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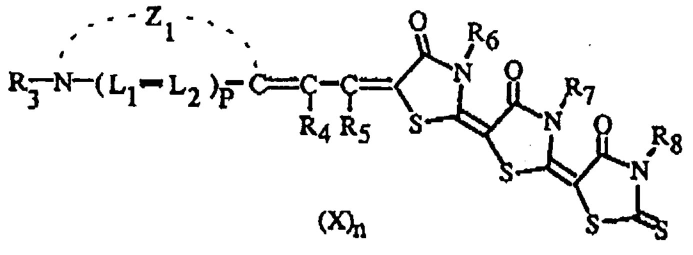
(54) Photographic elements with particular sensitized silver halide emulsions

(57) A photographic element (which is preferably a Graphic Arts element) a light sensitive silver halide emulsion sensitized with a dye of formula (I):



(I)

wherein:

R_3 is an alkyl group, alkenyl group, or aryl group
R_4 and R_5 are each hydrogen, an alkyl group, alkenyl or aryl group;
R_6, R_7 and R_8 are, independently, an alkyl group, alkenyl group, aryl group, or H;
the dye has at least three acid or acid salt substituents; and
each L independently represents a methine group;
p is 0 or 1;
Z_1 represents the atoms necessary to complete a 5- or 6-membered heterocyclic ring group;
$(X)_n$ represents counterions as needed to balance the charge on the molecule.

Dyes of formula (I) produce low stain in photographic elements of the present invention, while still providing the silver halide with good light sensitivity.

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Description

Field of the Invention

This invention relates to photographic elements sensitized with particular tetranuclear complex merocyanine dyes.

Background

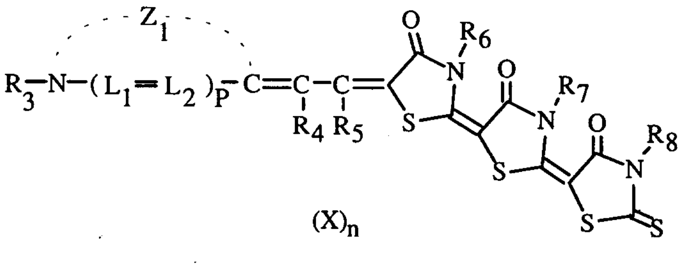
The procedures for spectrally sensitizing photographic silver halide emulsions so as to extend their sensitivity range are generally well known. In particular, for some Graphic Arts applications it may be necessary to sensitize the silver halide grains to specific wavelengths, for example to light of wavelength 633nm for helium-neon gas laser (HN) or about 670nm for laser diode (LD) and red light emitting diodes (LED) devices. There are numerous examples of suitable sensitizing dyes for these purposes, for example, see The Theory of the Photographic Process, T.H.James, editor, 4th edition, pages 195-234 for leading references. In British Patent Specification 1,471,701 is described the use of tri-nuclear cyanine dyes for such purposes. However, in Graphic Arts applications, sensitizing dyes are also required to provide many other qualities, such as low post-process stain while still providing good speed. Post-process stain is distracting and is therefore considered undesirable. It can in some circumstances cause undesirably high minimum ultraviolet light density.

The use of trinuclear merocyanine sensitizing dyes is described in US 5,116,722, EP 0 540 295, US 3,682,640 and USSR Inventor's Certificate No. 212,749. Specific tetranuclear merocyanine dyes for sensitizing photographic emulsions are described in GB 489,335.

However, it would be desirable to provide tetranuclear merocyanine dyes which have low stain and which still provide good sensitization.

Summary of the Invention

The present invention then, provides a photographic element comprising a light sensitive silver halide emulsion sensitized with a dye of formula (I):



(I)

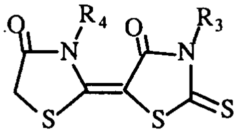
wherein:

R_3 is an alkyl group, alkenyl group, or aryl group
R_4 and R_5 are each hydrogen, an alkyl group, alkenyl or aryl group;
R_6, R_7 and R_8 are, independently, an alkyl group, alkenyl group, aryl group, or H;
the dye has at least three acid or acid salt substituents; and
each L independently represents a methine group;
p is 0 or 1;
Z_1 represents the atoms necessary to complete a 5- or 6-membered heterocyclic ring group;
$(X)_n$ represents counterions as needed to balance the charge on the molecule.

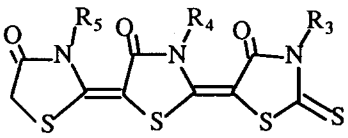
Dyes of formula (I) produce low dye stain in the photographic elements of the invention, while still providing the silver halide with good light sensitivity.

Embodiments of the Invention

It will be understood throughout this application that formulae shown for any dyes or precursor compounds of the present invention are to be interpreted as including all stereoisomers where possible. This is particularly true of isomers about a double bond. Thus, considering the following formulae:

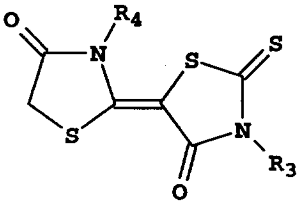


(Ib)

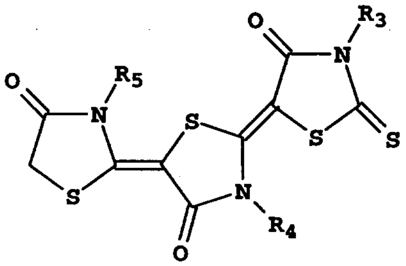


(Ic)

It will be understood that the above formulae, as written, will, for example, respectively include stereoisomers such as structures:



(Ib')



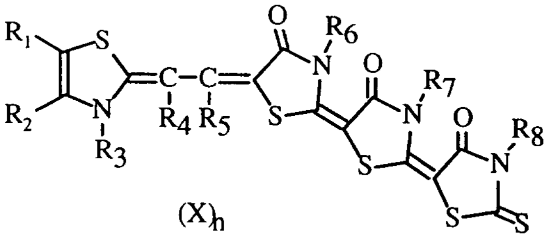
(Ic')

In the present application, reference to any chemical "group" (such as alkyl group, aryl group, heteroaryl group, and the like) includes the possibility of it being both substituted or unsubstituted (for example, alkyl group and aryl group include substituted and unsubstituted alkyl and substituted and unsubstituted aryl, respectively). Generally, unless otherwise specifically stated, substituent groups usable on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for the photographic utility. It will also be understood throughout this application that reference to a compound of a particular general formula includes those compounds of other more specific formula which fall within the general formula definition.

With regard to dyes of formula (I), Z_1 may particularly represent the atoms which complete an oxazole group, benzoxazole group, naphthoxazole group, thiazole group, benzthiazole group, naphthothiazole group, imidazole group, benzimidazole group, naphthimidazole group, pyridine group, quinoline group, 1,3,4-thiadiazole group, thiazoline group, selenazole group, benzoselenazole group, naphthoselenazole group, benzotellurazole group, or naphthotellurazole group.

Dyes of formula (I) preferably have at least R_6, R_7 and R_8 with an acid or acid salt substituent (with preferably one such substituent on each of R_6, R_7 and R_8). Furthermore, dyes of formula (I) may particularly have at least 4 acid or acid salt substituents (which includes the possibility of 5, 6 or more such substituents). Preferably at least three, and most preferably all four, of R_3, R_6, R_7 and R_8 have an acid or acid salt substituent (with each of them preferably having only one such substituent). However, the acid or acid salt substituents need not necessarily be located on the specified groups. For example, R_3, R_4 and/or R_5 could have one or more acid or acid salt substituents.

Preferably, the dye of formula (I) is of structure (Ia) below:



(Ia)

In the above formula (Ia), R_1 and R_2 independently represent an alkyl group (for example, methyl, ethyl, propyl, butyl), an alkenyl group, an alkoxy group (for example, methoxy, ethoxy, propyloxy, butoxy), an alkylthio group (for example, methylthio, ethylthio, propylthio, butylthio), an acyl group, an acyloxy group, an alkoxycarbonyl group, an alkylsulfonyl group, a carbamoyl group, or a sulfamoyl group. Additionally, R_1 and R_2 can independently represent an aryl group (such as phenyl) or an arylthio group. R_1 and R_2 can further independently represent a heteroaromatic group, hydrogen, hydroxy, halogen, carboxy, or cyano, or R_1 and R_2 together represent the atoms necessary to complete an annelated benzene, naphthalene or anthracene group (it will be understood that in any case where these are substituted, such "substituents" do not include another annellated aromatic ring, that is a benzene group does not include naphthalene).

In any of the above formulae, R_3, R_6, R_7 and R_8 may particularly independently be, a 1 to 5 carbon atom alkyl group. R_4 and R_5 may particularly independently be, a 1 to 5 carbon atom alkyl group or a hydrogen (preferably R_4 is hydrogen and R_5 is hydrogen or unsubstituted alkyl such as methyl or ethyl). As to the counterions $(X)_n$, X represents the counterion while n is 0 or a positive integer (for example, n is 1 to 4, or even to 5 or 6) depending on the charge of the counterion X and the number of them needed to balance the charge on the molecule. X, if required to be present to balance the charge, is preferably a substituted or unsubstituted ammonium ion or an alkali metal ion (for example, Na^+ or K^+). However, if the dye does not carry any acid salt groups (that is, any acid groups are present as the free acid form) then no counterions may be necessary.

All heterocyclic and aromatic groups (which includes aryl and arylthio) described above, may particularly have from 6 to 20, or from 6 to 15, carbon atoms. All heteroaryl groups may particularly have from 4 to 7 (or 5 or 6) carbon atoms, with 1, 2, 3 or 4 heteroatoms selected from 0, N, S or Si. Examples of aromatic groups include phenyl, tolyl, and the like, any of which may be substituted or unsubstituted. Examples of heteroaryl include thienyl, pyrrazolo, and furyl.

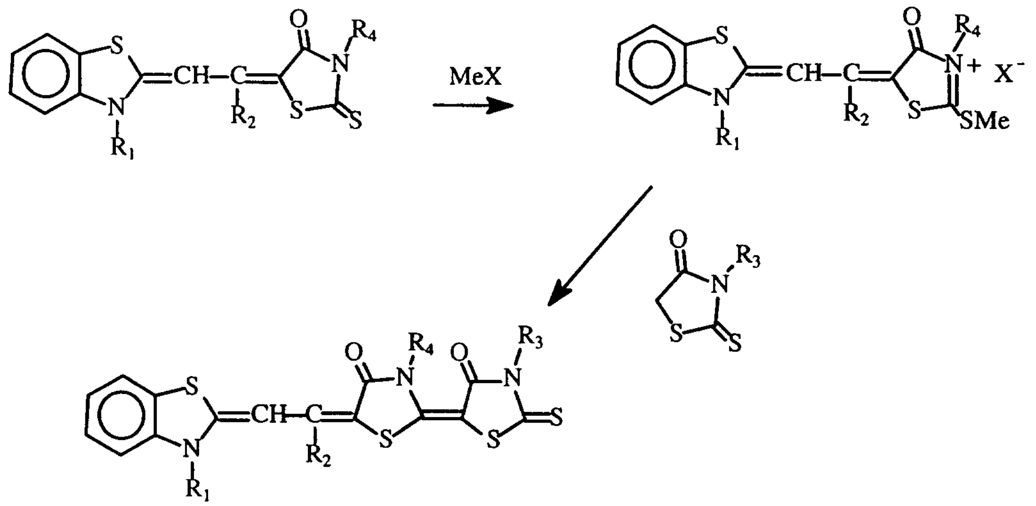
All alkyl, alkoxy, alkenyl, alkylthio, acyl, acyloxy, alkoxycarbonyl, alkylsulfonyl, carbamoyl, or sulfamoyl groups described herein, may particularly have from 1 to 20 carbon atoms (or 1 to 10 or 1 to 8 carbon atoms; or even 1, 2, 3 or 4 carbon atoms). All of these groups may be linear, branched or cyclic. Examples of alkyl include methyl, ethyl, propyl, and the like, and substituted alkyl groups (preferably a substituted lower alkyl containing from 1 to 8 carbon atoms) such as hydroxyalkyl group (for example, 2-hydroxyethyl), a sulfoalkyl group, (for example, 4-sulfobutyl, 3-sulfopropyl) and the like.

As to the acid or acid salt groups described above, such groups include carboxy, sulfo, phosphato, phosphono, sulfonamido, sulfamoyl, or acylsulfonamido (groups such as $-CH_2-CO-NH-SO_2-CH_3$) groups. Note that the foregoing words are used to define only the free acid groups or their corresponding salts, and do not include esters where there is no ionizable or ionized proton. Particularly preferred are the carboxy and sulfo groups (for example, 3-sulfobutyl, 4-sulfobutyl, 3-sulfopropyl, 2-sulfoethyl, carboxymethyl, carboxyethyl, carboxypropyl and the like).

Substituents on any of the specified substituent groups defined above, can include halogen (for example, chloro, fluoro, bromo), alkoxy (particularly 1 to 10 carbon atoms; for example, methoxy, ethoxy), substituted or unsubstituted alkyl (particularly of 1 to 10 carbon atoms, for example, methyl, trifluoromethyl), amido or carbamoyl (particularly of 1 to 10 or 1 to 6 carbon atoms), alkoxycarbonyl (particularly of 1 to 10 or 1 to 6 carbon atoms), and other known substituents, and substituted and unsubstituted aryl ((particularly of 1 to 10 or 1 to 6 carbon atoms) for example, phenyl, 5-chlorophenyl), thioalkyl (for example, methylthio or ethylthio), hydroxy or alkenyl (particularly of 1 to 10 or 1 to 6 carbon atoms) and others known in the art. Additionally, any of the substituents may optionally be non-aromatic.

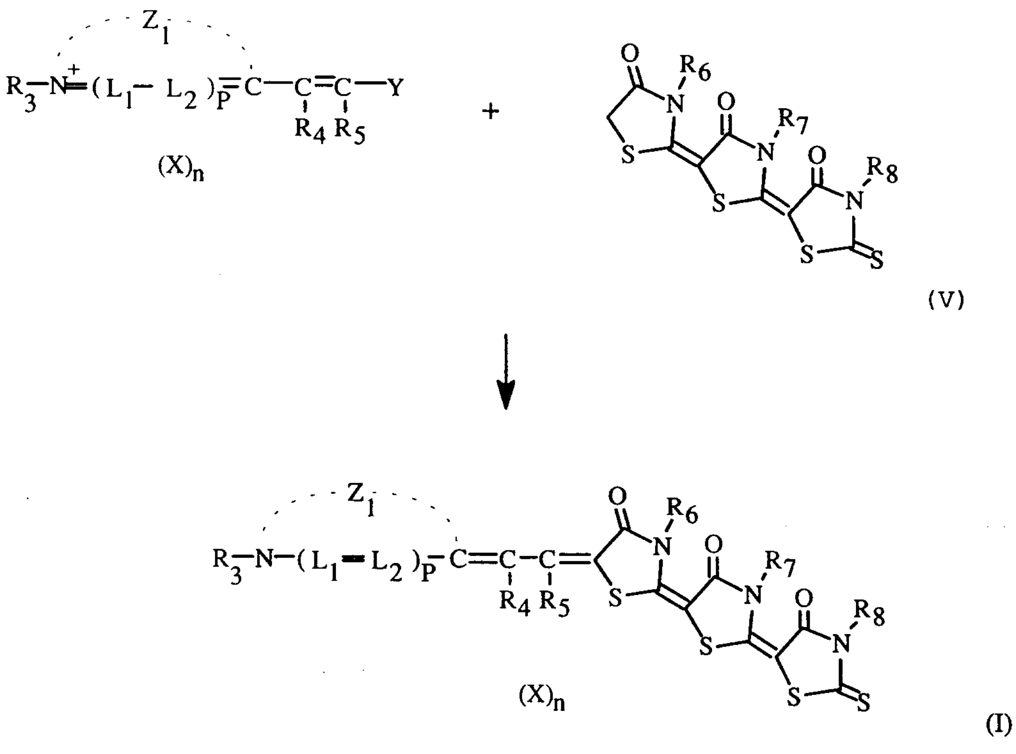
Dyes of formula (I) particularly provide on the light sensitive silver halide emulsion, a wavelength of maximum sensitivity ("λmax") which is between about 550 nm to 750 nm, but preferably between 600 to 690 nm (most preferably 620 to 680 nm).

Dyes of the type of formula (I) can be synthesized by using the usual method for the synthesis of complex trinuclear merocyanines. That is, trinuclear merocyanine dyes are known to be prepared by S-alkylation of the corresponding merocyanine, followed by displacement of the alkylthio group in the alkylated dye by a rhodanine, as shown in the following scheme.



Tetra-nuclear merocyanines are described in UK 489,335 and were synthesized in a manner analogous to that described above for tri-nuclear merocyanines, by using a tri-nuclear merocyanine as starting material. The tetranuclear merocyanine dyes of formula (I) can be prepared in a similar manner. However, such a method often gives poor yields and is inconvenient, in that a merocyanine dye must first be synthesized as the starting material for the synthesis. Therefore, it is preferred to prepare dyes of formula (I) using the method described in detail in U.S. patent application by Mee filed by Express Mail on February 28, 1995, and entitled "METHOD OF SYNTHESIZING DYES AND PRECURSOR COMPOUNDS THEREFOR" (Attorney Docket No. 69380GMS). The foregoing patent application and all other references cited in the present application, are incorporated herein by reference.

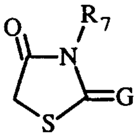
In particular, dyes of formula (I) are preferably prepared by the following reaction scheme:



wherein: Z_1, X, n, and each of R_3 through R_8 are as defined above in connection with formula (I), and Y is a leaving group. Examples of Y include an alkoxy or alkylthio (either particularly of 1 to 20, 1 to 10, or 1 to 6 carbon atoms), acetanilido or arylthio group (either particularly of 6 to 20, or 6 to 12 carbon atoms), or halogen (particularly chloro).

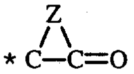
To produce low-staining dyes, including complex merocyanine sensitizing dyes, it is often desirable to provide the dye with one or more water solubilizing groups. Particularly useful as water solubilizing groups are carboxyalkyl and/or sulfoalkyl substituents. Any compounds of formulae (I) (including formula (Ia)) which contain N-carboxyalkyl substituents are advantageously synthesized with the carboxyl function protected as an ester. It is convenient to cleave the ester to a carboxylic acid, or a salt thereof, either before or after dye formation. This is preferably done by acid hydrolysis (since basic hydrolysis tends to induce decomposition of intermediates or dyes). The hydrolysis can be carried out typically between about 20°C to about 100°C. The optimum time and temperature for hydrolysis of each compound may vary (the optimum conditions being the best compromise between rapid hydrolysis and minimum decomposition). The acid may for example be aqueous HCl (for example, 20-30% by weight of HCl). In some cases the dye or intermediate may be insufficiently soluble in this medium and a co-solvent may be required. Trifluoracetic acid has been found to be particularly useful as a co-solvent.

Starting compounds of formula (V) in the above scheme are prepared by using a cyclic ketomethylene as the starting material. In general, the method used can be represented as a method of synthesizing a compound of formula (VIa):

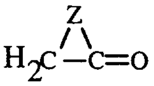


(VIa)

wherein R_7 is defined above in connection with the dye of formula (I), and G represents a ketomethylene group as shown below:

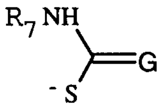


where * is the point of attachment of G as shown in formula (Ia), and Z represents the atoms necessary to complete a subsituted or unsubstituted 4 to 7-membered (preferably 5 or 6) alicyclic or heterocyclic ring. In particular, in synthesizing compound (V), Z will represent the rhodanine ring of formula (V) which carries the R_8 substituent on the nitrogen. The method in such case comprises reacting



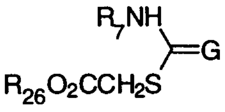
with an isothiocyanate of formula (VII) in the presence of a base to obtain a compound of formula (VIII):

$$R_7\text{-}N{=}C{=}S \qquad \text{(VII)}$$



(VIII)

Compound (VIII) is then reacted with a haloacetic acid or a haloacetic ester of formula $XCH_2CO_2R_{26}$, wherein X is a halogen and R_{26} is H, alkyl group or aryl group, to obtain compound (IX):



(IX)

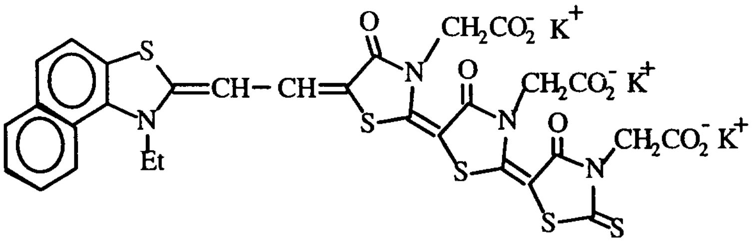
and then HOR_{26} is eliminated to form compound (VIa).

It will be seen that using the resulting product, the process can again be repeated to add another ring to obtain the compound of formula (V). In particular, a 1,3-thiazolidin-4-one ring can be added to such starting ketomethylene reagent which already has two rings.

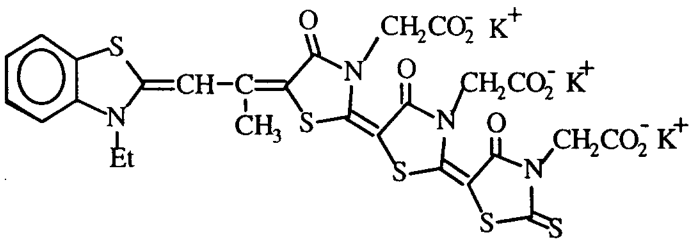
Suitable bases for carrying out the reaction of the ketomethylene or malononitrile with the isothiocyanate, are any base which is sufficiently strong to remove a proton from their methylene group, which then facilitates the attack of the carbon of the isothiocyanate group. Typically, such a base will have a pKa of at least 10, more preferably 12 (and most preferably 13). Preferred bases are organic bases such amidine compounds, such as 1,8-diazabicyclo[5.4.0] undec-7-ene ("DBU"), 1,5-diazabicyclo[4.3.0] non-5-ene ("DBN"), or 1,1,3,3,-tetramethylguanidine.

The step in which the water or alcohol is eliminated to form the 1,3-thiazolidin-4-one ring, may occur spontaneously or not depending upon the exact compound being sythesized. In the case where elimination and ring closure does not occur spontaneously or sufficiently fast, this can be aided by heating above room temperature (that is, heating above 20°C, preferably up to about 100°C or about 120° C, or even higher provided no decomposition of reagents or product occurs), as well as with the presence of an acid (for example, a sulfonic acid such as p-toluene sulfonic acid). All steps of the present method may be performed in any suitable solvent. Preferably, the solvent is an aprotic, polar solvent which of course, is itself subtantially inert to any of the reactants particlularly the isothiocyanate. Examples of suitable solvents include acetonitrile or other alkylnitrile solvents, N,N-dimethylformamide, N,N-dimethylacetamide and dimethylsulfoxide. In some cases an alcohol solvent (which is a protic solvent) may be suitable. However, an aprotic solvent is not necessary for the final step involving elimination of alcohol or water. For this final step, sometimes no solvent may be necessary, or a solvent such acetic acid may be suitable.

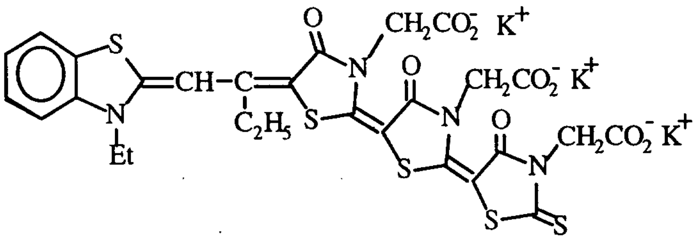
Examples of dyes of formula (I) are provided below:



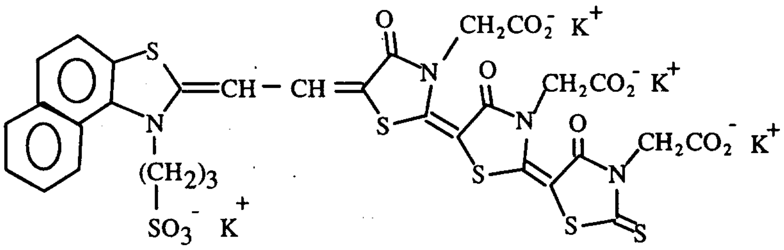
DYE 1



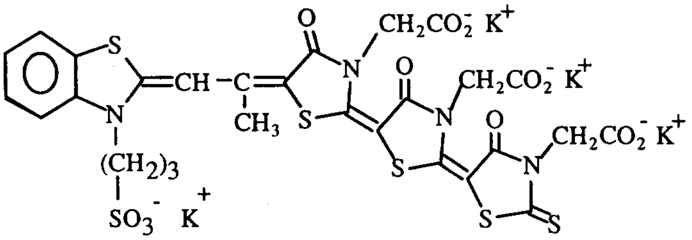
DYE 2



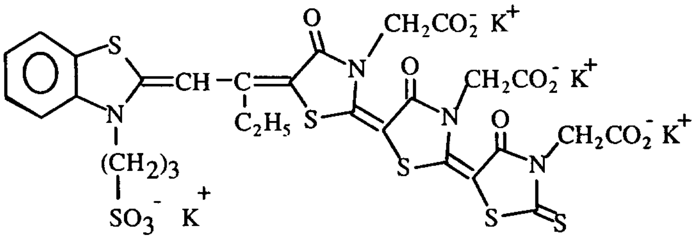
DYE 3



DYE 4



DYE 5



DYE 6

Photographic elements of the present invention will typically have at least one light sensitive silver halide emulsion layer and a support. They can be single color elements or multicolor elements, but are preferably black and white elements for use in Graphic Arts applications. In the case of photographic elements for graphic arts applications, there may optionally also be present a hydrazide nucleator and/or amine booster. Such elements and methods of processing them, are described in detail in U.S. Patent Application by Pich et al. for "PHOTOGRAPHIC ELEMENTS WITH TETRA-

NUCLEAR MEROCYANINE SENSITIZERS", filed by Express Mail on the same day as the present application, Attorney Docket No. 70997GMS (which application is also incorporated herein by reference).

However, the present sensitizing dyes can also be used in multicolor photographic elements. Such elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. However, multicolor photographic elements can also consist of image-forming units comprised of many other combinations of light sensitive silver halide emulsion layers associated with at least one dye-forming coupler.

Photographic elements of the present invention can also contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. All of the layers of photographic elements of the present invention, can be coated on a support which can be transparent or reflective (for example, a paper support). For paper materials, it is customary to employ a fluorescent brightening agent. These may be incorporated into the materials by known techniques, for example by dissolving a water-soluble brightener in the gelatin supercoat (the layer most remote from the support). In one embodiment a water-insoluble brightener may be used. It may be imbibed onto particles of a polymer dispersion as described in British Patent Specification 1,504,949 or 1,504,950 or dissolved in droplets of coupler solvents prior to incorporation in a layer of the material (for example, in the supercoat).

Photographic elements of the present invention may also usefully include a magnetic recording material as described in Research Disclosure, Item 34390, November 1992, or a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support as in US 4,279,945 and US 4,302,523. The element typically will have a total thickness (excluding the support) of from 5 to 30 microns. While the order of the color sensitive layers in a multicolor photographic element can be varied, they will normally be red-sensitive, green-sensitive and blue-sensitive, in that order on a transparent support, with the reverse order on a reflective support being typical.

Photographic elements of the present invention, particularly multicolor photographic elements, can be used in conventional cameras including what are often referred to as single use cameras (or "film with lens" units). These cameras are sold with film preloaded in them and the entire camera is returned to a processor with the exposed film remaining inside the camera. Such cameras may have glass or plastic lenses through which the photographic element is exposed. However, as already mentioned, photographic elements of the present invention are preferably graphic arts (and therefore, typically black and white) films.

In the following discussion of suitable materials for use in photographic elements, reference will be made to *Research Disclosure*, September 1994, Number 365, Item 36544, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, which will be identified hereafter by the term "Research Disclosure I." The Sections hereafter referred to are Sections of the Research Disclosure I.

The silver halide emulsions employed in the photographic elements may be negative-working, such as surface-sensitive emulsions or unfogged internal latent image forming emulsions, or positive working emulsions of internal latent image forming emulsions (that are either fogged in the element or fogged during processing). Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through V. Color materials and development modifiers are described in Sections V through XX. Vehicles which can be used in the photographic elements are described in Section II, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described, for example, in Sections VI through XIII. Manufacturing methods are described in all of the sections, layer arrangements particularly in Section XI, exposure alternatives in Section XVI, and processing methods and agents in Sections XIX and XX.

Supports for the photographic elements include polymeric films such as cellulose esters (for example, cellulose triacetate and diacetate) and polyesters of dibasic aromatic carboxylic acids with divalent alcohols (for example, poly(ethylene-terephthalate), poly(ethylene-napthalates)), paper and polymer coated paper. Such supports are described in further detail in Research Disclosure I, Section XV.

The photographic elements may also contain materials that accelerate or otherwise modify the processing steps of bleaching or fixing to improve the quality of the image. Bleach accelerators described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784 are particularly useful. Also contemplated is the use of nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

The elements may also contain filter dye layers comprising colloidal silver sol or yellow and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323.) Also, the couplers may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

The photographic elements may further contain other image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIR's). DIR compounds are disclosed, for example, in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in *Photographic Science and Engineering*, Vol. 13, p. 174 (1969), incorporated herein by reference. DIRs that have particular application in color reversal elements are disclosed in allowed U.S. patent applications Serial Numbers 08/004,019, 08/005,319, 08/005,472, and 08/007,440.

The emulsions and materials to form the photographic elements may be coated on pH adjusted support as described in U.S. 4,917,994; with epoxy solvents (EP 0 164 961); with additional stabilizers (as described, for example, in U.S. 4,346,165; U.S. 4,540,653 and U.S. 4,906,559); with ballasted chelating agents such as those in U.S. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium; and with stain reducing compounds such as described in U.S. 5,068,171 and U.S. 5,096,805. Other compounds useful in the above described photographic elements are disclosed in Japanese Published Applications 83-09,959; 83-62,586; 90-072,629, 90-072,630; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,096; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-101,937; 90-103,409; 90-151,577.

The silver halide used in the photographic elements may be silver iodobromide, silver bromide, silver chloride, silver chlorobromide, silver chloroiodobromide, and the like. For example, the silver halide used in the photographic elements of the present invention may contain at least 90% silver chloride or more (for example, at least 95%, 98%, 99% or 100% silver chloride). In the case of such high chloride silver halide emulsions, some silver bromide may be present but typically substantially no silver iodide. Substantially no silver iodide means the iodide concentration would be no more than 1%, and preferably less than 0.5 or 0.1%. In particular, in such a case the possibility is also contemplated that the silver chloride could be treated with a bromide source to increase its sensitivity, although the bulk concentration of bromide in the resulting emulsion will typically be no more than about 2 to 2.5% and preferably between about 0.6 to 1.2% (the remainder being silver chloride). The foregoing % figures are mole %.

However, the silver halide emulsion used for elements of the present invention, and which is sensitized by a dye of formula (I), is preferably of the type that provides a high contrast image as required in Graphic Arts applications. Such emulsions are customarily relatively high in silver chloride and low in silver iodide. They may contain both silver bromide and silver iodide in addition to silver chloride. Preferably the iodide content of these emulsions is less than 10 mole percent. Substantially pure silver chloride emulsions may be used for this purpose, although the preferred emulsions comprise 70 mole percent chloride and 30 mole percent bromide. As is known in the Graphic Arts field the grains may be doped with Rhodium, Ruthenium, Iridium or other Group VIII metals, preferably at levels in the range 10^{-9} to 10^{-3}, preferably 10^{-6} to 10^{-3}, mole metal per mole of silver. The preferred Group VIII metal is Rhodium.

The type of silver halide grains preferably include polymorphic, cubic, and octahedral. The grain size of the silver halide may have any distribution known to be useful in photographic compositions, and may be ether polydipersed or monodispersed. The silver halide emulsions employed in the photographic elements may be negative-working, such as surface-sensitive emulsions or unfogged internal latent image forming emulsions, or positive working emulsions of internal latent image forming emulsions (that are either fogged in the element or fogged during processing).

Tabular grain silver halide emulsions may also be used.
Tabular grains are those with two parallel major faces each clearly larger than any remaining grain face and tabular grain emulsions are those in which the tabular grains account for at least 30 percent, more typically at least 50 percent, preferably >70 percent and optimally >90 percent of total grain projected area. The tabular grains can account for substantially all (>97 percent) of total grain projected area. The tabular grain emulsions can be high aspect ratio tabular grain emulsions--i.e., ECD/t >8, where ECD is the diameter of a circle having an area equal to grain projected area and t is tabular grain thickness; intermediate aspect ratio tabular grain emulsions--i.e., ECD/t = 5 to 8; or low aspect ratio tabular grain emulsions--i.e., ECD/t = 2 to 5. The emulsions typically exhibit high tabularity (T), where T (i.e., ECD/t^2) > 25 and ECD and t are both measured in micrometers (μm). The tabular grains can be of any thickness compatible with achieving an aim average aspect ratio and/or average tabularity of the tabular grain emulsion. Preferably the tabular grains satisfying projected area requirements are those having thicknesses of <0.3 μm, thin (<0.2 μm) tabular grains being specifically preferred and ultrathin (<0.07 μm) tabular grains being contemplated for maximum tabular grain performance enhancements. When the native blue absorption of iodohalide tabular grains is relied upon for blue speed, thicker tabular grains, typically up to 0.5 μm in thickness, are contemplated.

High iodide tabular grain emulsions are illustrated by House U.S. Patent 4,490,458, Maskasky U.S. Patent 4,459,353 and Yagi et al EPO 0 410 410.

Tabular grains formed of silver halide(s) that form a face centered cubic (rock salt type) crystal lattice structure can have either {100} or {111} major faces. Emulsions containing {111} major face tabular grains, including those with controlled grain dispersities, halide distributions, twin plane spacing, edge structures and grain dislocations as well as adsorbed {111} grain face stabilizers, are illustrated in those references cited in Research Disclosure I, Section I.B.(3) (page 503).

The silver halide grains may be prepared according to methods known in the art, such as those described in Research Disclosure I and James, The Theory of the Photographic Process. These include methods such as ammoniacal emulsion making, neutral or acidic emulsion making, and others known in the art. These methods generally involve mixing a water soluble silver salt with a water soluble halide salt in the presence of a protective colloid, and controlling the temperature, pAg, pH values, etc, at suitable values during formation of the silver halide by precipitation.

The silver halide may be advantageously subjected to chemical sensitization with noble metal (for example, gold) sensitizers, middle chalcogen (for example, sulfur) sensitizers, reduction sensitizers and others known in the art. Compounds and techniques useful for chemical sensitization of silver halide are known in the art and described in Research Disclosure I and the references cited therein.

The photographic elements, as is typical, provide the silver halide in the form of an emulsion. Photographic emulsions generally include a vehicle for coating the emulsion as a layer of a photographic element. Useful vehicles include both naturally occurring substances such as proteins, protein derivatives, cellulose derivatives (e.g., cellulose esters), gelatin (e.g., alkali-treated gelatin such as cattle bone or hide gelatin, or acid treated gelatin such as pigskin gelatin), gelatin derivatives (e.g., acetylated gelatin, phthalated gelatin, and the like), and others as described in Research Disclosure I. Also useful as vehicles or vehicle extenders are hydrophilic water-permeable colloids. These include synthetic polymeric peptizers, carriers, and/or binders such as poly(vinyl alcohol), poly(vinyl lactams), acrylamide polymers, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, methacrylamide copolymers, and the like, as described in Research Disclosure I. The vehicle can be present in the emulsion in any amount useful in photographic emulsions. The emulsion can also include any of the addenda known to be useful in photographic emulsions. These include chemical sensitizers, such as active gelatin, sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, ruthenium, rhodium, phosphorous, or combinations thereof. Chemical sensitization is generally carried out at pAg levels of from 5 to 10, pH levels of from 3 to 8, and temperatures of from 30 to 80°C, as described in Research Disclosure I, Section IV (pages 510-511) and the references cited therein.

The sensitizing dye may be added to an emulsion of the silver halide grains and a hydrophilic colloid at any time prior to (e.g., during or after chemical sensitization) or simultaneous with the coating of the emulsion on a photographic element. The dyes may, for example, be added as a solution in water or an alcohol. The dye of formula (I) is typically used in a silver halide emulsion (typically in a silver halide emulsion containing layer) in an amount of from 5 to 500 mg per mole of silver halide (preferably from 50 to 350, and more preferably from 100 to 300 mg per mole of silver halide emulsion). The dye/silver halide emulsion may be mixed with a dispersion of color image-forming coupler immediately before coating or in advance of coating (for example, 2 hours).

The photographic elements can be imagewise exposed using any of the known techniques, including those described in Research Disclosure I, section XVI. In the case of multicolor elements, this typically involves exposure to light in the visible region of the spectrum (about 400-700nm). However, in the case of the preferred graphics arts films of the present invention, such exposure may include exposure to radiation having a wavelength of from about 500-800nm, preferably between about 600-700nm. Exposure may be to a real image through a lens. However, exposure may be by exposure to a computer stored or generated image by means of light emitting devices (such as light controlled by light valves, CRT and the like).

The photographic elements can be processed by any known process. Processing is described in Research Disclosure I, Sections XIX and XX, or in T.H. James, editor, The Theory of the Photographic Process, 4th Edition, Macmillan, New York, 1977.

In the case of preferred Graphic Arts films, the light sensitive silver halide contained in the photographic elements is preferably processed following exposure to form a visible image, by associating the silver halide with an alkaline medium in the presence of a developing agent contained in the medium or in the element. When the photographic elements contain incorporated developing agents, the elements can be processed in the presence of an activator.

Very high contrast images can be obtained in Graphic Arts films by processing at pH values in the range 11 to 12.3, but preferably lower pH values, for example below 11 and most preferably in the range 10.3 to 10.5 are preferably employed for processing the photographic recording materials as described herein.

The developers for the preferred Graphic Arts films are typically aqueous solutions, although organic solvents, such as diethylene glycol, can also be included to facilitate the solvency of organic components. The developers contain one or a combination of conventional developing agents, such as polyhydroxybenzene, aminophenol, para-phenylenediamine, ascorbic acid, pyrazolidone, pyrazolone, pyrimidime, dithionite, hydroxylamine, or other conventional developing agents.

It is preferred when processing the preferred Graphic Arts films constructed according to the present invention, to use hydroquinone and 3-pyrazolidone developing agents in combination. The pH of the developers can be adjusted with alkali metal hydroxides and carbonates, borax and other basic salts. To reduce gelatin swelling during development, compounds such as sodium sulfate can be incorporated into the developer. Also, compounds such as sodium thiocyanate can be present to reduce granularity. Chelating and sequestering agents, such as ethylenediaminetetraacetic acid or its sodium salt, can be present. Generally, any conventional developer composition suitable for Graphic Arts films, can be employed in the processing the preferred Graphic Arts films of this invention. Specific illustrative photographic developers are disclosed in the Handbook of Chemistry and Physics, 36th Edition, under the title "Photographic Formulae" at page 3001 et seq. and in Processing Chemicals and Formulae, 6th Edition, published by Eastman Kodak Company (1963). Graphic Arts elements elements can, of course, be processed with conventional developers for lithographic photographic elements, as illustrated by US Patent No.3,573,914 and UK Patent No. 376,600.

In the case of processing a negative working multicolor element, the element is treated with a color developer (that is one which will form the colored image dyes with the color couplers), and then with a oxidizer and a solvent to remove silver and silver halide. In the case of processing a reversal color element, the element is first treated with a black and white developer (that is, a developer which does not form colored dyes with the coupler compounds) followed by a treatment to fog silver halide (usually chemical fogging or light fogging), followed by treatment with a color developer. Preferred color developing agents are p-phenylenediamines. Especially preferred are:

4-amino N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N-ethyl-N-(β-(methanesulfonamido) ethylaniline sesquisulfate hydrate,
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate,
4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

Development is followed by bleach-fixing, to remove silver or silver halide, washing and drying.

The method of the present invention will be further described in the examples below.

Examples

The photosensitive materials used in this example consist of at least a light sensitive layer and a gel overcoat; coated on a polyethylene terephthalate base with an anti-halation back coat.

The light sensitive layer consists of a 70:30 chlorobromide cubic monodispersed emulsion (0.18μ edge length) doped with ammonium hexachlororhodate and coated at 3.3mg/m$^{2\cdot}$ Other addenda included in the light sensitive layer are the sensitizing dye, 2-methylmercapto-5-carboxy-6-methyl tetraazaindene, 1-(3-acetamidophenyl)-5-mercaptotetrazole, 4-carboxymethyl-4-thiazoline-2-thione and a latex copolymer of methyl acrylate, 2-acrylamido-2-methylpropanesulfonic acid and the sodium salt of 2-acetoxymethylmethyacrylate (88:5:7 by weight), 3,5-disulfocatechol, disodium salt and hydroquinone.

In these examples, the sensitizing dyes listed above as DYE1 to DYE6 were dissolved in water and were added at the rate of 100, 200 or 300 mg of dye per mole of silver to emulsion which had been previously chemically sensitized. After coating the treated emulsion on a polyethylene support the resulting coatings were exposed for 10^{-6} seconds using a solid state laser diode, having a maximum intensity at 670nm, to produce a 21 step, 0-2 logE (0.1 logE) step wedge. The coatings were processed for 30 seconds in a typical rapid access developer similar to Kodak RA2000 developer (1+4), fixed for 30 seconds in Kodak 3000 Fixer (1+3), and then dried. The densities of the step wedge silver images so produced were measured and plotted against the appropriate relative exposure level.

Several parameters were derived from the densitometry results, but in particular the minimum density ("Dmin") and "Sp.6" (the relative speed, in logarithmic units, of the coatings at a density of Dmin + 0.6), were measured. These data are shown in Table 1 below.

Table 1

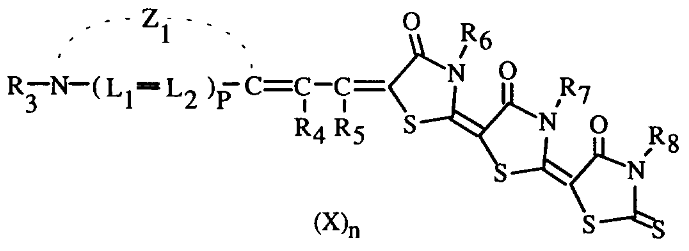
Dye	Level	Dmin	Sp.6	Stain
DYE1	100mg	0.017	0.43	Slight Blue
	200mg	0.023	0.6	Medium Blue
	300mg	0.032	0.73	High Blue
DYE2	100mg	0.013	0.65	Slight Blue
	200mg	0.015	0.91	Medium Blue
	300mg	0.019	0.99	High Blue
DYE3	100mg	0.017	0.71	Slight Blue
	200mg	0.014	0.92	Medium Blue
	300mg	0.024	1.02	High Blue
DYE4	100mg	0.017	0.46	Slight Blue
	200mg	0.015	0.65	Medium Blue
	300mg	0.022	0.73	High Blue
DYE5	100mg	0.013	0.62	None
	200mg	0.023	0.89	V.Slight Blue
	300mg	0.020	0.91	Slight Blue
DYE6	100mg	0.016	0.58	None
	200mg	0.018	0.86	None
	300mg	0.028	0.98	V.Slight Blue

It is clear from the above results that photographic elements of the present invention in which the silver halide is sensitized by a dye of formula (I), have low stain while still providing good spectral sensitivity to the emulsion.

The preceding examples are set forth to illustrate specific embodiments of this invention and are not intended to limit the scope of the compositions or materials of the invention. It will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. A photographic element comprising a light sensitive silver halide emulsion sensitized with a dye of formula (I):



(I)

wherein:

R_3 is an alkyl group, alkenyl group, or aryl group
R_4 and R_5 are each hydrogen, an alkyl group, alkenyl or aryl group;
R_6, R_7 and R_8 are, independently, an alkyl group, alkenyl group, aryl group, or H;

the dye has at least three acid or acid salt substituents; and

each L independently represents a methine group;

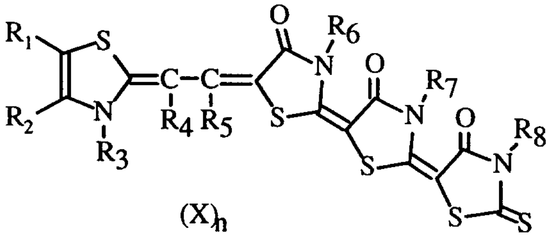
p is 0 or 1;

Z_1 represents the atoms necessary to complete a 5- or 6-membered heterocyclic ring group;

$(X)_n$ represents counterions as needed to balance the charge on the molecule.

2. A photographic element according to claim 2 wherein Z_1 represents the atoms which complete an oxazole group, benzoxazole group, naphthoxazole group, thiazole group, benzthiazole group, naphthothiazole group, imidazole group, benzimidazole group, naphthimidazole group, pyridine group, quinoline group, 1,3,4-thiadiazole group, thiazoline group, selenazole group, benzoselenazole group, naphthoselenazole group, benzotellurazole group, or naphthotellurazole group.

3. A photographic element according to claim 1, wherein the dye of formula (I) is of formula (Ia):



(Ia)

wherein:

wherein R_1 and R_2 independently represent hydrogen, hydroxy, a halogen atom, an aryl group, a heteroaromatic group, an alkyl group, an alkenyl group, an alkoxy group, an alkylthio group, an arylthio group, an acyl group, an acyloxy group, an alkoxycarbonyl group, an alkylsulfonyl group, a carbamoyl group, a sulfamoyl group, carboxy, or cyano, or R_1 and R_2 together represent the atoms necessary to complete an annellated benzene, naphthalene, anthracene group or heteroaromatic group;

R_4 and R_5 are each hydrogen, or an alkyl group;

R_3 is an alkyl group;

R_6, R_7 and R_8 are, independently, an alkyl group, at least three of R_3, R_6, R_7 and R_8 having an acid or acid salt substituent;

$(X)_n$ represents counterions as needed to balance the charge on the molecule.

4. A photographic element according to claim 1, claim 2 or claim 3, wherein at least R_6, R_7 and R_8 have an acid or acid salt substituent.

5. A photographic element according to claim 1, claim 2, or claim 3, wherein the dye has at least 4 acid or acid salt substituents, preferably carboxy or sulfo substituents.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0487

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y,D	GB-A-489 335 (D. J. FRY ET AL.) * page 1, line 6 - page 1, line 8 * * example 10 * ---	1-5	G03C1/26 C09B23/16
Y,D	EP-A-0 540 295 (KONICA CORPORATION) * page 2, line 3 - page 3, line 36 * * example 1 * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C C09B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	11 July 1996	Markowski, V

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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