United States Patent [19]

Hayakawa et al.

[11] **3,881,936**

[45] **May 6, 1975**

[54] **SILVER HALIDE PHOTOGRAPHIC EMULSION CONTAINING THREE SENSITIZING DYES**

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[22] Filed: **Jan. 23, 1974**

[21] Appl. No.: **435,816**

Related U.S. Application Data

[63] Continuation of Ser. No. 202,556, Nov. 26, 1971, abandoned.

[52] **U.S. Cl.** **96/216;** 96/30

[51] **Int. Cl.** **G03c 1/14**

[58] **Field of Search** 96/126, 139

[56] **References Cited**

UNITED STATES PATENTS

2,977,229	3/1961	Jones	96/126
3,574,631	4/1971	Gandino et al.	96/139
3,672,898	6/1972	Schwan et al.	96/126
3,713,828	1/1973	Hayashi et al.	96/139

Primary Examiner—J. Travis Brown

Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] **ABSTRACT**

Silver halide photographic emulsions which contain at least one green-sensitive sensitizing dye or one red-sensitive sensitizing dye in combination with at least one blue-sensitive apomerocyanine dye giving their maximum sensitization in the range of 430 to 530 m is disclosed.

6 Claims, No Drawings

SILVER HALIDE PHOTOGRAPHIC EMULSION CONTAINING THREE SENSITIZING DYES

This is a continuation of application Ser. No. 202,556, filed Nov. 26, 1971, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to improved silver halide photographic emulsions and especially to silver halide photographic emulsions, used for making color separations, which contain a blue-sensitive dye by which gamma balance of three colors is improved.

2. Description of the Prior Art

In the graphic arts industry, the technique of photoengraving has been commonly used to obtain color printing reproductions from a color original.

A continuous gradation black and white negative for color separations is obtainable from a color original by exposing a color film or color plate to light for three color separations through color separation filters and then developing. In this case, a previously prepared masking film is sometimes put between the color original and the sensitive element used for three color separation when the exposure is practiced.

Printing plates are produced from the thus resulting negatives by subsequent steps, and finally a color printing reproduction is obtained. However, printed materials having good color reproduction cannot be obtained when the continuous gradation separation negatives do not have a suitable gamma balance.

In a panchromatic silver halide sensitive element, it is well known that the gamma value in the intrinsic sensitivity range of the silver halide is lower than that in the optically sensitized wavelength range, and consequently, it is normal to prolong the period of developing a blue light exposed element in order to obtain a good gamma balance. However, this method in which the suitable gamma balance is kept by changing the development time is not preferred for the case of using automatic developing apparatus. Further, this method has the fault that the fog of the separation negative made through a blue filter increases if the development time is too long.

Hitherto, many attempts have been made to overcome these above disadvantages. For example, there are a methods which comprise mixing two or more emulsions which have a different optical sensitivity and a different gamma in the sensitive wavelength range (Belgium Pat. No. 703,146), methods which comprise correcting the wavelength range having the lowest gamma (usually the intrinsic sensitivity range) by providing another layer which is sensitive to said range (German Pat. No. 1,447,568) and methods which comprise controlling the gamma balance of the three separation negatives by introducing a filter dye which absorbs light of a high gamma wavelength range into the layers (French Pat. No. 1,551,489).

The processes of these three references are subject to the faults heretofore described.

SUMMARY OF THE INVENTION

We have found a novel means of overcoming the above faults which is quite different from the prior art methods, namely, the desired gamma balance of three color separations can be kept and the above-mentioned faults, that is, lack of suitability for automatic developing apparatus and fog of the blue filter separation negative can be removed by adding certain kinds of blue sensitive sensitizing dyes to silver halide photographic emulsions used for making color separations.

Accordingly, one object of the present invention is to provide a novel color separation film material which has an improved three color gamma balance by adding certain kinds of blue sensitive sensitizing dyes to panchromatically sensitized silver halide photographic emulsions.

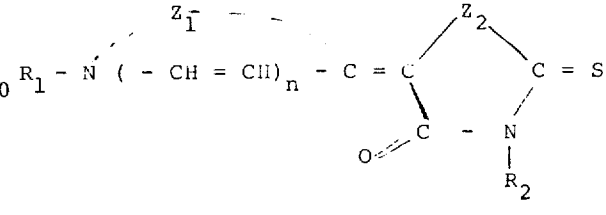
Other objects of this invention will be obvious to those skilled in the art as the description of this invention proceeds.

Preferred blue-sensitive sensitizing dyes used herein which have not been hitherto utilized for silver bromoiodide emulsions because the sensitizing wavelength range coincides with their intrinsic sensitive range, are apomerocyanine dyes giving their maximum sensitization in the range of 430–530mμ, most especially 450–500 mμ when incorporated in the silver halide emulsion.

In the field of graphic arts for color reproductions, the effect of an excellent gamma balance of the three color separations means that the difference between the gamma values obtained by using a blue filter and a green filter is small i.e. the blue gamma values is greater than 90 percent, preferably 95 percent and no greater than 105 percent of the green gamma values by using a green filter and that the gamma value obtained by using a red filter is preferably from 105 to 115 percent of the green gamma values.

DETAILED DESCRIPTION OF THE INVENTION

The blue sensitive sensitizing dyes desirably used in the present invention are represented by the following formula (1).



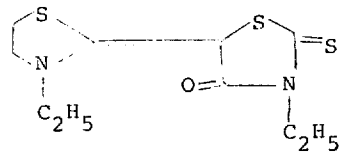
(I)

Z_1 represents a group of atoms necessary to form a 5- or 6- membered heterocyclic nucleus as is employed in the merocyanine dye, the heterocyclic nucleus including, for example, series of the thiazoline nucleus, thiazole nucleus, the benzothiazole nucleus, α-naphthothiazole nucleus, β, β-naphthothiazole nucleus, β-naphthothiazole nucleus, oxazole nucleus, benzoxazole nucleus, α-naphthoxazole nucleus, β, β-naphthoxazole nucleus, β-naphthoxazole nucleus, selenazole nucleus, benzoselenazole nucleus, naphthoselenazole nucleus, quinoline nucleus, pyridine nucleus, benzimidazole nucleus and naphthoimidazole nucleus; Z_2 represents an oxygen atom or sulfur atom; R_1 and R_2 each represent an alkyl group preferably having up to 4 carbon atoms, e.g., methyl group, ethyl group, n-propyl group and n-butyl group, a substituted alkyl group such as hydroxyalkyl group (e.g. β-hydroxyethyl) acetoxyalkyl group (e.g. β-acetoxyethyl), alkoxyalkyl group (e.g. β-methoxyethyl), alkyl group, (e.g. vinylmethyl), carboxylalkyl group (e.g. carboxymethyl group, β-carboxyethyl group, γ-carboxypropyl group, δ-carboxybutyl group),

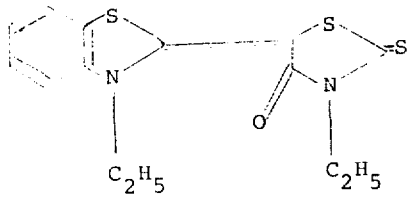
sulfoalkyl group (e.g., β-sulfoethyl group, γ-sulfopropyl group, δ-sulfobutyl group), aralkyl group (e.g. benzyl group, phenethyl group, p-carboxyphenethyl group and a p-sulfophenethyl group), or an aryl group(e.g. a phenyl group) with the proviso that R_2 may represent a hydrogen atom; and *n* represents 0 or 1.

The following blue sensitive sensitizing dyes are illustrative of those which are used in the present invention, but it will be obvious the present invention is not to be limited thereto.

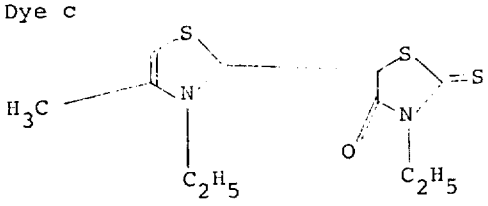
Dye a



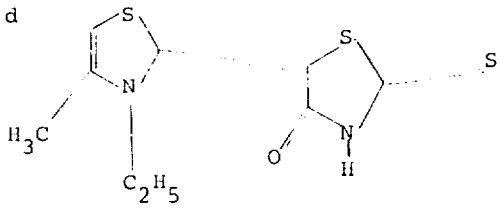
Dye b



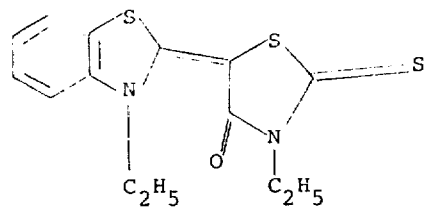
Dye c



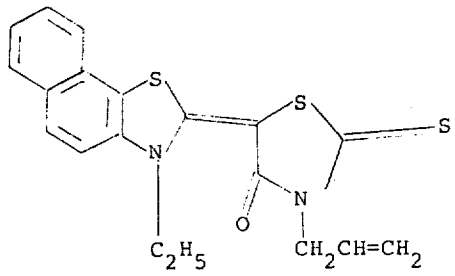
Dye d



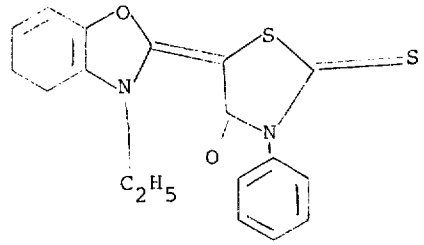
Dye e



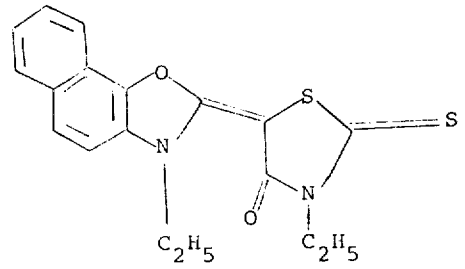
Dye f



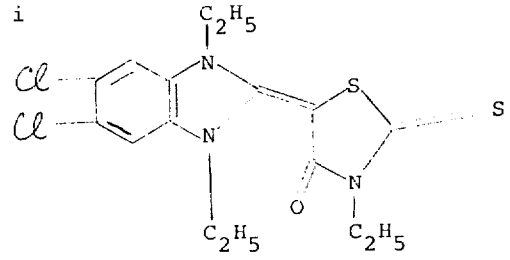
Dye g



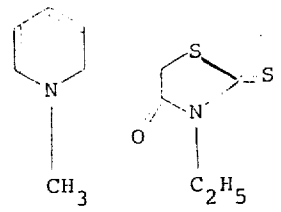
Dye h



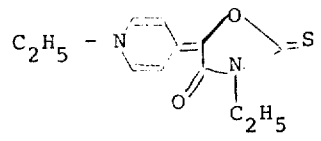
Dye i



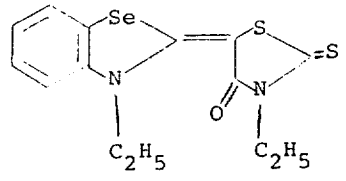
Dye j



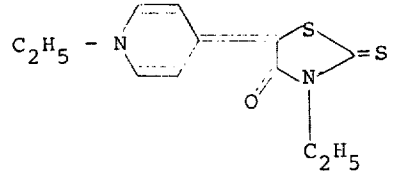
Dye k



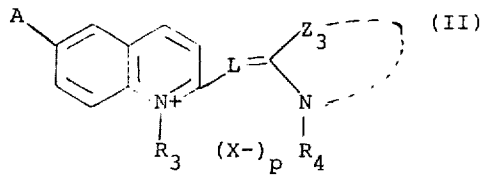
Dye l



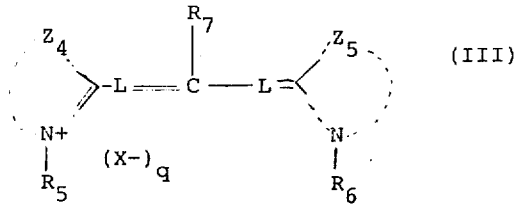
Dye m



Though the gist of the present invention lies in the use of silver halide emulsions containing a blue-sensitive sensitizing dye as described other dyes such as a green-sensitive sensitizing dye and/or a red-sensitive sensitizing due may be added to the emulsion together with the blue-sensitive sensitizing dye. As the green-sensitive sensitizing dye and the red-sensitive sensitizing dye, those which easily form J-aggregation and have a supersensiting relationship with each other are preferred from the viewpoint of obtaining high sensitization. As to J-aggregates, refer to articles from C. E. Mees & T. H. James "The Theory of the Photographic Process," Third Edition, 214ff, 240, 245, 258 and 266. For example, monomethine dyes represented by the following formula (II) of tri-methine dyes represented by the formula (III) are preferred to obtain the above mentioned effect:



(II)



(III)

wherein

Z_3 represents a group of atoms necessary to form a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus or a 2-quinoline nucleus. The term benzothiazole nucleus includes, for example, benzothiazole, 5-methylbenzothiazole, 5-chlorobenzothiazole, 5-methoxybenzothiazole, 5-hydroxybenzothiazole, 5-phenylbenzothiazole, 5,6-dimethylbenzothiazole, 5-methoxy-6-methylbenzothiazole, 5-ethoxy-6-methylbenzothiazole, 5-hydroxy-6-methylbenzothiazole, 5-carboxybenzothiazole and 5-methoxycarbonyl benzothiazole. The term naphthothiazole nucleus includes, for example, β-naphthothiazole and β, β-naphthotiazole. The term benzoselenazole nucleus includes, for example, benzoselenazole, 5-methylbenzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxy-benzoselenazole, 5-phenylbenzoselenazole, 5,6-dimethylbenzoselenazole, 5-methoxy-6-methylbenzoselenazole, 5-methoxy-6-methylbenzoselenazole, 5-ethoxy-6-methylbenzoselenazole and 5-hydroxy-6-methylbenzoselenazole. The term naphthoselenazole nucleus includes, for example, 62 -naphthoselenazole etc.; A represents a hydrogen atom, a lower alkyl group, an alkoxy group or a hydroxy group said alkyl or alkyl moiety being preferred to have up to four carbon atoms. The term lower alkyl group includes, for example, a methyl group and an ethyl group and the term alkoxy group includes, for example, a methoxy group and an ethoxy group;

Z_4 and Z_5 each represent a group of atoms necessary to form a benzimidazole nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus or naphthoselenazole nucleus, or Z_5 can represent a group of atoms necessary to form a benzimidazole nucleus when Z_4 represents an indolenine nucleus. The term benzimidazole nucleus includes, for example, alkyl benzimidazole (e.g., 1-methylbenzimidazole, 1-ethylbenzimidazole, 1-propylbenzimidazole), alkyl (halogeno) benzimidazole (e.g. 1-ethyl-5-chlorobenzimidazole, 1-ethyl-5,6-dichlorobenzimidazole, 1-ethyl-5-bromobenzimidazole, 1-ethyl-5-chloro-6-bromobenzimidazole, 1-ethyl-5,6-dibromobenzimidazole, 1-ethyl-5-fluorobenzimidazole, 1-ethyl-5,6-difluorobenzimidazole), alkyl (cyano)benzimidazole (e.g. 1-ethyl-5-cyanobenzimidazole), alkyl (trifluoromethyl) benzimidazole (e.g. 1-ethyl-5-trifluoromethylbenzimidazole), alkyl (alkyl sulfonyl) benzimidazole (e.g. 1-ethyl-5-methylsulfonylbenzimidazole), alkyl (morpholinosulfonyl) benzimidazole (e.g. 1-ethyl-5-morpholinosulfonylbenzimidazole), alkyl (piperidinosulfonyl) (halogeno) benzimidazole (e.g. 1-ethyl-5-piperidinosulfonyl-6-chlorobenzimidazole), alkyl (aryl) benzimidazole (e.g. 1-ethyl-5-phenylbenzimidazole), alkyl (trifluoromethyl) (sulfonyl) benzimidazole (e.g. 1-ethyl-5-trifluoromethylsulfonylbenzimidazole), alkyl (carboxy) benzimidazole (e.g. 1-ethyl-5-carboxylbenzimidazole) and alkyl (alkoxy carbonyl) benzimidazole (e.g. 1-ethyl-5-methoxycarbonyl-benzimidazole). The term alkyl benzoxazole (e.g. benzoxazole nucleus includes, for example, benzoxazole, 5-methylbenzoxazole, 5,6-dimethyl benzoxazole), halogeno benzoxazole (e.g. 5-fluorobenzoxazole, 5-chlorobenzoxazole), alkoxybenzoxazole (e.g. 5-methoxybenzoxazole) and arylbenzoxazole (e.g. 5-phenylbenzoxazole). The term naphthoxazole nucleus includes, for example, β-naphthoxazole and β,β-naphthoxazole. The term indolenine nucleus includes, for example, 3,3-dimethylindolenine, alkylindolenine (e.g. 3,3,5-trimethylindolenine, 3,3,5,6-tetramethylindolenine), halogenoindolenine (e.g. 3,3-dimethyl -5-chloroindolenine), and alkoxyindolenine (e.g. 3,3-dimethyl-5-methoxyindolenine). The term benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus and naphthoselenazole nucleus can each represent the same nuclei described for Z_3; R_3, R_4, R_5 and R_6 each represent a lower alkyl group of a substituted alkyl group. The term alkyl group includes, for example, a methyl group, ethyl group, n-propyl group and n-butyl group. The term substituted alkyl group includes, for example, a hydroxy alkyl group (e.g. β-hydroxyethyl group), acetoxy alkyl group (e.g. β-acetoxyethyl group, γ-acetoxypropyl group), alkoxy alkyl group (e.g. β-methoxyethyl group, γ-methoxypropyl group), carboxy alkyl group (e.g. β-carboxyethyl group, γ -carboxypropyl group, δ-carboxybutyl group), alkoxy carbonylalkyl group (e.g. β-ethoxycarbonylethyl group, γ-methoxycarbonylpropyl group), sulfoalkyl group (e.g. β-sulfoethyl group, γ-sulfopropyl group, γ-sulfobutyl group, δ-sulfobutyl group), alkyl group (e.g. vinylmethyl group), aralkyl group (e.g. benzyl group, phenethyl group, p-carboxybenzyl group, p-carboxyphenethyl group, p-sulfobenzyl group and p-sulfophenethyl group).

R_7 represents a lower alkyl group such as a methyl group, an ethyl group, a n-propyl group or an aralkyl group such as a phenethyl group. But R_7 represents a hydrogen atom when at least one of Z_4 and Z_5 forms a benzimidazole nucleus;

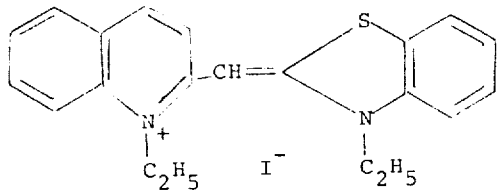
L represents a methine group. L may link to R_4, R_5 and R_6 by a polymethylene group;

p and *q* each represent 0 or 1, but p and q are 0 when the dye forms an inner salt; and

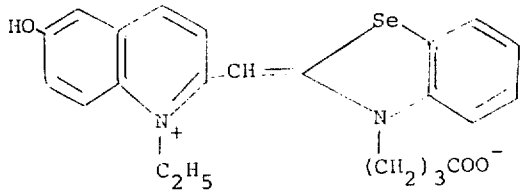
X represents an acid anion which is commonly used in the field of cyanine dyes, such as chloride ion, bromide ion, iodide ion, thiocyanate ion, perchlorate ion, p-toluenesulfonate ion, benzenesulfonate ion, methylsulfate ion and ethylsulfate ion.

In the following, green-sensitive sensitizing dyes and red-sensitive sensitizing dyes are described. But they are not intended to be limitative thereof.

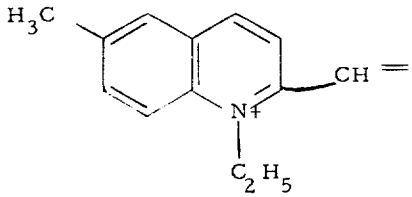
Dye I

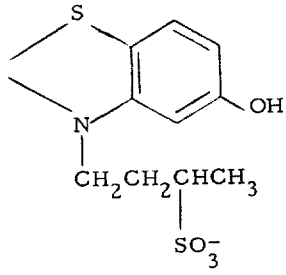


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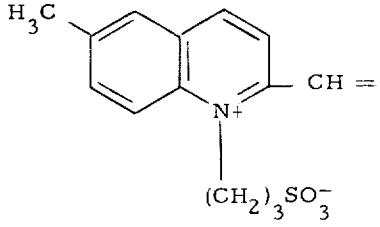


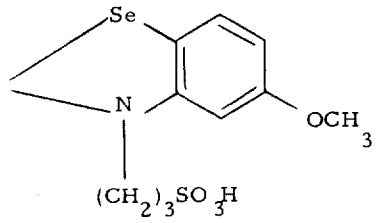
Dye III



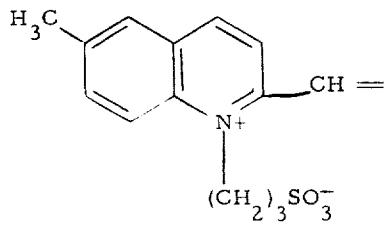


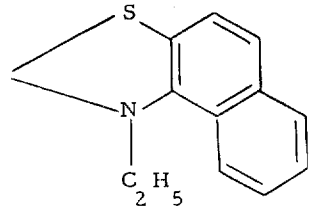
Dye IV



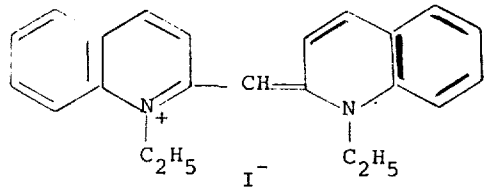


Dye V

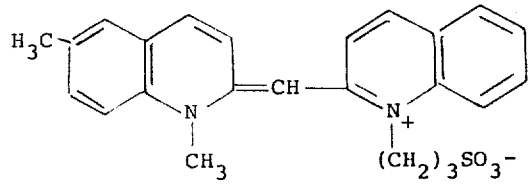




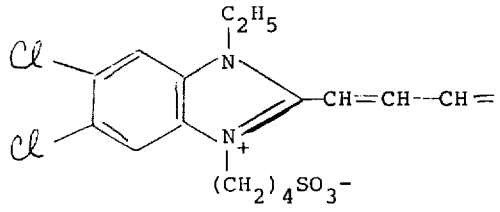
Dye VI

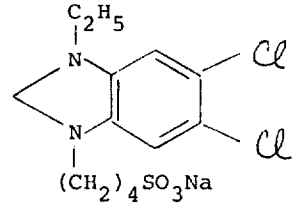


Dye VII

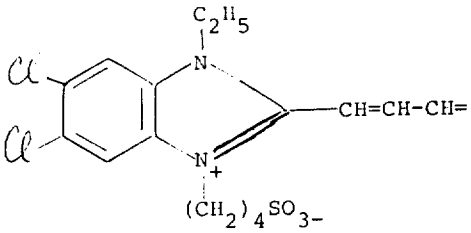


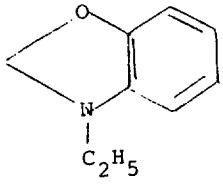
Dye VIII



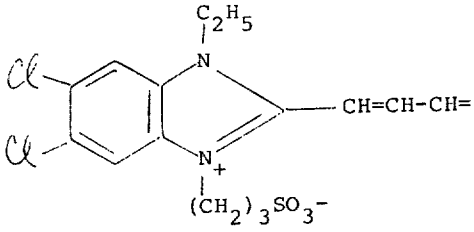


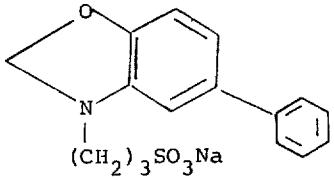
Dye IX



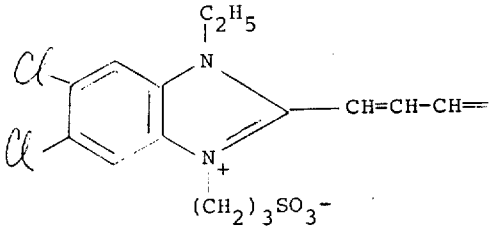


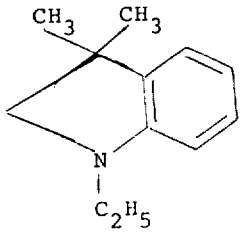
Dye X



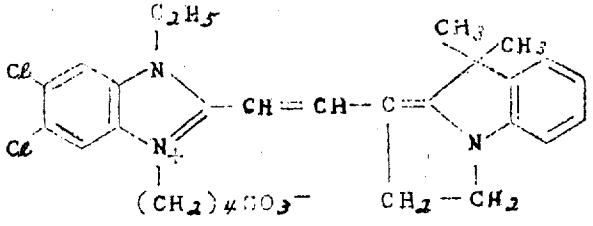


Dye XI

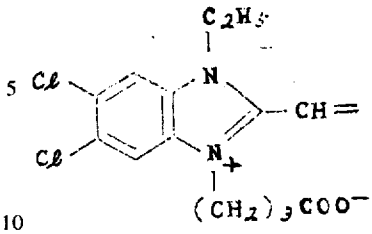


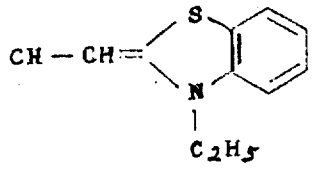


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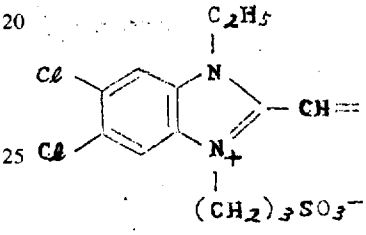


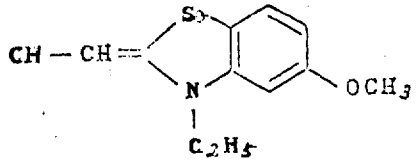
Dye XIII



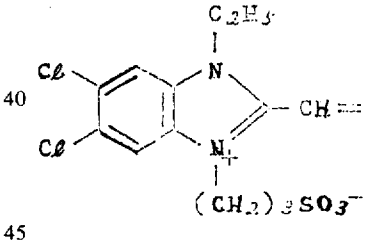


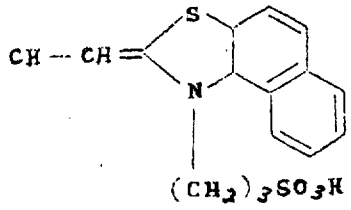
Dye XIV



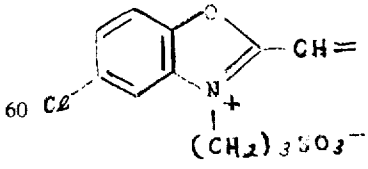


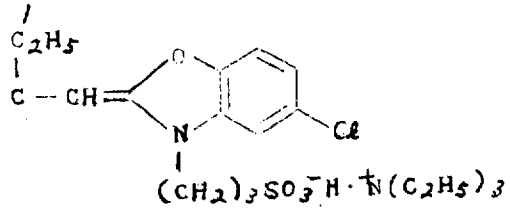
Dye XV



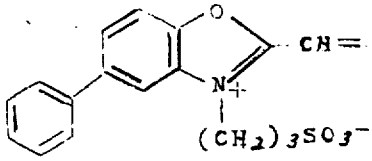


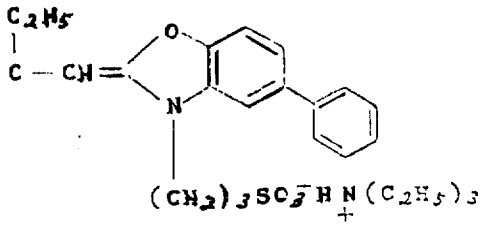
Dye XVI



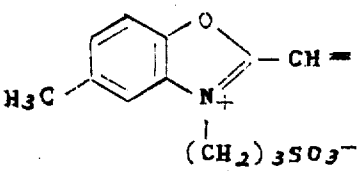


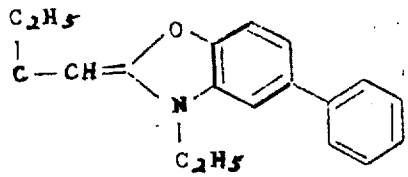
Dye XVII



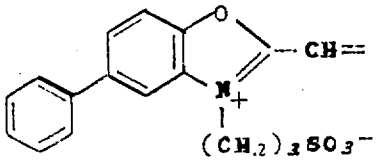


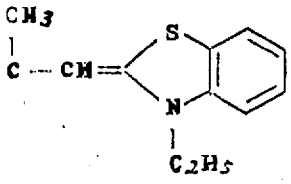
Dye XVIII



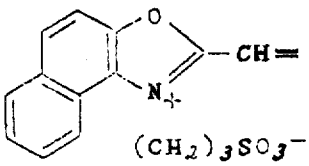


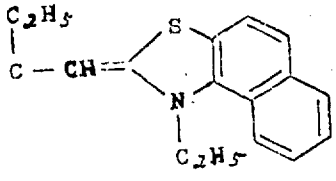
Dye XIX



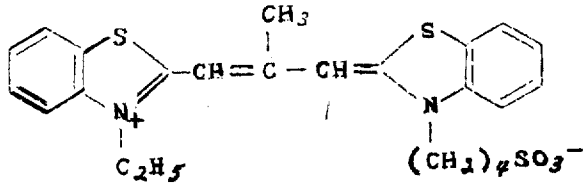


Dye XX

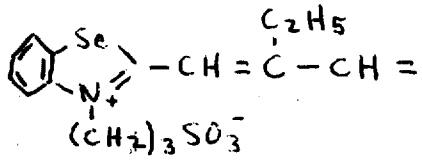


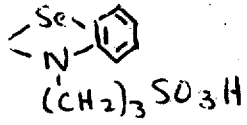


Dye XXI

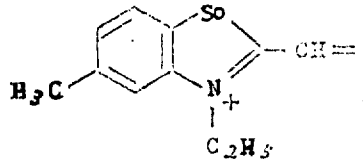


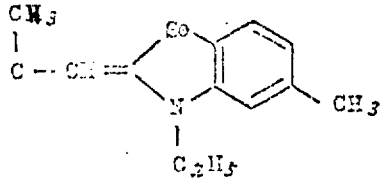
Dye XXII



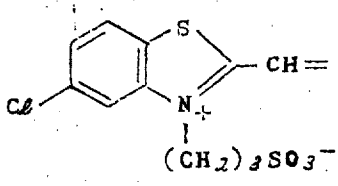


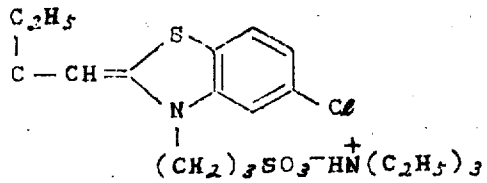
Dye XXIII



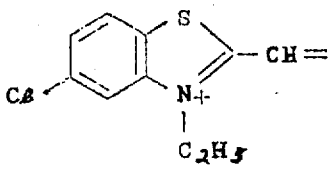


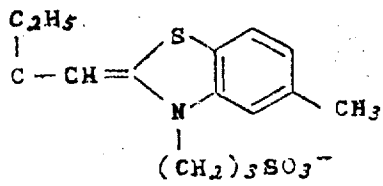
Dye XXIV



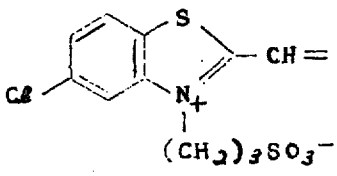


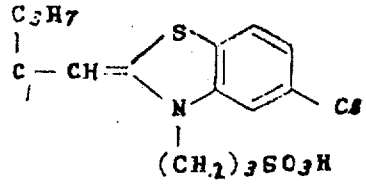
Dye XXV



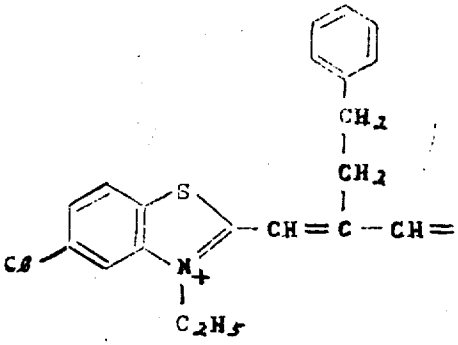


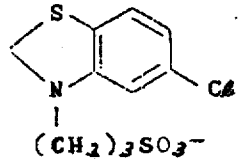
Dye XXVI



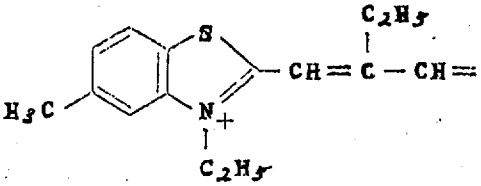


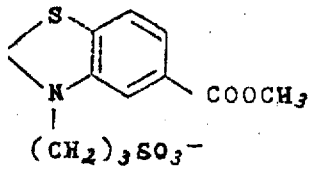
Dye XXVII



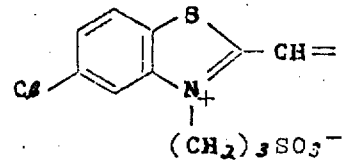


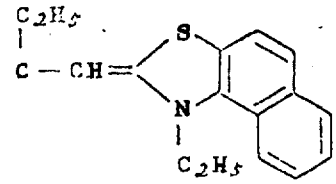
Due XXVIII



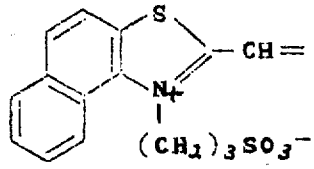


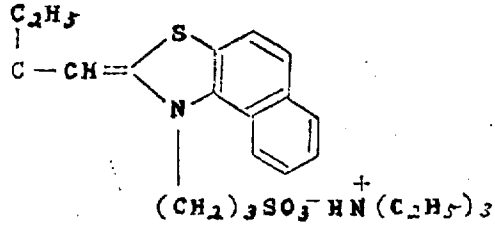
Dye XXIX



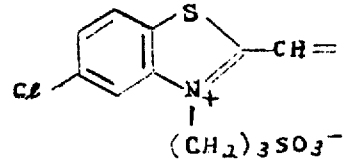


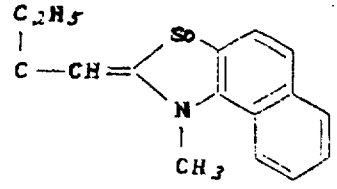
Dye XXX





Dye XXXI





The sensitizing dyes used in the present invention can be easily synthesized by persons skilled in the art with reference to "The Cyanine Dyes and Related Compounds" written by F. M. Hamer (Interscience Publishers), U.S. Pat. No. 2,493,747, U.S. Pat. No. 2,493,748, U.S. Pat. No. 2,519,001, U.S. Pat. No. 2,526,632, U.S. No. 2,503,776, German Pat. No. 929,080, British Pat. No. 840,223, U.S. Pat. No. 3,196,017, U.S. Pat. No. 3,177,210, German Pat. No. 1,072,765, U.S. Pat. No. 2,912,329, British Pat. No. 812,924, French Pat. No. 1,397,876 and French Pat. No. 1,337,260.

In the present invention, a mixed silver halide emulsion, particularly a silver bromoiodide emulsion is desirably used as the silver halide emulsion. A preferred emulsion contains 0.01–0.10 mols, particularly 0.03–0.06 mols, of silver iodide per one mol of silver in

the silver halide composition. Mixed silver halide emulsions may, of course, be used which contain a small amount of silver chloride (for example, less than 0.2 mols per one mole of silver) in order to improve gradation etc.

As the binder of the silver halide emulsions used for making color separations in the present invention, hydrophilic colloid such as gelatin, modified gelatin, albumin, cellulose derivatives and polyvinyl compounds may be used.

The silver halide emulsion can be produced by adding a silver salt solution to a halogen salt solution by the well known acid process, neutral process, or semi- or full ammonia process, or may be produced by adding a solution containing all or part of the halogen salt simultaneously with the silver salt solution to a gelatin solution free of the halogen salt or containing a part of the halogen salt.

The silver halide emulsion used for this invention may be chemically sensitized using a great variety of known material compounds containing unstable sulfur e.g. ammonium thiocyanate, allylthiourea (for example, refer to "P. Glafkides Chimie et Physique Photographiques," Third Edition Publications photo-cinema, Paul Montel, Paris, 1967, pages 350 and 351), or complex salts of monovalent gold and thiocyanic acid (refer to the above-mentioned book, page 354), or polyalkylene oxide derivatives or with a combination of these substances, which are well known in this art.

The emulsions may also be stabilized with various antifogging agents as are known to the art (refer to, for example, Kagaku Shashin Binran, Second Volume, pages 32–47, published by Maruzen Co., 1959, edited by Shinichi Kikuchi et al.) and may be hardened with various gelatin hardening agents as is well known to the art, such as aldehyde compounds (refer to Kagaku Shashin Binran, pages 30–32) polyfunctional ethyleneimine compounds (refer to, for example, Japanese Pat. No. 309,487), epoxy compounds (refer to, for example, Japanese Pat. No. 257,564), active halogen compounds (refer to, for example, French Pat. No. 1,379,255) and active vinyl compounds (refer to, for example, German Pat. No. 872,153).

The emulsions may further contain saponin and other well known coating agents, for example, nonionic surface active agents, anionic surface active agents and amphoteric surface active agents, such as polyoxyethylene nonylphenyl ethers, sodium alkylbenzene sulfonates and N-methyl alkyltaurides, or anionic surface active agents containing ethylene oxide chains, e.g., see Belgian Pat. No. 650,004.

Further, the emulsions may contain various gelatin plasticizers as are known to the art (for example, see British Pat. No. 1,111,930) and covering power increasing agents (for example see French Pat. No. 1,383,523).

In the present invention, though special means are not required for the use of the blue-sensitive sensitizing dyes, it is preferred to add the blue-sensitive sensitizing dyes to the emulsions prior to adding other sensitizing dyes so as to facilitate the preferential adsorption of the blue sensitive dyes onto the silver halide. In such a case, it is preferred to add the blue-sensitive dyes as a solution in an inert solvent, e.g., methanol, ethanol, acetone, methyl cellosolve etc. The blue-sensitive sensitizing dye can, of course, be used in combination with one or more other blue-sensitive sensitizing dyes.

The total amount of the blue-sensitive sensitzing dyes added is from 1×10^{-5} to 8×10^{-4} mols, preferably 3×10^{-5} to 3×10^{-4} mols per mol of silver halide which is present.

EXAMPLES 1–11

30cc of a 1/300 mol methanol solution of the above-described blue-sensitive sensitizing dyes *a* – *k* was added to 1 kg of an AgBrI emulsion containing 5 mol% of AgI, respectively. After one hour, a solution prepared by dissolving 100 mg of Dye IV, 30 mg of Dye XXII, and 20 mg of Dye XXIII in 100cc of methanol was added to the emulsion. A salt of the art anti-fogging agent, a hardener and a coating agent then was added. The resulting composition was applied to a polyethylene terephthalate base. As a comparison example, an identical emulsion free of blue-sensitive dye was prepared and applied to an identical base.

The resulting coated elements were exposed for 10 seconds to a 500 W tungsten lamp using Fuji color separation Filter No. 8 (red), No. 32 (green), No. 31 (blue) and a neutral filter. The elements were then developed at 20°C for 5 minutes using a developing solution having the following composition.

N-Methyl-p-aminophenol sulfate	1.0g
Anhydrous sodium sulfite	75.0g
Hydroquinone	9.0g
Sodium carbonate monohydrate	30.0g
Potassium bromide	5.0g
Water to make	1.0liter

The γ - values obtained by determining the density of each separation image are shown by the following tabulation.

Example No.	Dye	Red Filter	Green Filter	Blue Filter
Control	—	1.80	1.70	1.45
1	a	1.74	1.65	1.62
2	b	1.82	1.75	1.56
3	c	1.76	1.72	1.70
4	d	1.68	1.60	1.60
5	e	1.85	1.68	1.52
6	f	1.63	1.60	1.44
7	g	1.75	1.62	1.50
8	h	1.80	1.65	1.56
9	i	1.75	1.66	1.60
10	j	1.78	1.75	1.70
11	k	1.70	1.55	1.45

EXAMPLE 12

30cc of a 1/300 mol methanol solution of blue-sensitive sensitizing dye c was added to 1 kg of an AgClBrI emulsion containing 3 mol% AgI and 5 mol% of AgCl. After one hour, a solution prepared by dissolving 100 mg of Dye VII, 20 mg of Dye XXIII and 30 mg of Dye XXIV in 100cc of methanol was added to the emulsion. Then a standard antifogging agent, hardener and coating agent as are used by the art were added.

The resulting composition was applied to a polyethylene terephthalate base. As a comparison sample, an identical emulsion free of the blue-sensitive sensitizing dye was prepared and applied identically at the same thickness. The resulting coated elements were exposed and developed by the Examples 1 – 11. The values ob-

tained by determining the density of each separation image as shown by the following tabulation.

Example No.	Dye	Red Filter	Green Filter	Blue Filter
Control	—	2.10	2.03	1.70
12	c	2.00	1.88	1.85

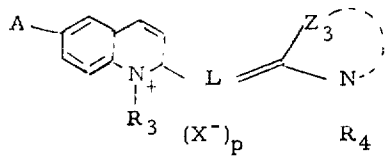
It will be understood from the above-mentioned examples that the effect of the present invention is excellent.

It will further be understood that the foregoing Examples are illustrative only and not intended to be limiting.

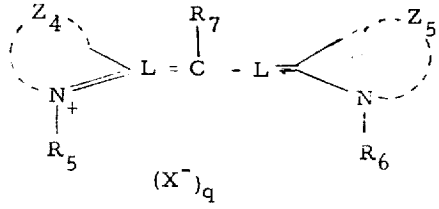
What is claimed is:

1. A black-and-white silver halide emulsion suitable for a three-color separation process, having the improved blue-to-green and red-to-green gamma balance, which contains at least one sensitizing dye represented by Formula II and at least one sensitizing dye represented by Formula III in combination with at least one apomerocyanine dye represented by the Formula I:

Formula (II):



Formula (III):



wherein

Z_3 represents the atoms necessary to form a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus or a 2-quinoline nucleus;

A represents a hydrogen atome, a lower alkyl group, an alkoxy group or a hydroxy group;

Z_4 and Z_5 each represent the atoms necessary to form a benzimidazole nucleus, benzoxazole nucleus, naphthoxazole nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus or naphthoselenazole nucleus, or Z_5 can represent the group of atoms necessary to form an indolenine nucleus when Z_4 represents a bonzimidazole nucleus;

R_3, R_4, R_6 each represent a lower alkyl group or a substituted alkyl group; wherein the substituted alkyl group represented by R_3, R_4, R_5 and R_6 is selected from the group consisting of hydroxyalkyl, acetoxyalkyl, alkoxyalkyl, carboxyalkyl, alkoxycarbonylalkyl, sulfoalkyl, allyl and aralkyl

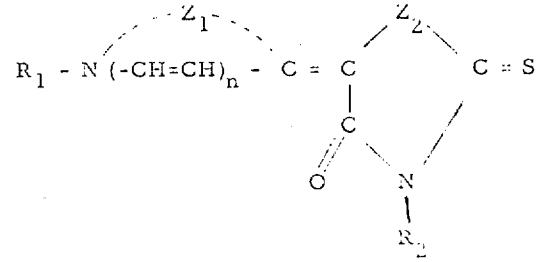
R_7 represents a lower alkyl group or an aralkyl group with the proviso that R_7 represents a hydrogen atom when at least one of Z_4 and Z_5 forms a benzimidazole nucleus;

L represents a methine group or may link to R_4, R_5 and R_6 by a polymethylene group;

p and q each represent 0 or 1 with the proviso that p and q are 0 when the dye forms an inner salt; and

X represents an acid anion,

Formula (I)



wherein:

Z_1 represents the atoms necessary to form a heterocyclic nucleus selected from the group consisting of a thiazoline nucleus, a thiazole nucleus, a benzolthiazole nucleus, an alpha-naphthothiazole nucleus, a beta, beta-naphthothiazole nucleus, a beta-naphtholthiazole nucleus, an oxazole nucleus, a benzolxazole nucleus, an alpha-naphthoxazole nucleus, a beta, beta-naphthoxazole nucleus, a beta-naphthoxazole nucleus, a selenazole nucleus, benzoselenazole nucleus, a naphthoxazole nucleus, a selenazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a quinoline nucleus, a pyridine nucleus, a benzimidazole nucleus and a naphthoimidazole nucleus;

Z_2 represents an oxygen atom or a sulfur atom, R_1 and R_2 represent an alkyl group, a substituted alkyl group selected from the group consisting of a hydroxyalkyl group, an acetoxyalkyl group, an alkyloxyalkyl group, an allyl group, a carboxyalkyl group, a sulfoalkyl group and an aralkyl group, or an aryl group, and further wherein R_2 may be hydrogen atom, and n represents an integer of 0 or 1.

2. The silver halide photographic emulsion of claim 1, wherein Z_3 of Formula II represents the group of atoms necessary to form a benzothiazole nucleus, a benzoselenazole nucleus or a 2-quinoline nucleus, A represents a lower alkyl group, Z_4 and Z_5 of Formula III each represents the group of atoms necessary to form a benzothiazole nucleus or a benzoselenazole nucleus, said benzothiazole nucleus or said benzoselenazole nucleus being unsubstituted or substituted by at least one lower alkyl group or halogen atom.

3. Silver halide photographic emulsion as claimed in claim 1 wherein the total amount of the blue-sensitive sensitizing dyes added is from 1×10^{-5} to 8×10^{-4} moles per one mole of silver halide.

4. Silver halide photographic emulsion as claimed in claim 1 wherein at least one of the green-sensitive sensitizing dye and the red-sensitive sensitizing dye is one which easily forms J-aggregation.

5. Silver halide photographic emulsion as claimed in claim 1 wherein the silver halide is silver bromoiodide or silver chlorobromoiodide.

6. A photographic sensitive material comprising an emulsion layer containing a silver halide photographic emulsion as claimed in claim 1.

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