3-[3-ethyl-2(3H)-benzothiazolylidene]propenylpyridinium iodide.

9. A photographic element comprising a support having thereon at least one sensitive silver halide emulsion layer, at least one layer of said photographic element containing the dye 1-benzoyl-3-[3-ethyl-2(3H)-benzothiazolylidene]propenylpyridinium iodide.

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