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3,684,517

## PHOTOGRAPHIC EMULSION CONTAINING NEW BENZIMIDAZOLE COMPOUNDS AS SENSITIZING DYES

Leslie G. S. Brooker and Earl J. Van Lare, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

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12 Claims

### ABSTRACT OF THE DISCLOSURE

New polymethine dyes of the cyanine and merocyanine types derived from new 2-methylbenzimidazole derivatives substituted on one of the ring nitrogen atoms by a 2-thiazolyl group or derivatives thereof and photographic silver halide emulsions sensitized therewith.

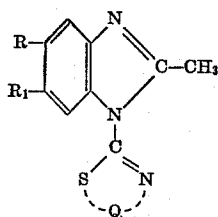
This invention relates to new benzimidazole compounds useful in the preparation of new cyanine and merocyanine dyes, to photographic silver halide emulsions sensitized with these dyes and to photographic elements containing the new photographic silver halide emulsions.

It is known in the photographic art to prepare polymethine dyes such as those of the cyanine and merocyanine classes from intermediates comprising methyl substituted nitrogenous heterocyclic nuclei the methyl groups of which can be made reactive by quaternization of the heterocyclic nuclei. It is also known that the photographic characteristics of the resulting dyes, with respect to photographic elements comprising silver halide emulsions, vary with the nuclei involved and their substituent groups. Accordingly, because of the constant demands of modern photographic processes for new and improved polymethine dyes, there is a continuing search for new heterocyclic nuclei and derivatives thereof from which such dyes can be prepared.

It is an object of this invention to provide new benzimidazole compounds which are useful for the preparation of polymethine dyes. Another object is to provide new cyanine and merocyanine dyes. A further object is to provide photographic silver halide emulsions sensitized with the new dyes of the invention. Another object is to provide photographic elements containing the new photographic silver halide emulsions. Other objects will become apparent from a consideration of the following descriptions and examples.

The new benzimidazole compounds of our invention include those represented by the following general formula:

(I)

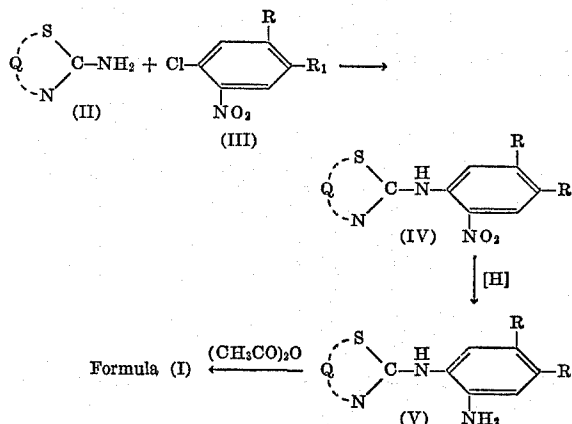


wherein R and R<sub>1</sub> are selected from the group consisting of hydrogen and chlorine atoms and Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing 5 atoms in the heterocyclic ring such as those selected from the group consisting of a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 5-methylthiazole, 4-phenylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), a thiazoline nucleus (e.g., thiazoline, 4-methylthiazoline, etc.), a benzothiazole nucleus (e.g., benzothiazole, 4-chloro-

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benzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, 6-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.), a naphthothiazole nucleus (e.g., naphtho[2,1]thiazole, naphtho[1,2]thiazole, 5-ethoxynaphtho[1,2]thiazole, 5-methoxynaphtho[1,2]thiazole, 7-methoxynaphtho[2,1]thiazole, 8-methoxynaphtho[2,1]thiazole, 7-ethoxynaphtho[2,1]thiazole, 8-ethoxynaphtho[2,1]thiazole, etc.), etc.

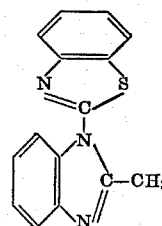
The novel benzimidazole compounds are conveniently prepared from well known materials by the reaction sequence illustrated hereinafter, wherein R, R<sub>1</sub>, and Q have the



meaning previously assigned to them, which comprises arylating the primary amino group of an appropriate 2-aminoheterocyclic compound (II) with an appropriate o-nitroaryl halide (III), reducing the pendant nitro group of the resulting secondary amine to —NH<sub>2</sub> (IV), and condensing the resulting o-phenylenediamine derivative (V) with acetic anhydride. Exemplary illustrations of this method of preparation are given in Examples 1-4.

### EXAMPLE 1

#### 1-(2-benzothiazolyl)-2-methylbenzimidazole



A mixture of 62.8 g. (1 mol.) of o-chloronitrobenzene, 60 g. (1 mol.) of 2-aminobenzothiazole, and 150 ml. of dimethylformamide was refluxed for 72 hours. The cooled reaction mixture was poured into 400 ml. of water and after stirring for 15 minutes the solid which had separated was filtered off and washed with water. An oil was also filtered off and this was separated from the water. The solid was suspended in 300 ml. of ethyl alcohol and the suspension was heated to boiling and then chilled. The

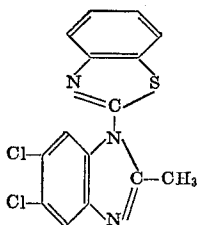
## 3

solid was filtered off and washed with ethyl alcohol. The oil and the alcoholic filtrates were combined and as much of the alcohol as possible was removed by evaporation. A residue of 80 g., 74%, of 2-(o-nitroanilino)benzothiazole, as a yellow oil, remained which was used in the next step without further purification.

To a hot, stirred solution of 80 g. (1 mol.) of 2-(o-nitroanilino)benzothiazole in 570 ml. of acetic acid and 120 ml. of acetic anhydride was added 115 g. (3 mols. + 100% excess) of zinc dust, in small portions. The temperature of the reaction mixture rose rapidly and soon the acetic acid refluxed vigorously after each addition. The addition of the zinc dust took 30 minutes. After the addition was complete, the mixture was heated on a steam bath with stirring for 5 hours. The reaction mixture was filtered hot and the solid was washed with acetic acid. The combined filtrates were concentrated as much as possible on a steam bath under reduced pressure and the residue was subjected to fractional distillation. The fraction boiling at 120–155° C./3 mm. was collected and re-fractionated to obtain 32.5 g. (43%) of 1-(2-benzothiazolyl)-2-methylbenzimidazole, B.P. 113–117° C./1.5 mm.

## EXAMPLE 2

1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole



A mixture of 15 g., (1 mol.) of 2-aminobenzothiazole, 22.7 g. (1 mol.) of 2,4,5-trichloronitrobenzene, and 75 ml. of dimethylformamide was heated for 1 week at 100° C. The reaction mixture was diluted with 100 ml. of ethyl alcohol and the mixture chilled. The solid was filtered off and washed with ethyl alcohol. The filtrate and washings were combined and the solvent removed under reduced pressure. After cooling, 12.5 g. (37%) of yellow, solid 2-(4,5-dichloro-2-nitroanilino) benzothiazole separated and was filtered off. After recrystallization from methanol, this product had a M.P. of 90–92° C.

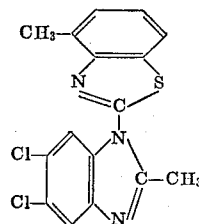
*Analysis.*—Calcd. for  $C_{13}H_7Cl_2N_3O_2S$  (percent): N, 12.35. Found (percent): N, 11.9.

To a well stirred suspension of 31.7 g. (1 mol.) of 2-(4,5-dichloro-2-nitroanilino)benzothiazole in 250 ml. of water and 1.1 ml. of concentrated hydrochloric acid at 60–70° C. was added 20.5 g. of iron powder in small portions over a period of 10 minutes. The reaction mixture was stirred for 6 hours at 70–80° C. After the addition of 30 cc. of Filter-cel, the mixture was filtered and the solid and liquid extracted separately with chloroform. The chloroform extracts were combined and treated with 20 ml. of acetic anhydride. The solvent was removed on a steam bath under reduced pressure. The residue was diluted with a small amount of ethyl alcohol, cooled, and the solid filtered off and washed with ethyl alcohol. This solid did not give a dye. The filtrate and washings were combined and concentrated as far as possible. The residue was treated with a small amount of diethyl ether and 8 g. (26%) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole, M.P. 95–98° C., was filtered off and washed with ether. On concentrating the ether solution an additional 4.2 g. (13%) of product was obtained.

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## EXAMPLE 3

5,6-dichloro-2-methyl-1-(4-methyl-2-benzothiazolyl)benzimidazole

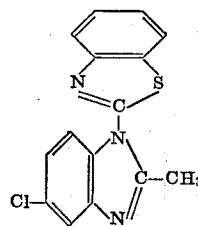


A mixture of 16.4 g. (1 mol.) of 2-amino-4-methylbenzothiazole, 22.7 g. (1 mol.) of 1,2,4-trichloro-5-nitrobenzothiazole, and 75 ml. of dimethyl acetamide was heated for 17 days at 100° C. The reaction mixture was treated with water and, after chilling, the solid was collected and taken up in 900 ml. of hot ethyl alcohol. On cooling, a solid impurity separated which was discarded after filtration. The filtrate was then concentrated to 100 ml., chilled, and the 18 g. (51%) of yellow, solid, 2-(4,5-dichloro-2-nitroanilino)-4-methylbenzothiazole was collected.

To a well stirred suspension of 25.7 g. (1 mol.) of 2-(4,5-dichloro-2-nitroanilino)-4-methylbenzothiazole and 1 ml. of concentrated hydrochloric acid in 150 ml. of water and 75 ml. of methyl alcohol at 70–80° C. was added 16.3 g. of iron powder in small portions over a period of 10 minutes. The reaction mixture was stirred for 6 hours at 80° C. The reaction mixture was cooled, 30 cc. of filter-cel was added, and the mixture was filtered. The solid and liquid were extracted separately with chloroform. The chloroform extracts were combined and the solvent was removed under reduced pressure. The residue was treated with 25 ml. of acetic anhydride and the mixture heated, allowing the acetic acid and excess acetic anhydride to distill off. The residue was extracted with 50 ml. of 4N hydrochloric acid, filtered, and cooled. The filtrate was made alkaline with solution of sodium carbonate and the solid 5,6-dichloro-2-methyl-1-(4-methyl-2-benzothiazolyl)-benzimidazole which separated was filtered off. This material was sufficiently pure to be used directly in the preparation of dyes. A sample recrystallized from methanol had a M.P. of 197–198° C.

## EXAMPLE 4

1-(2-benzothiazolyl)-5-chloro-2-methylbenzimidazole



A mixture of 15 g. (1 mol.) of 2-aminobenzothiazole, 19.2 g. (1 mol.) of 1,4-dichloro-2-nitrobenzene, and 60 ml. of dimethylacetamide was heated for 17 days at 100° C. The cooled reaction mixture was poured into 400 ml. of water and after stirring for 15 minutes, the solid was filtered off and washed with water. The oily layer of the filtrate was separated from the water and saved. The solid was crystallized from 100 ml. of ethanol and 12.5 g. of material was obtained which was not the desired product. The oil and the alcoholic filtrate were combined and as much alcohol as possible was removed under reduced pressure. There remained 11 g. of 2-(4-chloro-2-

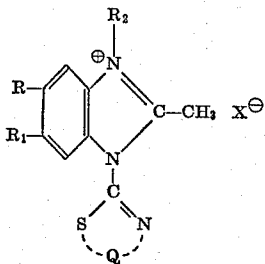
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nitroanilino)benzothiazole as an intense yellow oil which was used in the next step without further purification.

To a well stirred suspension of 11 g. (1 mol.) of 2-(4-chloro-2-nitroanilino)benzothiazole and 1 ml. of concentrated hydrochloric acid in 150 ml. of water and 75 ml. of methanol at 70–80° C. was added 8.1 g. of iron powder in small portions over a period of 10 minutes. The reaction mixture was stirred and refluxed for 4 hours. The mixture was cooled, 30 cc. of filter-cel was added, and the mixture was filtered. The solid and liquid were extracted separately with chloroform. The chloroform extracts were combined and the solvent was removed under reduced pressure. The residue was treated with 30 ml. of acetic anhydride and then refluxed for 1 hour. The acetic acid and the excess acetic anhydride were distilled off slowly until the residue reached a temperature of 220° C. The mixture was chilled and then boiled for 2 hours with 40 ml. of 4 N hydrochloric acid, filtered and cooled. The filtrate was made alkaline with aqueous sodium carbonate, cooled, and extracted with diethyl ether. The ether extract was dried and the ether removed. The oily residue of 1-(2-benzothiazolyl)-5-chloro-2-methylbenzimidazole (5 g., 48%) was used without further purification in the preparation of dyes.

To employ the new benzimidazole derivatives of our invention in the preparation of polymethine dyes, such as cyanine and merocyanine dyes, it is advantageous that they be quaternized with appropriate alkylating agents to provide intermediates having the following formula:

(VI)



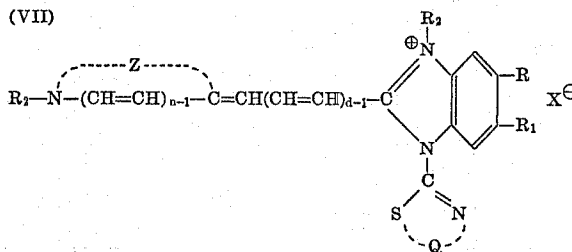
wherein R, R<sub>1</sub> and Q are as defined previously, R<sub>2</sub> represents an alkyl group, preferably an alkyl group having 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, octyl, decyl, etc., a carboxyalkyl group such as carboxymethyl, carboxyethyl, carboxypropyl or carboxybutyl, for example a sulfoalkyl group such as 2-sulfoethyl, 3-sulfopropyl or 4-sulfobutyl, for example, etc.; and X<sup>⊖</sup> represents an acid anion such as chloride, bromide, iodide, methylsulfate, ethylsulfate, benzenesulfonate, p-toluenesulfonate, thiocyanate, perchlorate, and sulfamate, for example. The manner of preparing quaternary compounds is well known to those skilled in the art to which this invention is directed and is illustrated hereinafter. The methyl group on the carbon atom adjacent to the quaternary nitrogen atom in the heterocyclic ring is very reactive and loses hydrogen readily in dye-forming condensation reactions. Such condensation reactions are well known in the art and can be employed to prepare both cyanine and merocyanine dyes from the intermediate compounds having the Formula VI. These condensation reactions are too numerous to be specifically mentioned, however, they are well documented in the literature (e.g., in Mees, "The Theory Of The Photographic Process," 3rd Ed., The Macmillan Co., pp. 199–232; Chem. Rev., 11, 273, (1932); Quart. Rev. (London), 4, 327 (1950); Hamer, "The Chemistry of Heterocyclic Compounds, vol. 18, The Cyanine Dyes and Related Compounds," Interscience Publishers, New York, 1964; etc.).

The new cyanine dyes which are a part of our inven-

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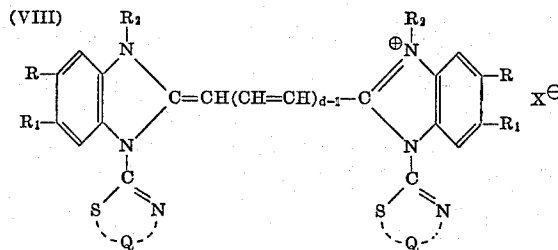
tion can be represented by the following general formulas:

(VII)



and

(VIII)

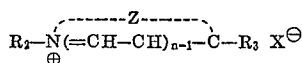


wherein R, R<sub>1</sub>, R<sub>2</sub>, Q and X<sup>⊖</sup> are as defined previously; d represents a positive integer of from 1–3; n represents a positive integer of from 1–2; and Z represents the non-metallic atoms necessary to complete a 5- to 6-membered heterocyclic nucleus selected from the group consisting of a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.); a benzothiazole nucleus (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.); a naphthothiazole nucleus (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole, 7-methoxy-α-naphthothiazole, etc.); a thianaphtheno-7',6',4,5-thiazole nucleus (e.g., 4'-methoxythianaphtheno-7',6',4,5-thiazole, etc.); an oxazole nucleus (e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.); benzoxazole nucleus (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 6-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.); a naphthoxazole nucleus (e.g., α-naphthoxazole, β-naphthoxazole, etc.); a selenazole nucleus (e.g., 4-methylselenazole, 4-phenylselenazole, etc.); a benzoselenazole nucleus (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.); a naphthoselenazole nucleus (e.g., α-naphthoselenazole, β-naphthoselenazole, etc.); a thiazoline nucleus (e.g., thiazoline 4-methylthiazoline, etc.); a 2-quinoline nucleus (e.g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.); a 4-quinoline nucleus (e.g., quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, etc.); a 1-isoquinoline nucleus (e.g., isoquinoline, 3,4-dihydroisoquinoline, etc.); a 3-isoquinoline nucleus (e.g., iso-

quinoline, etc.); a 3,3-dialkylindolenine nucleus (e.g., 3,3-dimethylindolenine, 5- or 6-nitro-3,3-dimethyl- or 5- or 6-cyano-3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.); a 2-pyridine nucleus (e.g., pyridine, 3-methylpyridine, 4-methylpyridine, 5-methylpyridine, 3,4-dimethylpyridine, 4-chloropyridine, 3-hydroxypyridine, 3-phenylpyridine, etc.); a 4-pyridine nucleus (e.g., 2-methylpyridine, 3-methylpyridine, 3-chloropyridine, 2,6-dimethylpyridine, 3-hydroxypyridine, etc.); a 1-alkylimidazole nucleus (e.g., 1-methylimidazole, 1-ethyl-4-phenylimidazole, 1-butyl-4,5-dimethylimidazole, etc.); a 1-alkylbenzimidazole nucleus (e.g., 1-methylbenzimidazole, 1-ethylbenzimidazole, 1-butyl-4-methylbenzimidazole, 1-ethyl-5,6-dichlorobenzimidazole, etc.), and a 1-alkylnaphthimidazole nucleus (e.g., 1-methyl- $\alpha$ -naphthimidazole, 1-ethyl- $\alpha$ -naphthimidazole, 1-methyl- $\beta$ -naphthimidazole, etc.).

The new cyanine dyes of our invention, as previously mentioned, can be prepared from cyclammonium salts having the general Formula VI by a variety of methods, e.g., unsymmetrical cyanines having the general Formula VII can be prepared by condensing cyclammonium salts having the Formula VI with compounds having the general formula:

(IX)

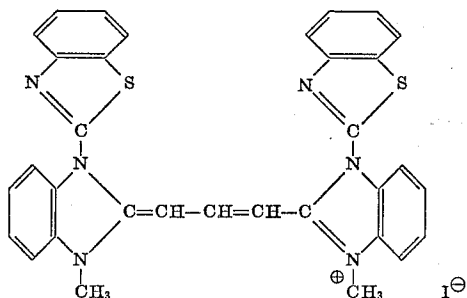


wherein  $\text{R}_2$ ,  $\text{X}^{\ominus}$ ,  $\text{Z}$  and  $n$  are as defined previously and  $\text{R}_3$  is a reactive group such as a halogen atom, e.g., chloro, bromo or iodo, an alkylmercapto group such as methylmercapto, for example, an arylmercapto group, such as phenylmercapto, for example, an alkoxy group such as methoxy or ethoxy, for example, the  $\beta$ -anilino-vinyl group, a  $\beta$ -acetanilidovinyl group, etc. Symmetrical cyanines having the Formula VIII can advantageously be prepared by reacting two molecules of a cycloammonium salt having the Formula VI with a bifunctional compound such as formaldehyde or diethoxymethyl acetate, an ortho ester of a carboxylic acid such as ethyl orthoformate, for example, a trihalomethane such as iodoform, for example, a dianil (or salt or anilide thereof) of the type  $\text{C}_6\text{H}_5-\text{NH}(\text{CH=CH})_d-\text{CH=N}-\text{C}_6\text{H}_5$  wherein  $d$  has the meaning previously assigned to it, etc.

Representative examples illustrating the synthesis of the cyanine dyes of our invention are provided in Examples 5-14. These examples illustrate but do not limit our invention.

## EXAMPLE 5

1,1'-di(2-benzothiazolyl)-3,3'-dimethylbenzimidazolo-carbocyanine iodide

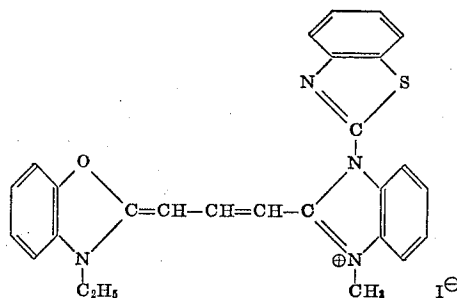


A mixture of 2.6 g. (2 mols.) of 1-(2-benzothiazolyl)-2-methylbenzimidazole and 3.7 g. (2 mols.+100% excess) of methyl p-toluenesulfonate was heated at 170° C. for 3 minutes. To the cooled melt was added a solution of 0.58 g. (5 mols.) of sodium in 40 ml. of ethyl alcohol, and then 1 g. (1 mol.) of chloral alcoholate (2,2,2-trichloro-1-ethoxyethanol). The reaction mixture was re-

fluxed for 2 hours and then chilled, and the solid filtered off and washed with ethyl alcohol. The filtrates were treated with a solution of 3.0 g. of sodium iodide in a small amount of water and the mixture was chilled. The solid, which had separated, was filtered off and washed with water. After recrystallization from methyl alcohol, 0.1 g. (3%) of brownish crystals was obtained, M.P. 285-286° C. (dec.).

## EXAMPLE 6

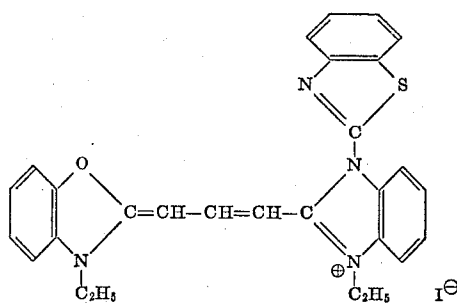
1-(2-benzothiazolyl)-3'-ethyl-3-methylbenzimidazolo-oxacarbocyanine iodide



A mixture of 1.3 g. (1 mol.) of 1-(2-benzothiazolyl)-2-methylbenzimidazole and 1.86 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was heated at 175° C. for 3 minutes. To the cooled melt were added 2.2 g. (1 mol.) of 2- $\beta$ -acetanilidovinyl-3-ethylbenzoxazolium iodide, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine and the mixture was refluxed for 1 hour. The reaction mixture was then cooled and treated with diethyl ether. The oil, which separated, was washed with diethyl ether and then with water. Addition of a small amount of ethyl alcohol caused the dye to crystallize. After chilling, the dye was filtered off and washed lightly with cold ethyl alcohol. After two recrystallizations from ethyl alcohol, 0.7 g. (24%) of pure dye was obtained as brick red crystals, M.P. 189-191° C. (dec.).

## EXAMPLE 7

1-(2-benzothiazolyl)-3,3'-diethylbenzimidazolo-oxacarbocyanine iodide



A mixture of 12 g. (1 mol.) of 1-(2-benzothiazolyl)-2-methylbenzimidazole and 10.5 g. (1 mol.+50% excess) of ethyl iodide was refluxed for 6 hours. The mixture was diluted with 20 ml. of acetone. After chilling, the solid 1-(2-benzothiazolyl)-3-ethyl-2-methylbenzimidazolium iodide was filtered off and washed with acetone. A yield of 4.5 g. (22%) of colorless crystals was obtained.

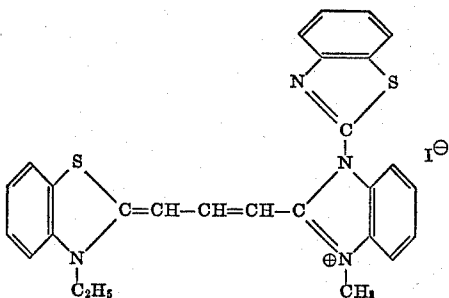
A mixture of 2 g. (1 mol.) of 1-(2-benzothiazolyl)-3-ethyl-2-methylbenzimidazolium iodide, 2.2 g. (1 mol.) of 2- $\beta$ -acetanilidovinyl-3-ethylbenzoxazolium iodide, 10 ml. of pyridine, and 0.5 g. (1 mol.) of triethylamine was refluxed for 1 hour. The reaction mixture was cooled and then treated with diethyl ether. The oil which separated

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was washed with diethyl ether and then with water. Addition of a small amount of ethyl alcohol caused the dye to crystallize. After chilling, the dye was filtered off and washed lightly with cold ethyl alcohol. After two recrystallizations from ethyl alcohol, 0.3 g. of pure dye was obtained as brownish yellow needles, M.P. 213–215° C. (dec.).

## EXAMPLE 8

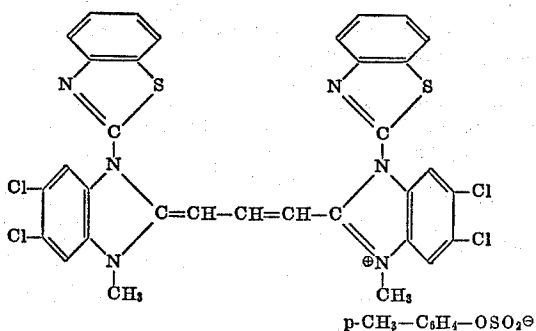
## 1-(2-benzothiazolyl)-3'-ethyl-3-methylbenzimidazolothiacarbocyanine iodide



A mixture of 1.3 g. (1 mol.) of 1-(2-benzothiazolyl)-2-methylbenzimidazole and 1.86 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was heated at 175° C. for 3 minutes. To the cooled melt were added 2.25 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine and the mixture was refluxed for 30 minutes. The reaction mixture was cooled and then treated with ether. The oil which separated was washed with diethyl ether and then with water. Addition of ethyl alcohol caused the dye to crystallize. After chilling, the dye was filtered off and washed lightly with cold ethyl alcohol. After two recrystallizations from ethyl alcohol, 0.5 g. (16%) of pure dye was obtained as bluish needles, M.P. 245–246° C. (dec.).

## EXAMPLE 9

## 1,1' - di(2 - benzothiazolyl) - 5,5',6,6' - tetrachloro-3,3'-dimethylbenzimidazolocarboxyanine p-toluenesulfonate

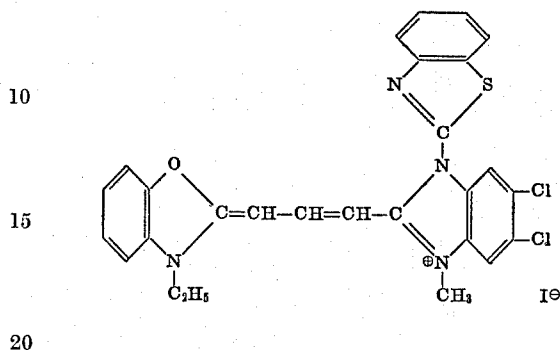


A mixture of 3.3 g. (2 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1.86 g. (2 mol.) of methyl p-toluenesulfonate was heated to 200° C. To the cooled melt was added a solution of 0.58 g. (5 mol.) of sodium in 40 ml. of ethyl alcohol and then 1 g. (1 mol.) of chloral alcoholate. The reaction mixture was refluxed for 2 hours and then chilled. The solid was filtered off and washed with water. The dye was left as a water insoluble purplish solid. After recrystallization from methyl alcohol, 0.2 g. (4%) of pure dye was obtained as red crystals with a bright reflex, M.P. 321–322° C. (dec.).

## 10

## EXAMPLE 10

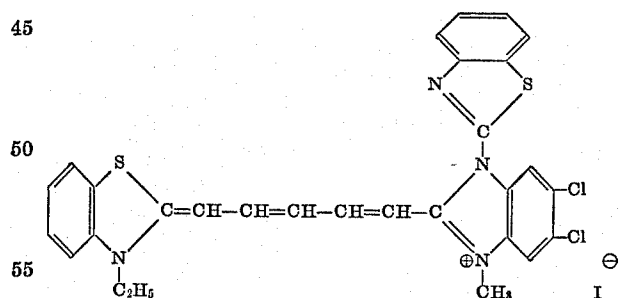
## 1-(2-benzothiazolyl)-5,6-dichloro-3'-ethyl-3-methylbenzimidazoloxacarbocyanine iodide



A mixture of 1.7 g. (1 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1.86 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was heated to 200° C. To the cooled melt were added 2.2 g. (1 mol.) of 2-β-acetanilido-3-ethylbenzoxazolium iodide, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine and the mixture was refluxed for 1 hour. The reaction mixture was then cooled and treated with diethyl ether. The oil which separated was washed with diethyl ether and then with water. Addition of ethyl alcohol caused the dye to crystallize. After chilling, the dye was filtered off and washed lightly with cold ethyl alcohol. After two recrystallizations from methyl alcohol, 0.3 g. (9%) of pure dye was obtained as stout purple needles, M.P. 276–277° C. (dec.).

## EXAMPLE 11

## 1-(2-benzothiazolyl)-5,6-dichloro-3'-ethyl-3-methylbenzimidazolthiadicarboxyanine iodide

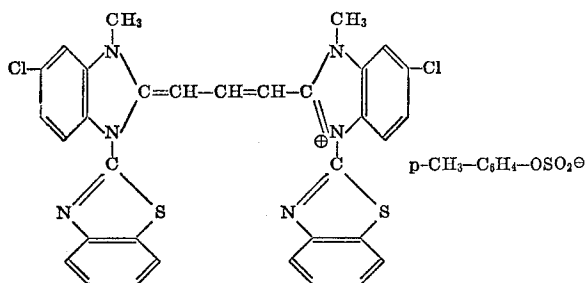


A mixture of 1.7 g. (1 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1.86 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was heated to 200° C. To the cooled melt were added 2.38 g. (1 mol.) of 2-(4-acetanilido-1,3-butadienyl)-3-ethylbenzothiazolium iodide, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine and the mixture was refluxed for 20 minutes. The reaction mixture was cooled and then treated with diethyl ether. The oil which separated was washed with diethyl ether and then with water. Addition of a small amount of ethyl alcohol caused the dye to crystallize. After chilling, the dye was filtered off and washed with ethyl alcohol. After two recrystallizations from methyl alcohol, 0.2 g. (6%) of pure dye was obtained as blue crystals, M.P. 235–237° C. (dec.).

# 11

## EXAMPLE 12

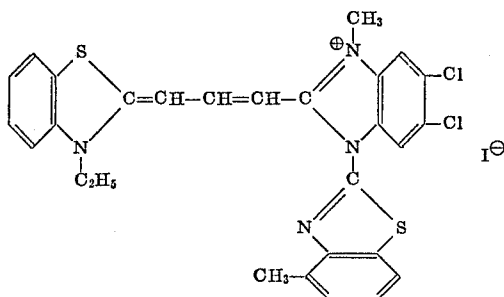
1,1'-di-(2-benzothiazolyl)-5,5'-dichloro-3,3'-dimethylbenzimidazolocarboaniline p-toluenesulfonate



A mixture of 2 g. (2 mol.) of 1-(benzothiazolyl)-5-chloro-2-methylbenzimidazole and 2.5 g. (2 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 3 minutes. To the cooled melt was added a solution of 0.5 g. of sodium in 40 ml. of ethyl alcohol, and then 0.8 g. (1 mol.) chloral alcoholate. The reaction mixture was refluxed for 2 hours and then chilled. The solid was filtered off and washed with water and then stirred with a small amount of acetone. After recrystallization from methyl alcohol, 0.1 g. (4%) of pure dye was obtained as dark red crystals, M.P. 249–252° C. (dec.).

## EXAMPLE 13

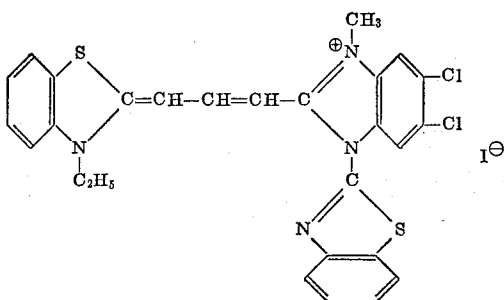
5,6-dichloro-3'-ethyl-1-methyl-3-(4-methyl-2-benzothiazolyl)benzimidazolothiacarboaniline iodide



A mixture of 1.75 g. (1 mol.) of 5,6-dichloro-2-methyl-1-(4-methyl-2-benzothiazolyl)benzimidazole and 1.86 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 2 minutes. To the cooled melt were added 2.25 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide, 10 ml. of pyridine and 1 g. (1 mol.+100% excess) of triethylamine and the mixture was refluxed for 20 minutes. After chilling, the reaction mixture was treated with water and the water layer decanted. Treatment of the oily residue with diethyl ether caused the crude dye to crystallize. After chilling, the crude dye was filtered off and washed lightly with cold ethyl alcohol. After two recrystallizations from methanol, 0.15 g. (4%) of pure dye was obtained as bluish crystals, M.P. 284–285° C. (dec.).

## EXAMPLE 14

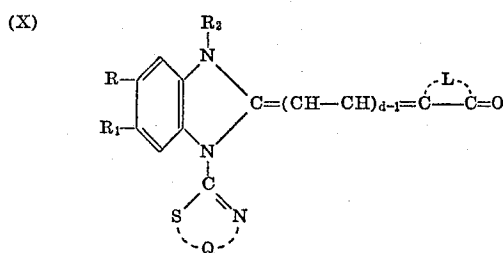
1-(2-benzothiazolyl)-5-chloro-3'-ethyl-3-methylbenzimidazolothiacarboaniline iodide



# 12

A mixture of 1.5 g. (1 mol.) of 1-(2-benzothiazolyl)-5-chloro-2-methylbenzimidazole and 1.8 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 2 minutes. To the cooled melt were added 2.25 g. (1 mol.) of 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine and the mixture was refluxed for 30 minutes. After chilling, the reaction mixture was filtered and the solid discarded. The filtrate was treated with water and the water layer decanted. The oily residue was stirred with acetone and chilled. The crude dye was filtered off and washed with acetone. The crude dye was dissolved in chloroform and purified by chromatography on alumina. After developing the column with 10 liters of chloroform, the slowest moving band was extruded from the column. The dye was extracted from the alumina with methyl alcohol. After the alcoholic solution was concentrated to a small volume and chilled, 0.1 g. (3%) of pure dye was obtained as brownish orange crystals, M.P. 244–246° C. (dec.).

The new merocyanine dyes of our invention have the following general formula:

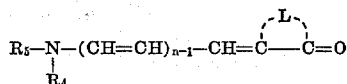


wherein R, R<sub>1</sub>, R<sub>2</sub>, Q and d have the meaning previously assigned to them and L represents the non-metallic atoms required to complete a 5- to 6-membered heterocyclic nucleus such as those selected from the class consisting of a 2-pyrazolin-5-one nucleus (e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.), an isoxazolone nucleus (e.g., 3-phenyl-5(4H)-isoxazolone, 3-methyl-5(4H)-isoxazolone, etc.), an oxindole nucleus (e.g., 1-alkyl-2, 3-dihydro-2-oxindoles, etc.), a 2,4,6-triketohexahydropyrimidine nucleus (e.g., barbituric acid or 2-thio-barbituric acid as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-propyl, 1-heptyl, etc.), or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β-methoxyethyl, etc.), or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl, etc.), or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl, 1-p-ethoxycarbonylphenyl, etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-heptyl-3-phenyl, etc. derivatives), a rhodanine nucleus (i.e., 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkylrhodanines (e.g., 2-methylrhodanine, 3-ethylrhodanine, etc.), 3-allylrhodanine, 3-carboxyalkylrhodanines (e.g., 3-(2-carboxyethyl)rhodanine, 3-(4-carboxybutyl)rhodanine, etc.), 3-sulfoalkylrhodanines (e.g., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfopropyl)rhodanine, 3-(4-sulfobutyl)rhodanine, etc.), or 3-arylrhodanines (e.g., 3-phenylrhodanine, etc.), etc., a 2(3H)-imidazo[1,2-a]pyridone nucleus, a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus (e.g., 5-, 7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.), a 2-thio-2,4-oxazolidinedione nucleus (i.e., a 2-thio-2,4-(3H,5H)-oxazolidinedione nucleus) e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-oxazolidinedione, 3-(3-carboxypropyl)-2-thio-2,4-oxazolidinedione, etc.), a thianaphthenone nucleus (e.g., 3(2H)-thianaphthenone, etc.), 2-thio-2,5-thiazolidinedione nucleus (i.e., the 2-thio-2,5(3H,4H)-thiazolidinedione nucleus) (e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.), a 2,4-thiazolidinedione nucleus (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione-

dione, 3- $\alpha$ -naphthyl-2,4-thiazolidinedione, etc.), a thiazolidinone nucleus (e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone, 3- $\alpha$ -naphthyl-4-thiazolidinone, etc.), a 2-thiazolin-4-one nucleus (e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkylphenylamino-2-thiazolin-4-one, 2-diphenylamino-2-thiazolin-4-one, etc.), a 2-imino-4-oxazolidinone (i.e., pseudohydantoin) nucleus series, a 2,4-imidazolidinedione (hydantoin) nucleus (e.g., 2,4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3- $\alpha$ -naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2,4-imidazolidinedione, ethyl-3- $\alpha$ -naphthyl-2,4-imidazolidinedione, 1,3-diphenyl-2,4-imidazolidinedione, etc.), a 2-thio-2,4-imidazolidinedione (i.e., 2-thiohydantoin) nucleus (e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-imidazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolidinedione, 3-phenyl-2-thio-2,4-imidazolidinedione, 3- $\alpha$ -naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3- $\alpha$ -naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diphenyl-2-thio-2,4-imidazolidinedione, etc.), a 2-imidazolin-5-one nucleus (e.g., 2-propylmercapto-2-imidazolin-5-one, etc.), etc.

Although the new merocyanine dyes of our invention can be prepared in a variety of ways from the cyclammonium salts having the general Formula VI, or derivatives thereof, we find it advantageous to prepare them by reacting cyclammonium salts having the general formula:

(XI)

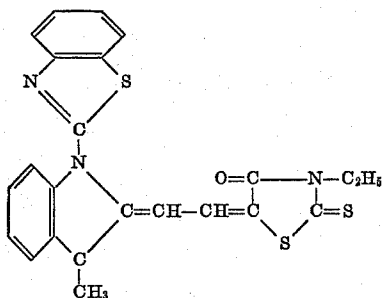


wherein  $n$  and  $L$  have the meaning previously assigned to them,  $R_5$  represents a hydrogen atom or an acyl group such as formyl, acetyl, propionyl, butyryl, benzoyl, *o*-toluoyl, *m*-toluoyl, or *p*-toluoyl, for example, and  $R_4$  represents an aryl group such as phenyl, methylphenyl e.g. (*o*-, *m*-, *p*-tolyl), chlorophenyl, bromophenyl, alkoxyphenyl such as methoxyphenyl and ethoxyphenyl, for example, sulfophenyl and naphthyl.

Examples 15-22 hereinafter illustrate the preparation of the new merocyanine dye compounds of the invention but are not limitative of our new merocyanine dye compounds or their preparation.

## EXAMPLE 15

5-[[1-(2-benzothiazolyl)-2-methyl-2-benzimidazolylidene]ethylidene]-3-ethylrhodanine

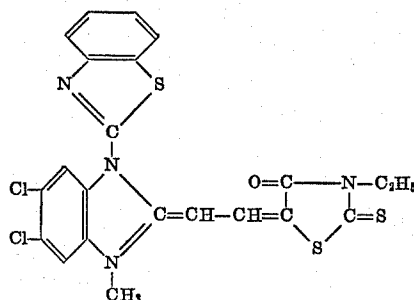


A mixture of 1.3 g. (1 mol.) of 1-(2-benzothiazolyl)-2-methylbenzimidazole and 1.86 g. (1 mol.+100% excess) of methyl *p*-toluenesulfonate was heated at 175° C. for 3 minutes. To the cooled melt were added 1.6 g. (1 mol.) of 5-acetanilidomethylene-3-ethylrhodanine, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine, and the mixture was refluxed for 1 3/4 hours. The reaction mixture was cooled and then treated with diethyl ether. The oil which separated was washed with diethyl ether and then with water. Addition of a small amount of ethyl alcohol caused the dye to crystallize. After chilling, the dye was filtered off and washed lightly

with cold ethyl alcohol. The dye was purified by precipitation from a pyridine solution with methyl alcohol. The yield of pure dye, as fine orange needles, was 0.2 g. (9%), M.P. 293-294° C. (dec.).

## EXAMPLE 16

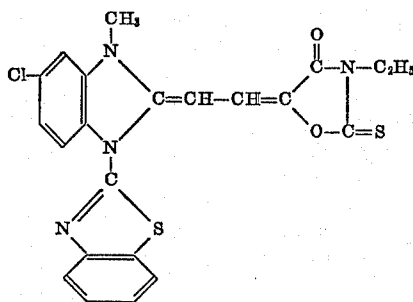
5-[[1-(2-benzothiazolyl)-5,6-dichloro-3-methyl-2-benzimidazolylidene]ethylidene]-3-ethylrhodanine



A mixture of 1.7 g. (1 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1.86 g. (1 mol.+100% excess) of methyl *p*-toluenesulfonate was heated at 175° C. for 3 minutes. To the cooled melt were added 1.6 g. (1 mol.) of 5-acetanilidomethylene-3-ethylrhodanine, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine, and the mixture was refluxed for 1 1/2 hours. The reaction mixture was cooled and then treated with diethyl ether. The oil which separated was washed with diethyl ether and then with water. Addition of a small amount of ethyl alcohol caused the dye to crystallize. After chilling, the dye was filtered off and washed with ethyl alcohol. After two recrystallizations from pyridine, 0.4 g. (14%) of pure dye was obtained as maroon crystals, M.P. 326-327° C. (dec.).

## EXAMPLE 17

5-[[1-(2-benzothiazolyl)-5,6-dichloro-3-methyl-2-benzimidazolylidene]ethylidene]-3-ethyl-2-thio-2,4-oxazolidinedione

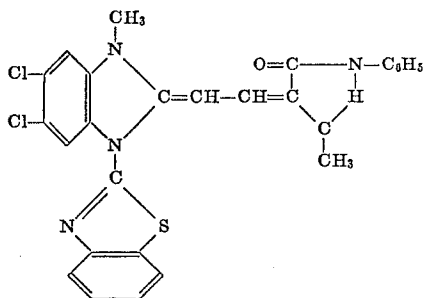


A mixture of 0.9 g. (1 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1 g. (1 mol.+100% excess) of methyl *p*-toluenesulfonate was fused at about 180° C. for 3 minutes. To the cooled melt were added 0.85 g. (1 mol.) of 5-acetanilidomethylene-3-ethyl-2-thio-2,4-oxazolidinedione, 10 ml. of dimethylacetamide, and 0.5 g. (1 mol.+100% excess) of triethylamine, and the mixture was heated at 125-135° C. for 30 minutes. The reaction mixture was chilled and the crude dye filtered off and washed with ethyl alcohol. After two recrystallizations from pyridine, 0.1 g. (7%) of pure dye was obtained as orange crystals, M.P., above 310° C.

# 15

## EXAMPLE 18

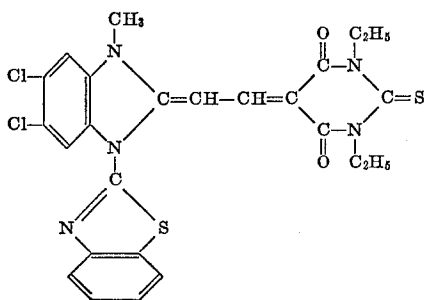
4-[[1-(2-benzothiazolyl)-5,6-dichloro-3-methyl-2-benzimidazolinyldene]ethylidene]-3-methyl-1-phenyl-2-pyrazolin-5-one



A mixture of 0.9 g. (1 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 3 minutes. To the cooled melt were added 0.8 g. (1 mol.) of 4-anilinomethylene-3-methyl-1-phenyl-2-pyrazolin-5-one, 10 ml. of dimethylacetamide, 0.3 ml. of acetic anhydride, and 0.5 g. (2 mol.) of triethylamine, and the mixture was heated at 125° C. for 30 minutes. The reaction mixture was chilled and the crude dye was filtered off and washed with water and then with methyl alcohol. After two recrystallizations from pyridine, 0.1 g. (7%) of pure dye was obtained as orange crystals, M.P., 267–270° C. (dec.).

# EXAMPLE 19

5-[[1-(2-benzothiazolyl)-5,6-dichloro-3-methyl-2-benzimidazolinyldene]ethylidene]-1,3-diethyl-2-thiobarbituric acid

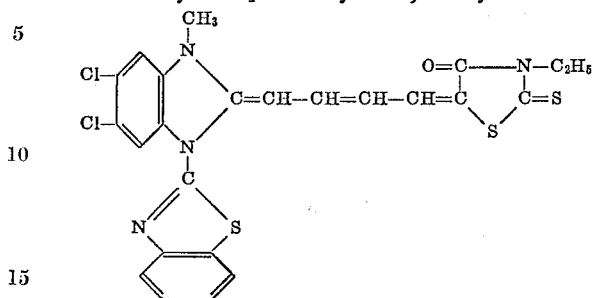


A mixture of 0.9 g. (1 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 3 minutes. To the cooled melt were added 0.8 g. (1 mol.) of 5-anilinomethylene-1,3-diethyl-2-thiobarbituric acid, 10 ml. of dimethylacetamide, 0.3 ml. of acetic anhydride, and 0.5 g. (2 mols.) of triethylamine, and the mixture was refluxed for 2 minutes and then heated at 125° C. for 30 minutes. The reaction mixture was chilled and the crude dye was filtered off and washed with ethyl alcohol. After two recrystallizations from pyridine, 0.15 g. (10%) of pure dye was obtained as orange crystals, M.P., above 320° C.

# 16

## EXAMPLE 20

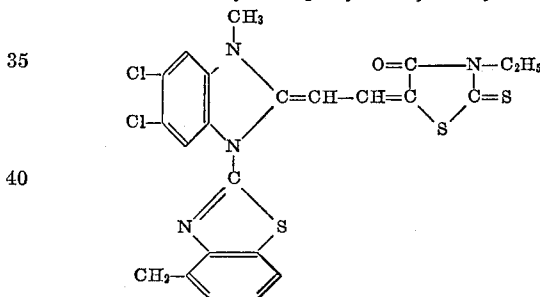
5-[[1-(2-benzothiazolyl)-5,6-dichloro-3-methyl-2-benzimidazolinyldene]-2-butenylidene]-3-ethylrhodanine



A mixture of 0.9 g. (1 mol.) of 1-(2-benzothiazolyl)-5,6-dichloro-2-methylbenzimidazole and 1 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 3 minutes. To the cooled melt were added 0.85 g. (1 mol.) of 5-acetanilidoallylidene-3-ethylrhodanine, 7 ml. of dimethylacetamide, and 0.5 g. (1 mol.+100%) of triethylamine and the mixture was refluxed for 2 minutes and then heated at 125° C. for 30 minutes. The reaction mixture was chilled and the crude dye was filtered off and washed with methyl alcohol. After two recrystallizations from pyridine, 0.05 g. (3%) of pure dye was obtained as a green powder, M.P., 294–295° C. (dec.).

# EXAMPLE 21

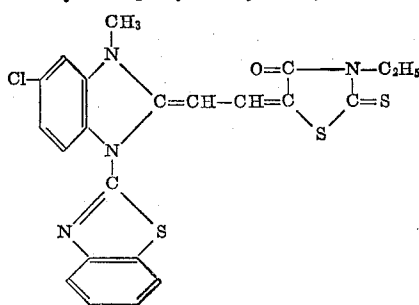
5-[[5,6-dichloro-3-methyl-1-(4-methyl-2-benzothiazolyl)-2-benzimidazolinyldene]ethylidene]-3-ethylrhodanine



A mixture of 1.75 g. (1 mol.) of 5,6-dichloro-2-methyl-1-(4-methyl-2-benzothiazolyl)benzimidazole and 1.86 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 3 minutes. To the cooled melt were added 1.6 g. (1 mol.) of 5-acetanilidomethylene-3-ethylrhodanine, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine, and the mixture was refluxed for 1 hour. The reaction mixture was chilled and then stirred for 15 minutes with a mixture of diethyl ether and water. The crude dye was filtered off and washed first with water and then with diethyl ether. The dye was purified by dissolving it in pyridine and treating the pyridine solution with methyl alcohol. The pure dye, 0.13 g. (5%), was obtained as red crystals, M.P., above 320° C.

# EXAMPLE 22

5-[[2-(benzothiazolyl)-5-chloro-3-methyl-2-benzimidazolinyldene]ethylidene]-3-ethylrhodanine





A mixture of 1.5 g. (1 mol.) of 1-(2-benzothiazolyl)-5-chloro-2-methylbenzimidazole and 1.8 g. (1 mol.+100% excess) of methyl p-toluenesulfonate was fused at 180° C. for 3 minutes. To the cooled melt were added 16 g. (1 mol.) of 5-acetanilido-methylene-3-ethylrhodanine, 10 ml. of pyridine, and 1 g. (1 mol.+100% excess) of triethylamine, and the mixture was refluxed for 1½ hours. The reaction mixture was chilled and the crude dye filtered off and washed with ethyl alcohol. After two recrystallizations from pyridine, 0.5 g. (17%) of pure dye was obtained as orange crystals, M.P. 288–289° C. (dec.).

It will be obvious to those skilled in the art that, operating in a manner similar to that described hereinbefore, naphthimidazole derivatives similar to the hereinbefore described benzimidazole derivatives can be prepared by employing o-nitronaphthyl halides such as 2-chloro-3-nitro-naphthalene, 1-chloro-2-nitronaphthalene, and 2-chloro-1-nitronaphthalene, for example, as the o-nitro-aryl halide reactants in Equation 1, hereinbefore. It will be equally obvious that these naphthimidazole derivatives can then be employed to prepare cyanine and merocyanine dyes which are benzologs of the dyes represented by Formulas VII, VIII, and X.

The new cyanine and merocyanine dyes of our invention having the Formulas VII, VIII, and X, are spectral sensitizers for photographic silver halide emulsions being particularly useful in manufacturing photographic gelatin-silver halide emulsions of the developing-out type. The dyes are advantageously incorporated into washed, finished, emulsions and should, of course, be uniformly distributed throughout the emulsions.

The methods of incorporating dyes into photographic emulsions are simple and well known to those skilled in the art of emulsion making. For example, the dyes can be added from solutions in appropriate organic solvents which are compatible with the emulsions and free from deleterious effects on the light sensitive materials. Methanol, isopropanol, and pyridine, alone or in admixture, have proven satisfactory as solvents for the dyes.

The types of silver halide emulsions that can be sensitized with the new dyes of this invention include those prepared from hydrophilic colloids that are known to be satisfactory vehicles for dispersed silver halides, for example, emulsions comprising natural materials such as gelatin, gelatin derivatives, agar-agar, albumin, gum arabic, alginic acid, etc., and synthetic resins such as poly(vinyl alcohol), poly(vinyl pyrrolidone), polyacrylamide, cellulose ethers and carboxylated derivatives thereof, partially hydrolyzed cellulose acetate, certain copolymers of acrylic and methacrylic acids, polymeric hydrosols or latexes, mixtures of these, and the like.

The concentration of the new dyes in the emulsion can vary widely, e.g., from about 5 to about 100 mg. per liter of flowable emulsion. The specific concentration will vary according to the type of light sensitive material in the emulsion and the effects desired. The suitable and most economical concentration for a given emulsion will be apparent to those skilled in the art upon making the tests and observations customarily used in the art of emulsion making.

To prepare a gelatin-silver halide emulsion sensitized with one of the dyes of this invention, the following procedure is satisfactory: A quantity of the dye is dissolved in a suitable solvent and a quantity of this solution containing from 5 to 100 mg. of dye is slowly added to one liter of a gelatin-silver halide emulsion. With most of the dyes, 10 to 20 mg. of dye per liter of emulsion suffices to produce the maximum sensitizing effect with the ordinary gelatin-silver bromide (including bromiodide and chlorobromide) emulsions. With fine grain emulsions, which include most of the ordinarily employed gelatin-silver chloride emulsions, somewhat larger concentrations of dye may be necessary to obtain optimum sensitizing

effects. While this procedure has dealt with emulsions comprising gelatin, it will be appreciated that these remarks apply generally to any emulsion wherein all or part of the gelatin is substituted by another suitable hydrophilic colloid as mentioned above. It will also be appreciated that this description is merely illustrative and should not be construed as limiting the invention in any sense since it is apparent that the new dyes can be incorporated by other methods in many of the photographic silver halide emulsions and hydrophilic colloid layers customarily used in the art. For example, the dyes can be incorporated by bathing a plate or film bearing a silver halide sensitized layer in an aqueous solution of one of the dyes. Bathing methods, however, are not normally preferred.

Photographic silver halide emulsions containing the sensitizing dyes of this invention can also contain other addenda such as chemical sensitizers, e.g., sulfur sensitizers such as allyl thiocarbamide, thiourea, allyl isothiocyanate, cystine, etc., selenium and tellurium sensitizers, various gold compounds such as potassium chloroaurate, auric trichloride, etc. (see U.S. Pats. 2,540,085; 2,597,856, and 2,597,915), various palladium compounds such as palladium chloride (U.S. Pat. 2,540,086), potassium chloropalladate (U.S. Pat. 2,598,079), etc., or mixtures of such sensitizers; antifoggants such as ammonium chloroplatinate (U.S. Pat. 2,566,263), benzonitrazole, nitrobenzimidazoles, 5-nitroindazole, mercaptans, etc., (see Mees, "The Theory of the Photographic Process," Macmillan Pub., 1942, p. 460); or mixtures thereof.

Photographic silver halide emulsion layers and other layers present in the photographic elements made according to the invention may contain developing agents such as hydroquinones, catechols, 1,3-pyrazolidones, aminophenols, etc.; and the layers can be hardened with any suitable hardener such as aldehyde hardeners, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides, mixtures of these, and the like. The layers present in photographic elements made according to the invention may also contain color couplers, such as those described in U.S. Pats. 2,423,730 and 2,640,776, et al., or mixtures of such addenda. Dispersing agents for color couplers such as those set forth in U.S. Pats. 2,322,027 and 2,304,940, and non-ionic, anionic, and amphoteric coating aids, can also be employed in the above described emulsions and colloid layers. The photographic emulsions can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including stabilizers, for example, particularly the water soluble inorganic acid salts of cadmium, cobalt, manganese, and zinc such as disclosed in U.S. Pat. 2,829,404, and the substituted triazaindolizines such as those disclosed in U.S. Pats. 2,444,605 and 2,444,607; other spectral sensitizing dyes; speed increasing materials such as polyalkylene glycols, onium salts, thioethers, etc.; plasticizers; filter dyes; mixtures of these additives; and the like.

The sensitizing effects of representative new dyes of our invention are illustrated in the following tabulation where the sensitizing range and sensitizing maximum values are shown for these dyes. The dyes were tested in silver bromiodide and silver chlorobromide emulsions. The dyes, dissolved in suitable solvents, were added to separate portions of either a silver bromiodide (99.3:0.65) or a silver chlorobromide (40–60) emulsion, as indicated in the table, at the concentrations indicated. After digestion at 50° C. for 10 minutes, the emulsions were coated on a cellulose acetate film support at a coverage of 459 mg., of silver and 1040 mg., of gelatin per square foot. A sample of each coating was then exposed on an Eastman 1B Sensitometer and to a wedge spectrograph, processed for 3 minutes in Kodak Developer D–19, fixed, washed, and dried.

## SENSITIZING DATA

Dye of example number—	Emulsion type	Dye conc. (grams per mole)	Sensitizing range (m $\mu$ ) to—	Sensitizing maximum (m $\mu$ )
5.....	BrI	0.08	600	560
5.....	ClBr	0.13	610	540, 575
6.....	BrI	0.08	560	515
6.....	ClBr	0.13	580	535
7.....	BrI	0.08	540	515
7.....	ClBr	0.13	545	515
8.....	BrI	0.08	670	540, 600
8.....	ClBr	0.13	660	560, 605
9.....	BrI	0.08	625	595
9.....	ClBr	0.13	630	595
10.....	BrI	0.08	600	560
10.....	ClBr	0.13	600	560
11.....	BrI	0.08	720	555, 665
11.....	ClBr	0.13	720	665
12.....	BrI	0.08	690	565
13.....	BrI	0.08	660	590
13.....	ClBr	0.13	635	560
14.....	BrI	0.08	640	555
15.....	BrI	0.08	640	530, 580
15.....	ClBr	0.13	635	500, 570
16.....	BrI	0.08	630	580
16.....	ClBr	0.13	620	575
17.....	ClBr	0.13	610	535
18.....	ClBr	0.13	550	490
19.....	ClBr	0.13	540	495
20.....	ClBr	0.13	700	650
21.....	ClBr	0.13	680	575
22.....	ClBr	0.13	620	580

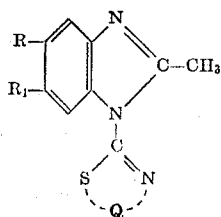
Although the above photographic element examples show coatings made on cellulose acetate film support, it is to be understood that the photographic silver halide emulsions may be coated advantageously on any of the support materials commonly used in photographic elements including glass, metals, paper, cellulose nitrate, and synthetic film forming resinous materials such as polystyrene, polyolefins, polyesters, polyamides, polycarbonates, poly(vinyl acetals), etc., supports such as papers which are partially acetylated or coated with an a-olefin polymer, particularly a polymer derived from an a-olefin containing 2-10 carbon atoms as exemplified by polyethylene and polypropylene, ethylene-butene copolymers, and the like, also give good results.

The term "filter-cel" mentioned in certain examples refers to a diatomaceous earth filter aid. Any inert diatomite filter aid can be employed such as that sold by Johns-Manville under the registered trade-mark "Celite."

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

## We claim:

1. A photographic silver halide emulsion containing a compound having the formula:



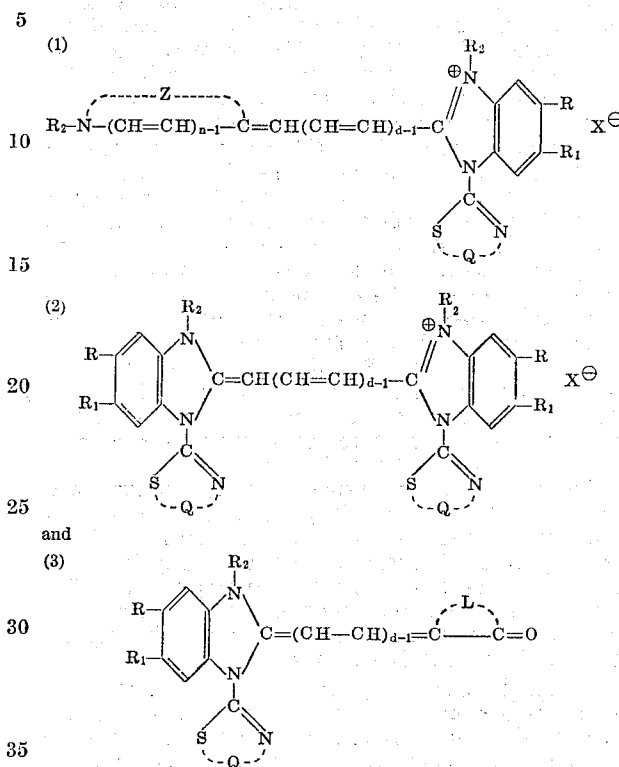
wherein R and R<sub>1</sub> each represents the same or different member selected from the group consisting of a hydrogen atom or a chlorine atom, and Q represents the nonmetallic atoms required to complete a 5-membered heterocyclic nucleus selected from the group consisting of a thiazole nucleus, a thiazoline nucleus, a benzothiazole nucleus and a naphthothiazole nucleus.

2. A photographic emulsion according to claim 1 wherein Q represents the nonmetallic atoms necessary to complete a benzothiazole nucleus.

3. A photographic element comprising a support having thereon at least one layer containing a photographic emulsion according to claim 1.

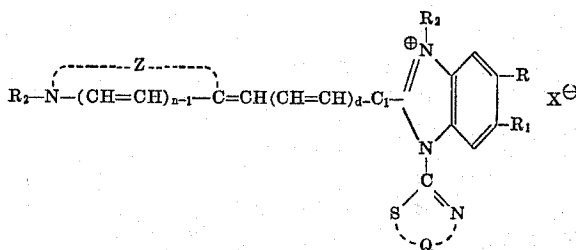
4. A photographic silver halide emulsion containing at

least one compound selected from the compounds having the formulae:

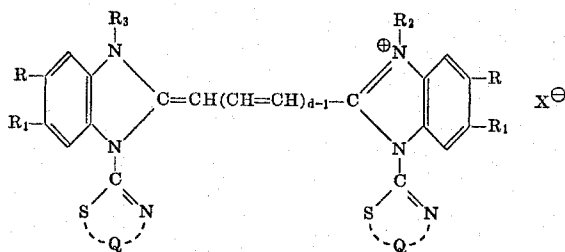


wherein R and R<sub>1</sub> each represents the same or different member selected from the group consisting of a hydrogen atom or a chlorine atom; R<sub>2</sub> represents a member selected from the group consisting of an alkyl group, a carboxy-alkyl group, a sulfoalkyl group and a phenyl group; d represents a positive integer of from 1 to 3; n represents a positive integer of from 1 to 2; Q represents the non-metallic atoms required to complete a 5-membered heterocyclic nucleus selected from the group consisting of a thiazole nucleus, a thiazoline nucleus, a benzothiazole nucleus and a naphthothiazole nucleus; Z represents the nonmetallic atoms required to complete a 5- to 6-membered heterocyclic nucleus selected from the class consisting of a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a thianaphtheno-7',6',4,5-thiazole nucleus, an oxazole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a selenazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a thiazoline nucleus, a 2-pyridine nucleus, a 4-pyridine nucleus, a 2-quinoline nucleus, a 4-quinoline nucleus, a 1-isoquinoline nucleus, a 3-isoquinoline nucleus, a 3,3-dialkylindolenine nucleus, an imidazole nucleus, a benzimidazole nucleus, and a naphthimidazole nucleus; L represents the non-metallic atoms required to complete a heterocyclic nucleus selected from the class consisting of a 2-pyrazoline-5-one nucleus, an isoaxazolone nucleus, an oxindole nucleus, a barbituric acid nucleus, a 2-thiobarbituric acid nucleus, a rhodanine nucleus, a 2(3H)-imidazo-[1,2-a]pyridone nucleus, a 5,7-dioxo-6,7-dihydro-5-thiazolo-[3,2-a]pyrimidine nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a thianaphthenone nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a thiazolidinone nucleus, a 2-thiazolin-4-one nucleus, a 2-imino-2,4-oxazolidinone nucleus, a 2,4-imidazolidinedione nucleus, a 2-thio-2,4-imidazolidinedione nucleus, and a 2-imidazoline-5-one nucleus; and X<sup>⊖</sup> represents an acid anion.

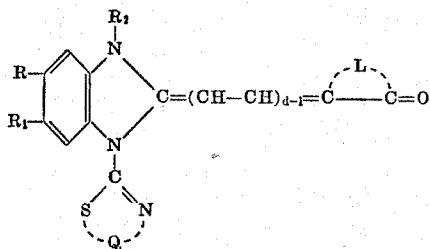
5. A photographic silver halide emulsion according to claim 4 wherein said compound has the formula:



6. A photographic silver halide emulsion according to claim 4 wherein said compound has the formula:

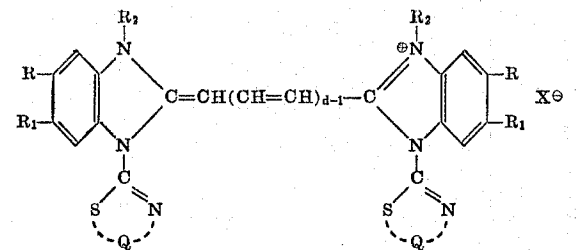
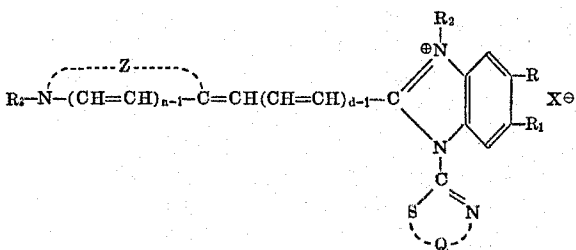


7. A photographic silver halide emulsion according to claim 4 wherein said compound has the formula:

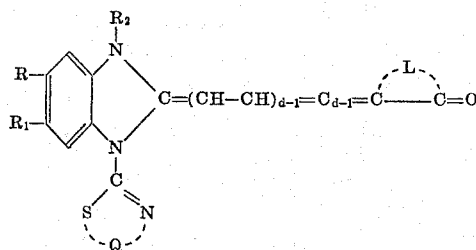


8. A photographic element comprising a support and having thereon at least one layer containing a silver halide emulsion according to claim 4.

9. A photographic element comprising a support and at least one layer coated thereon containing silver halide and a compound selected from the formulae:



and



wherein R and R<sub>2</sub> each represents the same or different member selected from the group consisting of a hydrogen atom or a chlorine atom; R<sub>2</sub> represents a member selected from the group consisting of an alkyl group, a carboxy-alkyl group, a sulfoalkyl group and a phenyl group; d represents a positive integer of from 1 to 3; n represents a positive integer of from 1 to 2; Q represents the non-metallic atoms required to complete a 5-membered heterocyclic nucleus selected from the group consisting of a thiazole nucleus, a thiazoline nucleus, a benzothiazole nucleus and a naphthothiazole nucleus; Z represents the nonmetallic atoms required to complete a 5- to 6-membered heterocyclic nucleus selected from the class consisting of a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a thianaphtho-7',6',4,5-thiazole nucleus, an oxazole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a selenazole nucleus, a benzo-selenazole nucleus, a naphthoselenazole nucleus, a thiazoline nucleus, a 2-pyridine nucleus, a 4-pyridine nucleus, a 2-quinoline nucleus, a 4-quinoline nucleus, a 1-isoquinoline nucleus, a 3-isoquinoline nucleus, a 3,3-di-alkylindolenine nucleus, an imidazole nucleus, a benzimidazole nucleus, and a naphthimidazole nucleus; L represents the nonmetallic atoms required to complete a heterocyclic nucleus selected from the class consisting of a 2-pyrazolin-5-one nucleus, an isoxazolone nucleus, an oxindole nucleus, a barbituric acid nucleus, a 2-thiabarbituric acid nucleus, a rhodanine nucleus, a 2(3H)-imidazo-[1,2-a]pyridone nucleus, a 5,7-dioxo-6,7-dihydro-5-thiazolo-[3,2-a]pyrimidine nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a thianaphthenone nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a thiazolidinone nucleus, a 2-thiazolin-4-one nucleus, a 2-imino-2,4-oxazolidinone nucleus, a 2,4-imidazolidinedione nucleus, a 2-thio-2,4-imidazolidinedione nucleus, and a 2-imidazolin-5-one nucleus; and X<sup>⊖</sup> represents an acid anion.

10. A photographic element according to claim 9 wherein said compound is 1,1'-di(2-benzothiazolyl)-3,3'-dimethylbenzimidazolocarbo-cyanine iodide.

11. A photographic element according to claim 9 wherein said compound is 1-(2-benzothiazolyl)-3'-ethyl-3-methylbenzimidazolothiacarbo-cyanine iodide.

12. A photographic element according to claim 9 wherein said compound is 5-{[1-(2-benzothiazolyl)-5-chloro-3-methyl-2-benzimidazolinylidene]ethylidene}-3-ethylrhodanine.

#### References Cited

##### UNITED STATES PATENTS

3,443,955	3/1969	Gandino et al.	96-128
3,243,298	2/1966	Libeer et al.	96-127
3,615,638	6/1971	Kimura et al.	96-127

NORMAN G. TORCHIN, Primary Examiner

E. C. KIMLIN, Assistant Examiner

U.S. Cl. X.R.

96-127

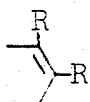
UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,684,517 Dated August 15, 1972

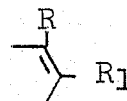
Inventor(s) Leslie G. S. Brooker and Earl J. VanLare

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

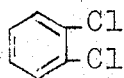
Column 1, line 2, "EMULSION" should read --EMULSIONS--. Column 2, lines 2-3, "5-5-methylbenzothiazole" should read -- 5-methylbenzothiazole --; line 29, that part of formula reading:



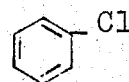
should read



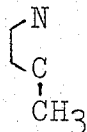
Column 3, line 19, "fracitonal" should read --fractional--; line 20, "mg." should read --mm.--; line 69, "fitrate" should read --filtrate--. Column 4, line 2, after "-benzothiazolyl", --)-- should be inserted; line 43, "asolution" should read --a solution --; line 47, "recrysatlized" should read --recrystallized--; line 69, "wtih" should read --with--. Column 7, line 32, "analkylmercapto" should read --an alkylmercapto--. Column 11, line 16, that part of formula reading "1-(benzothiazolyl)" should read -- 1-(2-benzothiazolyl) --; line 25, "form" should read --from--; line 67, that part of formula reading:



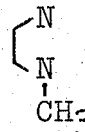
should read



Column 12, line 56, "2-methylrhodanine" should read -- 3-methylrhodanine--. Column 13, line 60, that part of formula reading:



should read



Column 14, line 8, that part of formula reading "methyl2" should read -- methyl-2 --; line 21, that part of formula reading:

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,684,517 Dated August 15, 1972

Inventor(s) Leslie G. S. Brooker and Earl J. VanLare

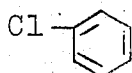
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:



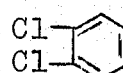
should read



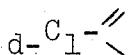
line 53, that part of formula reading:



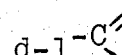
should read



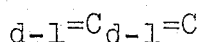
Column 16, line 44, that part of formula reading "CH<sub>2</sub>" should read --CH<sub>3</sub>--; line 62, that part of formula reading "{2-" should read -- {1-(2- ---. Column 18, line 27, "benzonitrazole" should read --benzotriazole--; line 66, "40-60" should read --40:60--. Column 20, line 64, that part of formula reading "pyrazoline" should read --pyrazolin--; line 65, "isoaxazolone" should read --isoxazolone--; line 74, that part of formula reading "imidazoline" should read --imidazolin--. Column 21, line 6, that part of formula reading:



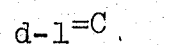
should read



Column 22, line 6, that part of formula reading:



should read



line 13, "R<sub>2</sub>" should read --R<sub>1</sub>--; line 51, that part of formula reading "benzothiazoly" should read --benzothiazolyl--; line 54, "wehein" should read --wherein--.

Page 2 of 2 pages

Signed and sealed this 8th day of May 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents