(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 540 656 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification : **28.09.94 Bulletin 94/39**

(51) Int. Cl.[5] : **G03C 1/015,** G03C 1/12, G03C 7/34

(21) Application number : **91914483.2**

(22) Date of filing : **28.06.91**

(86) International application number : **PCT/US91/04593**

(87) International publication number : **WO 92/01970 06.02.92 Gazette 92/04**

(54) **LIGHT-SENSITIVE SILVER HALIDE COLOR PHOTOGRAPHIC ELEMENTS COMPRISING PHENOL CYAN COUPLERS AND SPECTRAL SENSITIZING DYES.**

(30) Priority : **20.07.90 IT 2099790**

(43) Date of publication of application : **12.05.93 Bulletin 93/19**

(45) Publication of the grant of the patent : **28.09.94 Bulletin 94/39**

(84) Designated Contracting States : **BE DE FR GB NL**

(56) References cited :
DE-A- 3 641 861
JP-A-63 146 032
US-A- 4 334 012

(73) Proprietor : **MINNESOTA MINING AND MANUFACTURING COMPANY**
3M Center,
P.O. Box 33427
St. Paul, Minnesota 55133-3427 (US)

(72) Inventor : **BELTRAMINI, Walter**
3M Italia Ricerche S.p.A.
I-17018 Ferrania (IT)

(74) Representative : **Baillie, Iain Cameron et al**
c/o Ladas & Parry
Altheimer Eck 2
D-80331 München (DE)

EP 0 540 656 B1

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

FIELD OF THE INVENTION

This invention refers to light-sensitive silver halide color photographic elements having at least one layer comprising a silver halide photographic emulsion, at least one 2,5-diacylamino phenol cyan coupler and at least one sulfo-substituted spectral sensitizing dye, wherein such spectral sensitizing dye is added to the silver halide photographic emulsion after the desalting step process in the preparation of such emulsion.

BACKGROUND OF THE INVENTION

The spectral sensitizing technique of adding certain sensitizing dyes to a silver halide photographic emulsion to expand its light-sensitive wavelength region to the longer wavelength side is well known in the art for preparing silver halide color photographic emulsions.

The degree of spectral sensitization is influenced by the chemical structure of the sensitizing dye, by many properties of the emulsion (for example, composition of silver halides, crystal habit, crystal form, silver ion concentration) and the like. It is also influenced by the photographic additives present in the emulsiop, such as stabilizer agents, antifoggants, colour couplers, etc.

Combination of the sensitizing dye and the coupler to form a salt, causing the sensitizer molecules to be desorbed from the grain surface, has been long recognised in the art (H.Meier, Spectral Sensitization, The Focal Press, 1968, p.52).

2,5-Diacylamino phenol cyan couplers are known to produce cyan dyes having excellent resistance against fading as described, for example, in US Patent Nos. 4,333,999; 4,451,559; 4,465,766 and 4,554,244.

The combination of said 2,5-diacylamino phenol cyan couplers with conventional cationic cyanine dyes shows no sensitometric problem if the coupler is added to a red sensitized emulsion immediately before coating, whereas it causes a dramatic loss of red sensitivity (desensitization) if the finalled emulsion is held several hours at high temperature before coating.

DE-A-3 641 861 describes multilayer colour photographic elements comprising a 2,5-diacylaminophenol cyan coupler and a silver halide emulsion red-sensitized with a sulfo-substituted thiacarbocyanine dye.

With cyanine dyes having two sulfoalkyl groups, desensitization is reduced, but such cyanine dyes cause an increased sensitization of the adjacent layers of the coated film (diffusion sensitization) since they can diffuse into the adjacent layers under high temperature and humidity. This diffusion is a serious problem in practical use.

US Patent No.4,513,081 describes a silver halide photographic emulsion comprising a 2,5-diacylamino phenol cyan coupler and a merocyanine sensitizing dye which does not undergo desensitization and diffusion sensitization.

European Patent Application No. 291,339 describes a high sensitivity light-sensitive photographic element having one layer comprising a silver halide photographic emulsion, wherein said silver halide emulsion is obtained by addition of a spectral sensitizing dye during the desalting step in obtaining such emulsion.

SUMMARY OF THE INVENTION

The present invention provides a light-sensitive silver halide color photographic element having at least one layer comprising a silver halide photographic emulsion containing sensitizing cyanine dyes and 2,5-diacylamino phenol cyan couplers to overcome desensitization and diffusion sensitization defects.

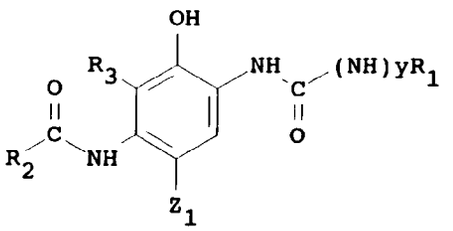
The present invention provides light-sensitive silver halide color photographic elements having at least one layer comprising a silver halide photographic emulsion containing sulfo-substituted thiacarbocyanine sensitizing dyes and 2,5-diacylamino phenol cyan couplers, wherein such sensitizing dyes are added to the silver halide photographic emulsion after the desalting step in the preparation of said emulsion and before the addition of dispersing medium to reconstitute the emulsion to provide substantially no migration of the spectral sensitizing dye into adjacent layers.

BRIEF DESCRIPTION OF THE DRAWINGS

An embodiment of the invention selected by way of example will be herein below described with reference to the accompaying diagrammatic drawings in which FIGS. 1 and 2 represent the sensitization spectra of silver halide color photographic elements.

DETAILED DESCRIPTION OF THE INVENTION

The 2,5-diacylamino non-leuco phenol cyan couplers for use in the present invention are represented by the formula (I):



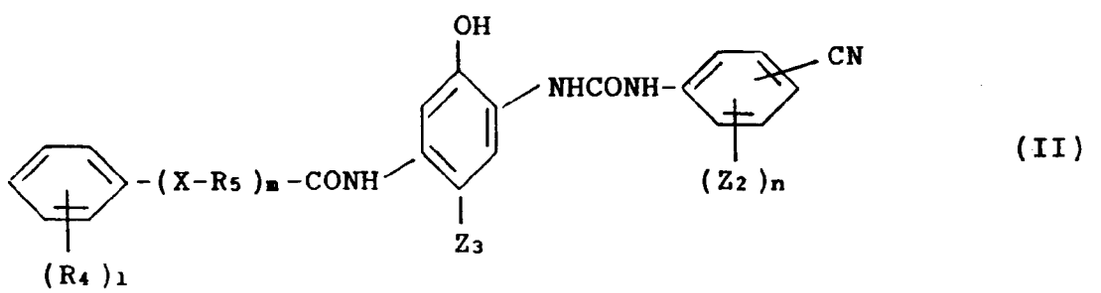
(I)

wherein R_1 is an aryl group (preferably up to 30 carbon atoms), R_2 is an alkyl group of up to 20 carbon atoms such as methyl, ethyl, butyl, dodecyl, etc.) or an aryl group of up to 20 carbon atoms, R_3 is a hydrogen atom, a halogen atom (such as fluorine, bromine, chlorine, etc.), an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.) or an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.), and Z_1 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent (e.g., a leaving group useful on a phenol color photographic coupler); y is 0 or 1.

The aryl group represented by R_1 of formula (I) is, e.g., a phenyl group, a naphthyl group, or other aryl group of up to 30 carbon atoms, and preferably is a phenyl group. This group is allowed to have a single substituent or a plurality of substituents; for example, typical substituents introducible to the aryl group include halogen atoms (such as fluorine, chlorine, bromine, etc.), alkyl groups (such as methyl, ethyl, propyl, butyl, dodecyl, etc.), hydroxyl group, cyano group, nitro group, alkoxy groups (such as methoxy, ethoxy, etc.), alkylsulfonamido groups (such as methylsulfonamido, octylsulfonamido, etc.), arylsulfonamido groups (such as phenylsulfonamido, naphthylsulfonamido, etc.), alkylsulfamoyl groups (such as butylsulfamoyl), arylsulfamoyl (such as phenylsulfamoyl), alkyloxycarbonyl groups (such as methyloxycarbonyl), aryloxycarbonyl groups (such as phenyloxycarbonyl), aminosulfonamido groups, acylamino groups, carbamoyl groups, sulfonyl groups, sulfinyl groups, sulfoxy groups, sulfo groups, aryloxy groups, alkoxy groups, alkylcarbonyl groups, arylcarbonyl groups, aminocarbonyl groups, and the like. Two different members of these groups are allowed to be introduced to the aryl group. The preferred group represented by R_1 is a phenyl group, the more preferred is a phenyl group having one or more substituents including halogen atoms and cyano groups.

When the term "group" is used in the present invention to describe a chemical compound or substituent, the described chemical material includes the basic group and that group with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent, only an unsubstituted chemical material is intended to be included. For example, "alkyl group" includes not only alkyl moieties as methyl, ethyl, octyl, dodecyl, etc., but also such moieties bearing sustituent groups such as halogen, cyano, hydroxyl, nitro, amine, carboxylate, etc. On the other hand, "alkyl moiety" includes only methyl, ethyl, octyl, dodecyl, etc.

In the present invention, the preferred cyan couplers having Formula (I) are the compounds having the following formula (II):



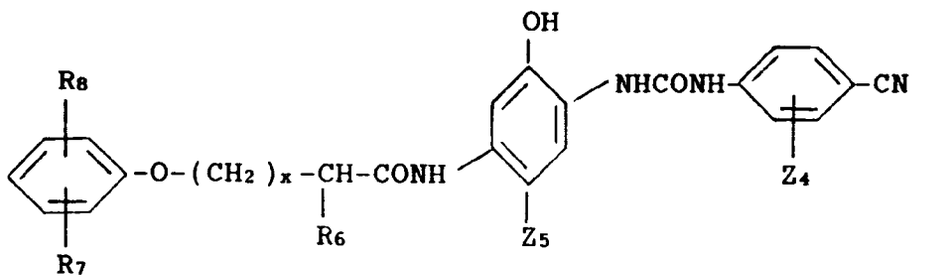
(II)

wherein Z_2 is a hydrogen atom, a halogen atom (such as fluorine, bromine, chlorine, etc.) or a monovalent organic group, R_4 is a hydrogen atom or a substituent exemplified by a halogen atom (such as fluorine, bromine, chlorine, etc.), a hydroxyl group, a nitro group, an alkyl group of up to 20 carbon atoms (such as methyl, ethyl,

iso-propyl, tert.-butyl, n-octyl, n-dodecyl, etc.), an alkyloxycarbonyl group (such as methyloxycarbonyl), an aryloxycarbonyl group (such as phenyloxycarbonyl), an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.), an aryloxy group (such as phenoxy), an alkylcarbonyl group (such as methylcarbonyl, propylcarbonyl, octylcarbonyl, etc.), an arylcarbonyl (such as phenylcarbonyl), an acyloxy group (such as acetoxy, benzoyloxy, etc.), an alkylsulfonyl group (such as methylsulfonyl, ootylsulfonyl, etc.), an arylsulfonyl group (such as phenylsulfonyl), an acyl group (such as acetyl), an acylamino group, a sulfonamido group (such as methylsulfonamido, octylsulfonamido, phenylsulfonamido, etc.), a sulfamoyl group (such as butylsulfamoyl, phenylsulfamoyl, etc.), and the like; X is an oxygen atom or a sulfur atom, R_5 is a straight-chain or a branched-chain alkylene group, n is an integer of 0 to 3, m is an integer of 0 to 4 and 1 is an integer of 1 to 4, and Z_3 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidised product of an aromatic primary amine-type color developing agent.

Examples of monovalent organic group represented by Z_2 include a halogen atom, a nitro group, an amino group, a cyano group, a hydroxy group, a carboxy group, an alkyl group (such as methyl, ethyl, propyl, isopropyl, t-butyl, octyl, etc.), an aralkyl group (such as benzyl, phenethyl, etc.), an alkoxy group (such as methoxy, ethoxy, benzyloxy, etc.), an aryloxy group (such as phenoxy, p-nitrophenoxy, etc.), an acylamino group (such as acetylamino, propionylamino, benzoylamino, phenoxyacetylamino, etc.), a carbamoyl group (such as methylcarbamoyl, dimethylcarbamoyl, phenylcarbamoyl, diphenylcarbamoyl, etc.), a sulfonamido group (such as methanesulfonamido, butanesulfonamido, benzenesulfonamido, p-toluene- sulfonamido, etc.), a sulfamoyl group (such as methylsulfamoyl, dimethylsulfamoyl, phenylsulfamoyl, etc.), an alkylcarbonyl group (such as methylcarbonyl, propylcarbonyl, octylcarbonyl, etc.), an arylcarbonyl group (such as phenylcarbonyl), an alkyoxycarbonyl group (such as methyloxycarbonyl, ethyloxycarbonyl, butyloxycarbonyl, t-butyloxycarbonyl, etc.), an aryloxycarbonyl group (such as phenyloxycarbonyl), and the like.

In the present invention, the more preferred cyan couplers having formula (I) are the compounds having the following formula (III):



(III)

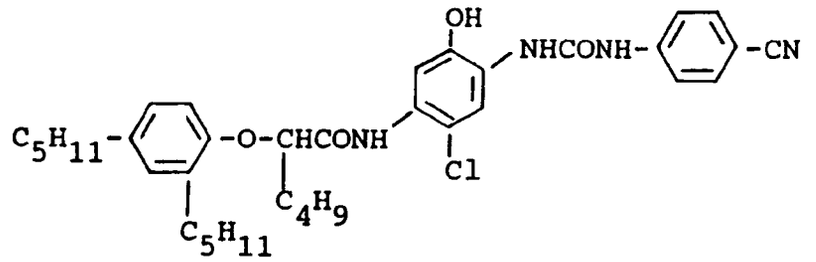
wherein Z_4 is a hydrogen atom or a halogen atom (such as fluorine, chlorine, bromine, etc.), Z_5 is a hydrogen atom or a chlorine atom, R_6 is a hydrogen atom or an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, propyl, butyl, octyl, dodecyl, etc.), R_7 and R_8 may be either the same or different and each is a hydrogen atom, an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.) or an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.), provided. that the sum of carbon atoms of R_6, R_7 and R_5 is from 8 to 20, and x is an integer of 0 to 2.

In formulas (I), and (II), the groups that can be split off by the reaction of these couplers with the oxidized product of the aromatic primary amine-type color developing agents, represented by Z_1 and Z_3, are all known to those skilled in the art. Any of these groups changes the reactivity of the coupler or is split from the coupler to fulfill its development-inhibiting, bleach-inhibiting and color-compensation inhibiting functions to thereby advantageously act in the coupler-containing layers or other layers of the silver halide color photographic material. Typcal examples os such groups include, for example, alkoxy groups, aryloxy groups, arylazo groups, thiether, carbamoyloxy groups, acyloxy groups, imido groups, sulfonamido groups, thiocyano group or heterocyclic groups (such as oxazolyl, diazolyl, triazolyl, tetrazolyl, etc.), and the like. The particularly preferred examples represented by Z_1 and Z_3 are a hydrogen atom or a chlorine atom.

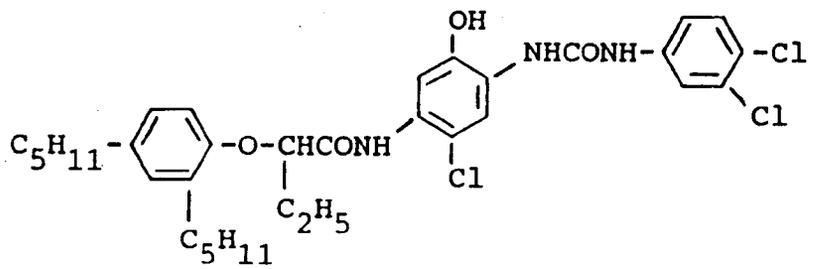
The cyan couplers of formula (I) can readily be synthesized by use of methods well known in the art such as described, for example, in US Patents 3,758,308, 4,333,999 and 4,451,559.

Specific examples of cyan couplers represented by the formula (I) are illustrated below, but the present invention is not limited thereby.

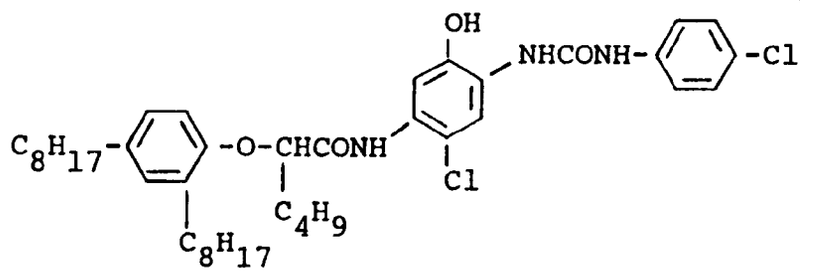
(I-1)



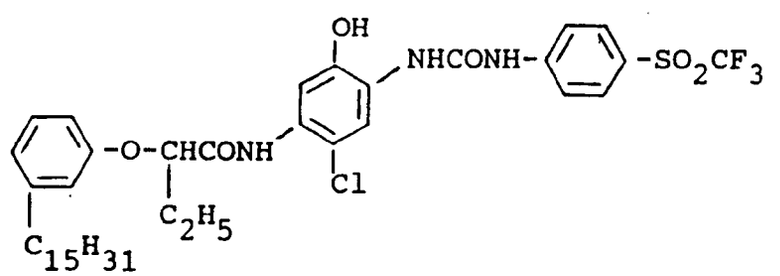
(I-2)



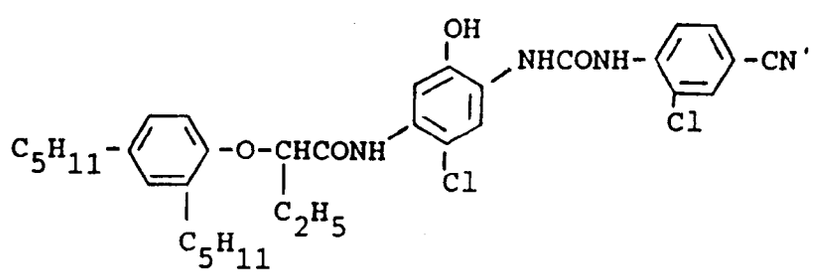
(I-3)



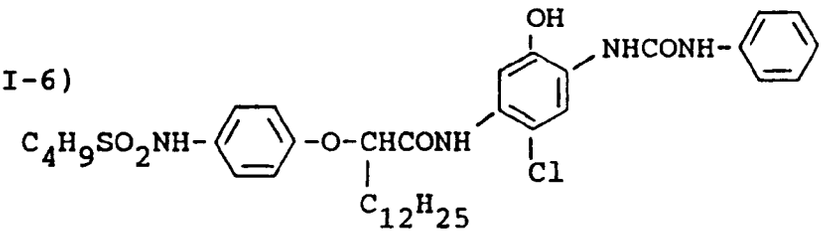
(I-4)



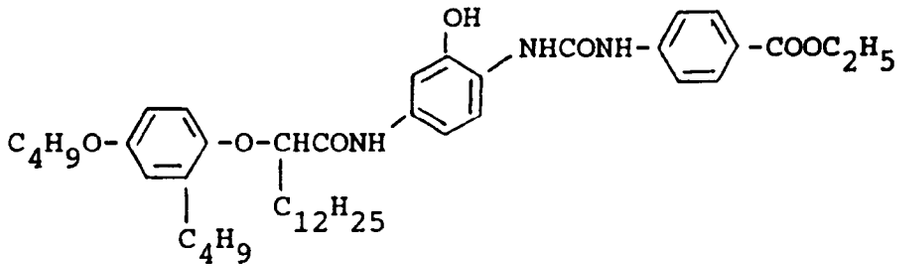
(I-5)



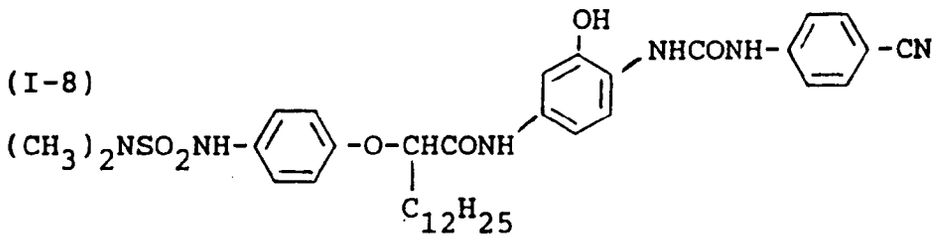
(I-6)



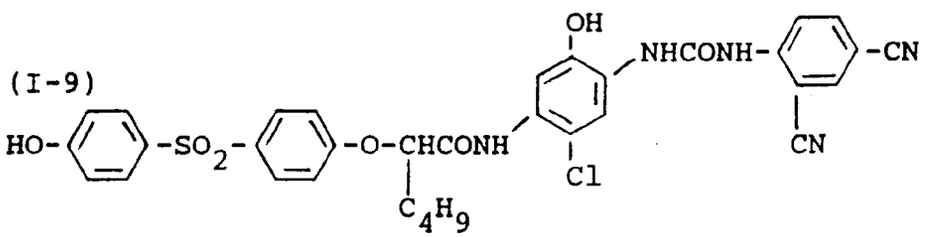
(I-7)



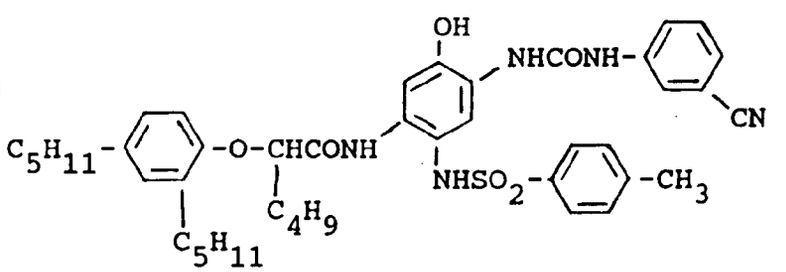
(I-8)



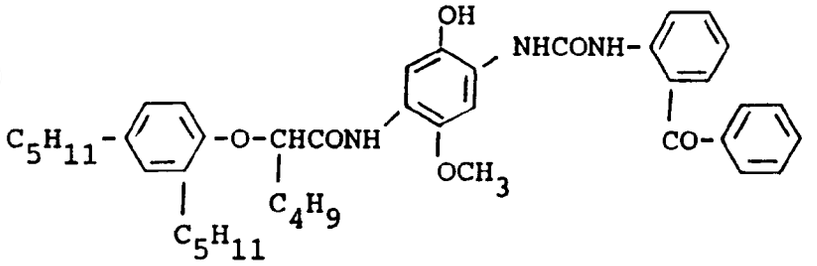
(I-9)



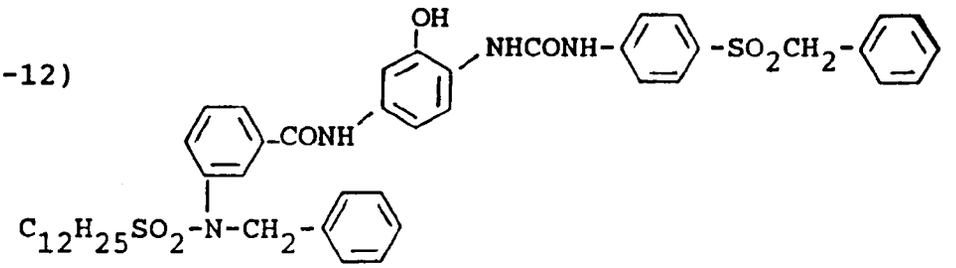
(I-10)



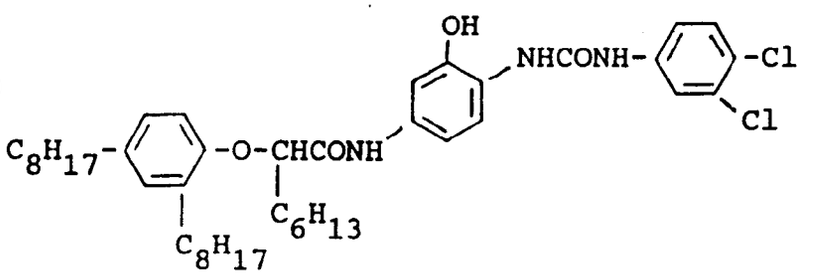
(I-11)



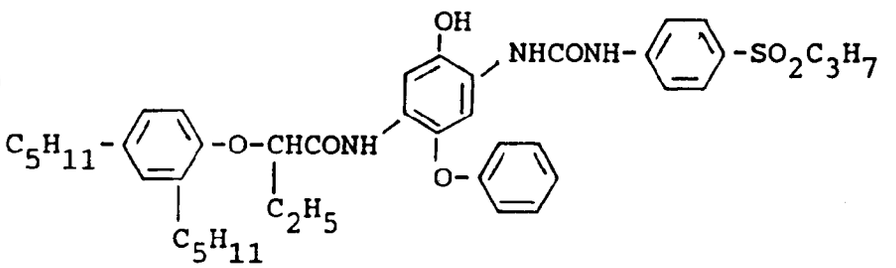
(I-12)



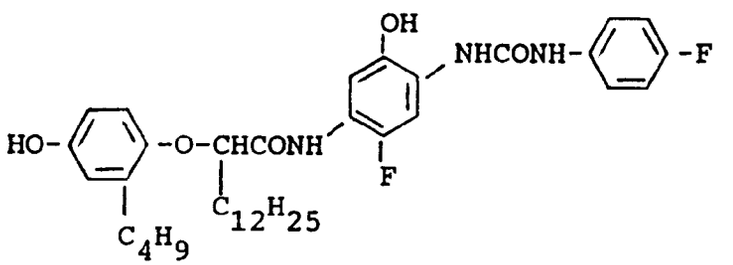
(I-13)



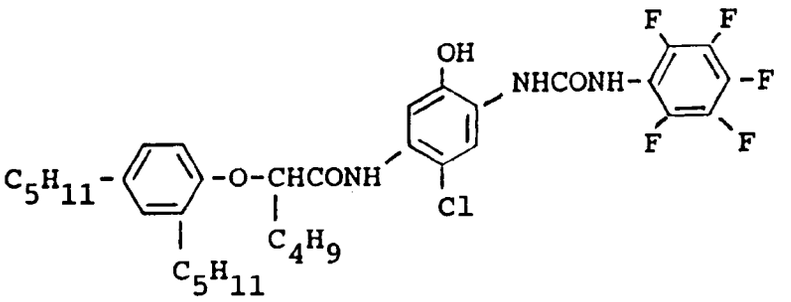
(I-14)



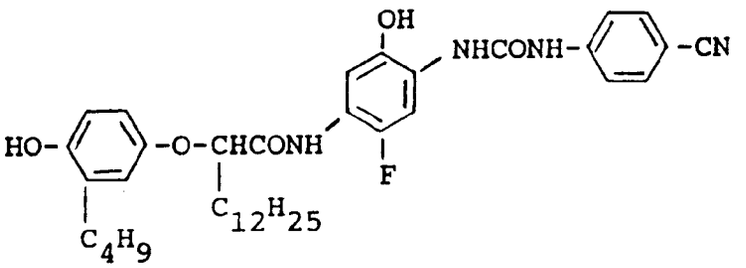
(I-15)



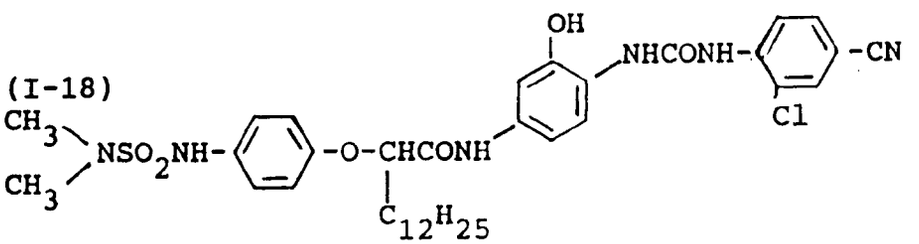
(I-16)



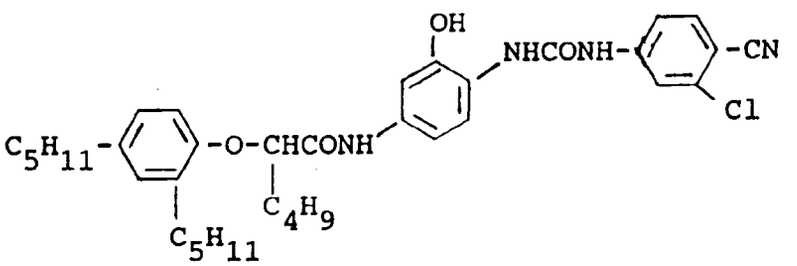
(I-17)



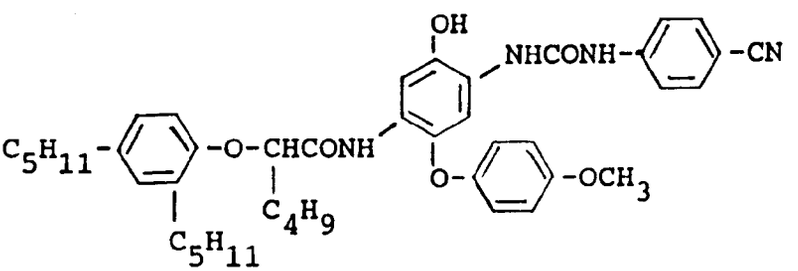
(I-18)



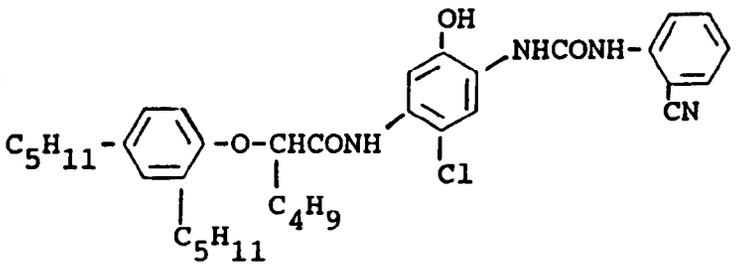
(I-19)



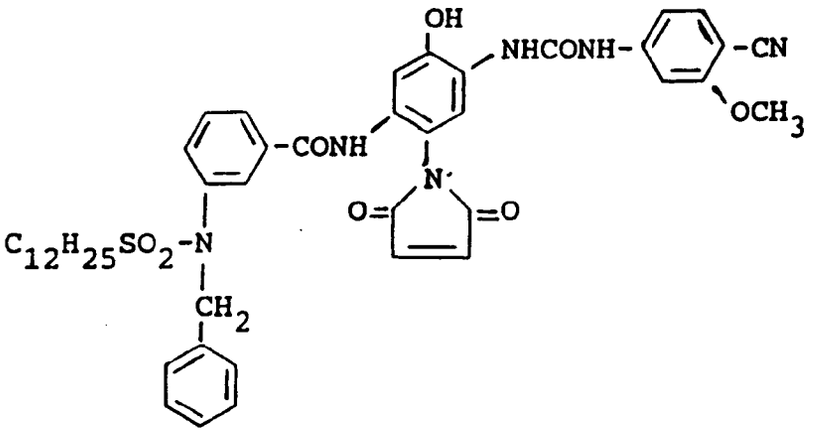
(I-20)



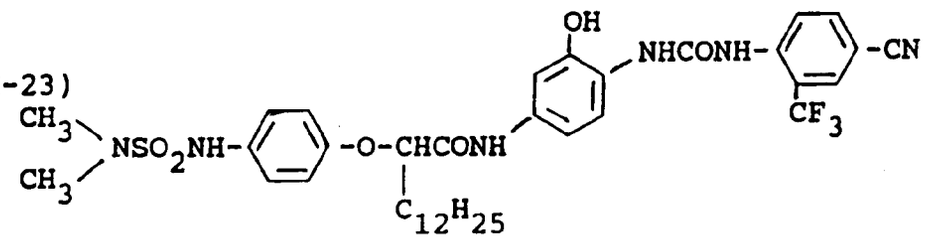
(I-21)



(I-22)



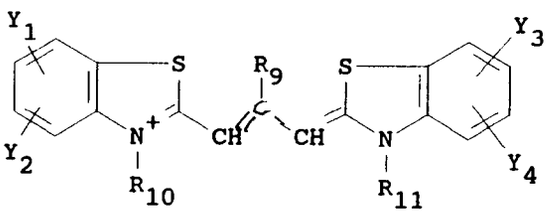
(I-23)



The sulfo substituted thiacarbocyanine sensitizing dyes for use in the present invention comprise two basic heterocyclic nuclei joined by a linkage of three methine groups, at least one of said heterocyclic nucleus being a benzothiazolium nucleus. The heterocyclic nuclei preferably include fused benzene rings.

Examples of heterocyclic nuclei include quinolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium and naphthoselenazolium quaternary salts.

The preferred sulfo substituted sensitizing cyanine dyes are thiacarbocyanine sensitizing dyes represented by the following formula (IV):



(IV)

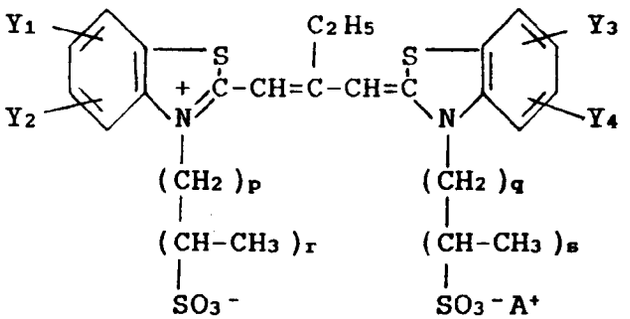
wherein Y_1, Y_2, Y_3 and Y_4 each represents a hydrogen atom, a halogen atom (e.g. chlorine, bromine, iodine and fluorine), a hydroxy group, an alkoxy group (e.g. methoxy, ethoxy, etc.), an amino group (e.g. amino, methylamino, dimethylamino, etc.), an acylamido group (e.g. acetamido, propionamido, etc.), an acyloxy group (e.g. acetoxy group, etc.), an alkoxycarbonyl group (e.g. methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl,

etc.), an alkyl group (e.g. methyl, ethyl, isopropyl, etc.), an alkoxycarbonylamino group (e.g. ethoxycarbonylamino, etc.), or an aryl group (e.g. phenyl, tolyl, etc.), or Y_1 and Y_2, and respectively Y_3 and Y_4, can be the atoms necessary to form a benzene nucleus (so that the heterocyclic nucleus results to be, for example, an α-naphthothiazole nucleus, a β-naphthothiazole or a β,β'-naphthothiazole); R_9 represents a hydrogen atom or an alkyl group (e.g. methyl, ethyl, etc.); R_{10} and R_{11} may be either the same or different and each is an alkyl group associated with a sulfo group (e.g. 2-sulfoethyl, 3-sulfopropyl, 4-sulfobutyl, 2-hydroxy-3-sulfopropyl, 2-(3-sulfopropoxy)-propyl, p-sulfobenzyl, p-sulfophenethyl, etc.), A is a hydrogen atom or a cationic group (e.g. lithium salt, potassium salt, sodium salt, quaternary ammonium salt, pyridinium salt, etc..).

The alkyl groups included in said substituents Y_1, Y_2, Y_3, Y_4, R_9, R_{10} and R_{11} and, more particularly, the alkyl portions of said alkoxy, alkoxycarbonyl, alkoxycarbonylamino, hydroxyalkyl, acetoxyalkyl groups and of the alkyl groups associated with a sulfo group each preferably contain from 1 to 12, more preferably from 1 to 4 carbon atoms, the total number of carbon atoms included in said groups preferably being no more than 20.

The aryl groups included in said substituents Y_1, Y_2, Y_3 and Y_4 each preferably contain from 6 to 18, more preferably from 6 to 10 carbon atoms, the total number of carbon atoms included in said groups arriving up to 20 carbon atoms.

In the present invention, the preferred sulfo-substituted thiacarbocyanine spectral sensitizing dyes having formula (IV) are the compounds having the following formula (V):

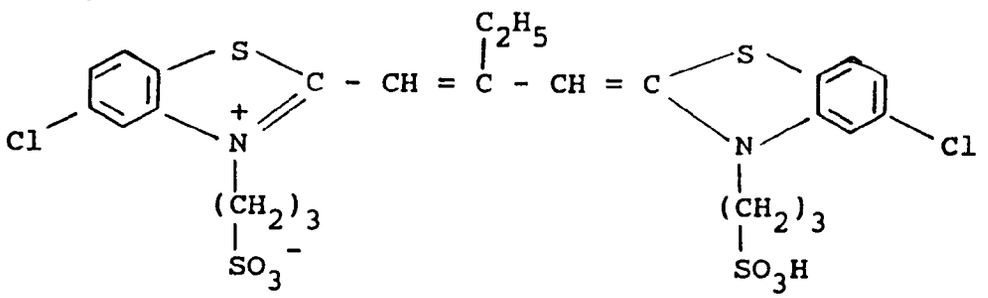


(V)

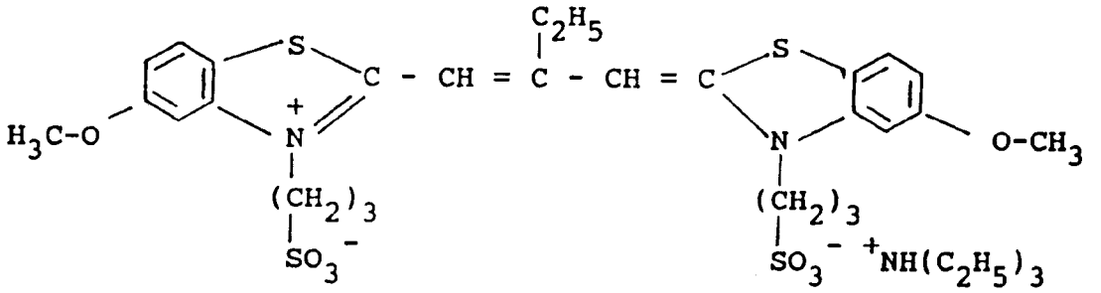
wherein Y_1, Y_2, Y_3 and Y_4 are the same as before; p and q are integers of 1 to 4; r and s are integers of 0 to 1; and A is a hydrogen atom or a cationic group (e.g. lithium salt, potassium salt, sodium salt, quaternary ammonium salt, pyridinium salt, etc..).

The following are specific examples of sulfo substituted thiacarbocyanine spectral sensitizing dyes belonging to those represented by the general formula (IV):

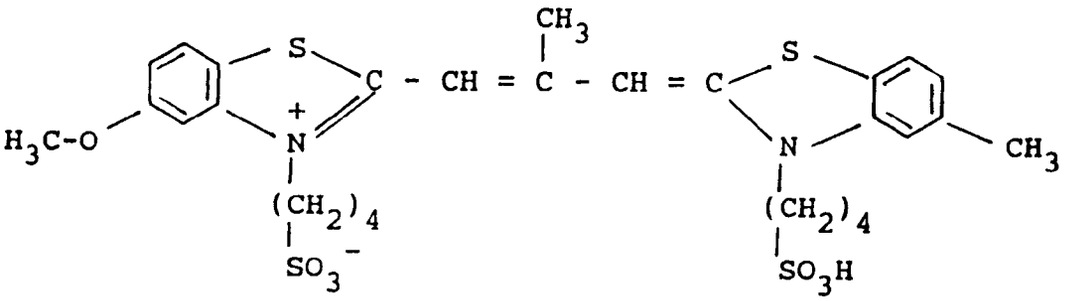
(S-1)



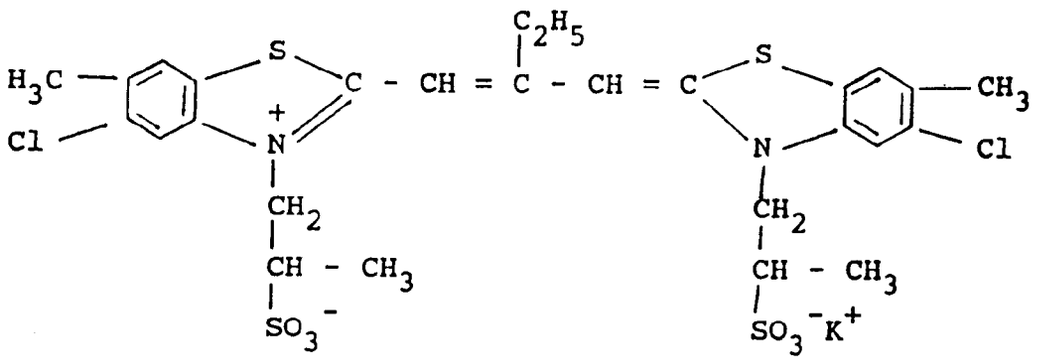
(S-2)



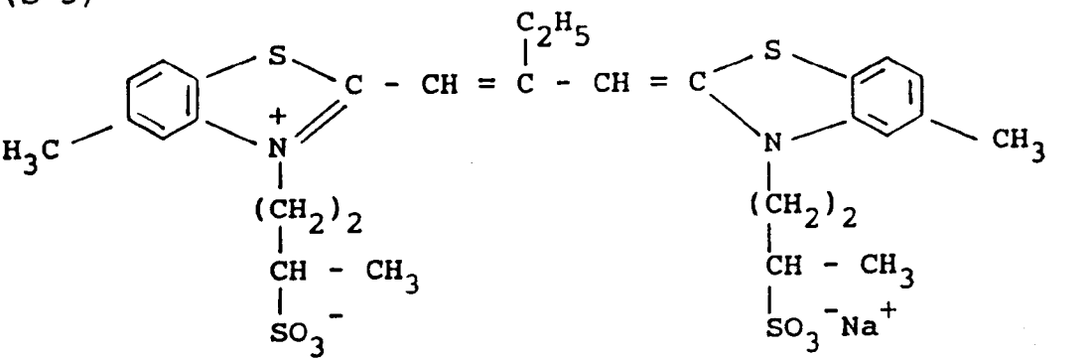
(S-3)



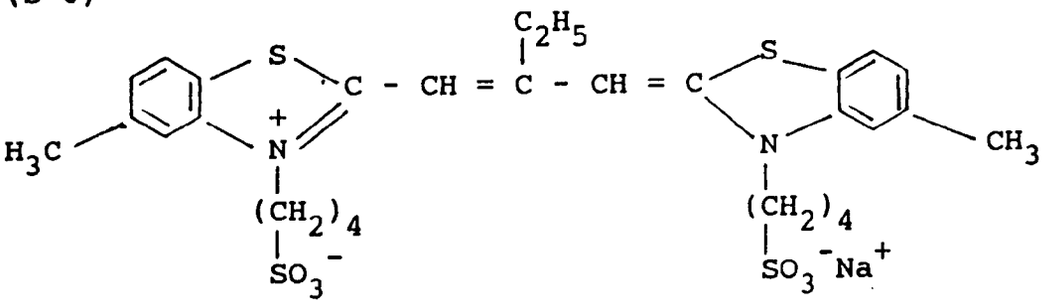
(S-4)



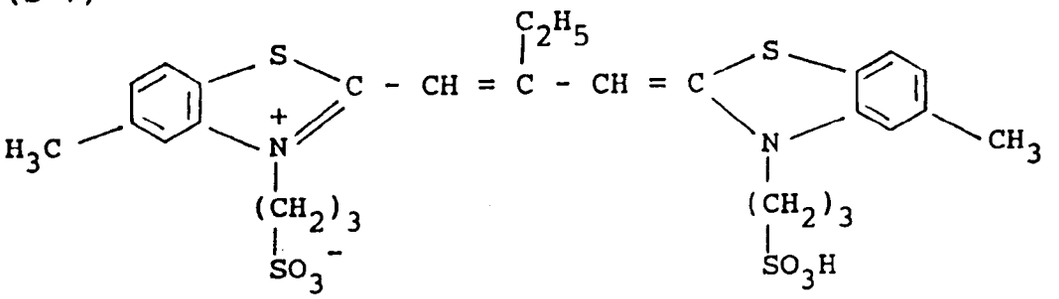
(S-5)



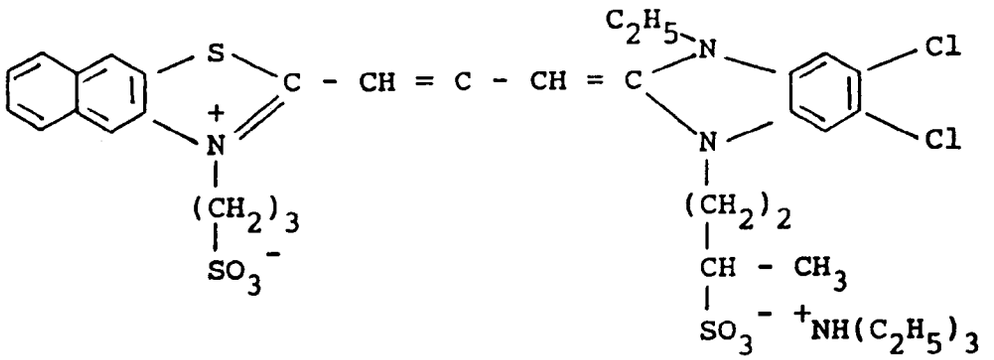
(S-6)



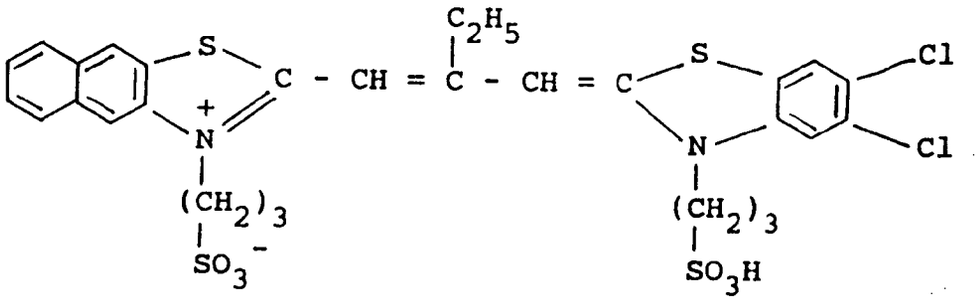
(S-7)



(S-8)



(S-9)



It is known in the art that a photographic material is obtained through sequential processing steps, comprising mixing water soluble silver salt and halide salt solutions in a dispersing medium contained in a reaction vessel under stirring to form silver halide grains, chemically sensitizing, spectrally sensitizing, incorporating additives useful in photography, such as couplers, hardeners stabilizers and coating the resulting composition onto a photographic support base. The sulfo-substituted thia-carbocyanine spectral sensitizing dyes are added to the silver halide photographic emulsion according to the present invention after a desalting step in obtaining

said emulsion. The desalting step refers to the step of removing soluble salts which are formed during the precipitation of silver halide grains.

It is known that silver halide photographic emulsions can be formed by precipitating silver halide grains in an aqueous dispersing medium comprising a binder, gelatin preferably being used as a binder. The silver halide grains are precipitated by reaction of aqueous solutions of silver salts with aqueous solutions of halide salts during which water soluble salts are formed.

In order to avoid soluble salts in the emulsion layers of a photographic material from crystallizing out after coating and other photographic or mechanical disadvantages (stickiness, brittlenes, etc.), the soluble salts formed during precipitation have to be removed.

There are various methods for desalting a silver halide photographic emulsion, such as the water washing method of gelled and noodled gelatin emulsion and the precipitation (or flocculation) method by using inorganic salts (e.g. sodium sulfate), anionic surfactants, anionic polymers (e.g. polystyrene sulfonic acid) or gelatin derivatives (e.g. carbamoylated gelatin).

Other suitable desalting methods are those wherein the dispersing medium and soluble salts dissolved therein can be removed from the silver halide emulsion on a continous basis, such as, for example, a combination of dialysis or electrodialysis for the removal of soluble salts or a combination of osmosis or reverse osmosis for the removal of the dispersing medium.

In a particularly preferred enmbodiment, among the known techniques for removing the dispersing medium and soluble salts while retaining silver halide grains in the remaining dispersion, ultrafiltration is a particularly advantageous cleaning arrangement for the purpose of this invention. The use of ultrafiltration for removing soluble salts is illustrated in Research Disclosures 10208 (1972), 13122 (1975), 13577 (1975) and 16351 (1977) and in BE 818,237, in US 4,334,012; 4,336,328; 4,758,505 and in DE 2,555,364. Typically, an ultrafiltration unit comprising membranes of inert, non-ionic polymers is used as a cleaning arrangement. Since silver halide grains are large in comparison with the dispersing medium and the soluble salts or ions, silver halide grains are retained by said membranes while the dispersing medium and the soluble salts dissolved therein are removed.

The action mechanism of preferred membranes is described in GB 1,307,331. The membranes used in the ultra-filtration comprise a very thin layer of extremely fine pore texture supported upon a thicker porous structure. Suitable membranes consist of polymers such as polyvinylacetate, polyvinylalcohol, polyvinylformate, polyvinylethers, polyamides, polyimides, polyvinyl and polyvinylidene chloride, aromatic polymers, such as aromatic polyesters, polytetrafluoroethylene, regenerated cellulose, cellulose esters, such as cellulose acetate, or mixed cellulose esters. The membranes in question have anisotropic, semipermeable properties, show considerable mechanical, thermal and chemical stability and are photographically inert. The membranes are preferably permeable to molecules having molecular weights of up to about 300,000 and, more especially, of up to about 50,000.

The pressure of the emulsion contacting the ultrafiltration membrane can vary over a wide range. Typically, the pressure within the reaction vessel contacting the ultrafiltration membrane is about 700 kPa, while the outlet pressure of the retentate is up about 70 kPa. The pressure difference across the membrane is typically in the range of from about 280 to 420 kPa. It is however within the skilled in the art to operate at pressures outside of these ranges, depending upon the construction of the reaction vessel and the ultrafiltration unit, the viscosity of the emulsion, the concentration of the retentate, and the purity of the retentate desired.

As said before, ultrafiltration is the preferred desalting method to separate dispersing media and/or soluble salts according to the purpose of this invention and offers a number of advantages versus other cleaning techniques. One of the advantages of the ultrafiltration is that the time required for separating dispersing media and soluble salts is very short, so that the total time of silver halide precipitation is not substantially increased by the ultrafiltration process.

It has been found in the present invention that diffusion sensitization due to migration of sulfo-substituted thiacarbocyanine spectral sensitizing dyes does not occur when the addition of those dyes to the silver halide photographic emulsion is p made at the end of the silve4r halide emulsion making, after the desalting step process which consists in an ultrafiltration process, and before the addition of the gelatin to reconstitute the silver halide emulsion.

It has been found that by ultrafiltering at the end of the silver halide emulsion making, as shown before, a concentrate of silver halide emulsion grains of a given ionic conductivity and high silver/gelatine ratio can be obtained, stored and then conveniently processed to get a more effective optical sensitization.

Thanks to the poor shelling of the silver halide grain by the gelatine there, a lower amount of cyanine dyes is required to layer the crystal surfaces than is needed by doing it after the chemical ripening, as it is a common use.

The more effective the adsorption of dyes on the crystal, the less the molecules trapped by the gelatine

in the layer, the lower the diffusion into the adjacent magenta layer, as has been checked by conditioning the coated films 7 days at 38°C and 75% relative humidity.

The silver halide emulsions may be chemically sensitized using the usual sensitizing agents. Sulfur containing compounds, gold and noble metal compounds, polyoxyalkylene compounds are particularly suitable. Methods for chemically sensitizing silver halide emulsions are described, for example, in Research Disclosure 17643, Section III, 1978.

The usual antifoggants and stabilizers may be used as described in Research Disclosure 17643, Section VI, 1978, such as azaindenes.

Other suitable addenda, such as hardeners, coating aids, plasticizers, matting agents, developing agents, color couplers, absorbing and scattering materials, which may be added to the silver halide emulsions are described in Research Disclosure 17643, 1978.

The silver halide color photographic elements of the present invention comprise at least one blue-sensitive silver silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one silver-halide red-sensitive silver halide emulsion layer, said layers being associated with yellow, magenta and cyan dye-forming couplers. As used herein, the word "associated" means that the cyan dye-forming couplers according to the present invention and the silver halide emulsions are positioned in such a way as to imagewise produce in the photographic layers upon coupling with the oxidized aromatic primary amine-type developing agents very stable cyan indoaniline dyes. Such cyan couplers may be incorporated in the silver halide emulsion layers, in an adjacent layer or in the processing solutions. In a preferred form, the cyan couplers are incorporated in the silver halide emulsion layer.

In order to introduce the couplers for use in the present invention into the silver halide emulsion layer, some conventional methods known to the skilled in the art can be employed. According to US patents 2,322,027, 2,801,170, 2,801,171 and 2,991,177, the couplers can be incorporated into the silver halide emulsion layer by the dispersion technique, which consists of dissolving the coupler in a water-immiscible high-boiling organic solvent and then dispersing such a solution in a hydrophilic colloidal binder under the form of very small droplets. The preferred colloidal binder is gelatin, even if some other kinds of binders can be used.

Another type of introduction of the couplers into the silver halide emulsion layer consists of the so-called "loaded-latex technique". A detailed description of such technique can be found in BE patents 853,512 and 869,816, in US patents 4,214,047 and 4,199,363 and in EP patent 14,921. It consists of mixing a solution of the couplers in a water-miscible organic solvent with a polymeric latex consisting of water as a continous phase and of polymeric particles having a mean diameter ranging from 0.02 to 0.2 micrometers as a dispersed phase.

Another useful method is the Fisher process. According to such a process, couplers having a water-soluble group, such as a carboxyl group, a hydroxy group, a sulfonic group or a sulfonamido group, can be added to the photographic layer for example by dissolving them in an alkaline water solution.

The cyan couplers for use in the present invention are generally incorporated into a red-sensitive silver halide emulsion layer to form one of the differently sensitized silver halide emulsion layers of a multilayer color photographic material. Such material generally comprises a support base having coated thereon one or more red-sensitive silver halide emulsion layers, one or more green-sensitive silver halide emulsion layers, one or more blue-sensitive silver halide emulsion layers and additionally filter layers, interlayers, protective layers and sub-layers. The layer units can be coated in any conventional order, but in a preferred layer arrangement the red-sensitive layes are coated nearest the support and are overcoated by the green-sensitive layers, a yellow filter layer and the blue-sensitive layers.

More preferably, the red-sensitive silver halide emulsion layer, associated according to this invention with the cyan couplers of Formula (I), is composed of two or more silver halide emulsion layers sensitized to the same spectral region of the visible spectrum, the uppermost silver halide emulsion layer of which having the highest sensitivity and the lowermost silver halide emulsion layer having the lowest sensitivity, as described in GB patent 923,045, in FR patent 2,043,433 and in US patent 4,582,780. Most preferably, the uppermost red-sensitive silver halide emulsion layer having the highest sensitivity comprises the cyan couplers of Formula (I).

The most useful yellow-forming couplers are conventional open-chain ketomethylene type couplers. Particular examples of such couplers are benzoylacetanilide type and pivaloyl acetanilide type compounds. Yellow-forming couplers that can be used are specifically described in US patents 2,875,057, 3,265,506, 3,408,194, 3,551,151, 3,682,322, 3,725,072 and 3,891,445, in DE patents 2,219,917, 2,261,361 and 2,414,006, in GB patent 1,425,020, in JP patent 10,783/76 and in JP patent applications 26,133/72, 73,147/73, 102,636/76, 6,341/75, 123,342/75, 130,442/75, 1,827/76, 87,650/75, 82,424/77 and 115,219/77.

The most useful magenta-forming couplers are conventional pyrazolone type compounds, indazolone type compounds, cyanoacetyl compounds, pyrazoletriazole type compounds, etc, and particularly preferred couplers are pyrazolone type compounds. Magenta-forming couplers are described for example in US patents

2,600,788, 2,983,608, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,834,908 and 3,891,445,in DE patent 1,810,464, in DE patent applications 2,408,665, 2,417,945, 2,418,959 and 2,424,467 and in JP patent applications 20,826/76, 58,922/77, 129,538/74, 74,027/74, 159,336/75, 42,121/77, 74,028/74, 60,233/75, 26,541/76 and 55,122/78.

Colored couplers can be used which include those described for example in US patents 3,476,560, 2,521,908 and 3,034,892, in JP patent publications 2,016/69, 22,335/63, 11,304/67 and 32,461/69, in JP patent applications 26,034/76 and 42,121/77 and in DE patent application 2,418,959.

DIR (Development Inhibitor Releasing) couplers can be used which include those described for example in US patents 3,227,554, 3,617,291, 3,701,783, 3,790,384 and 3,632,345, in DE patent applications 2,414,006, 2,454,301 and 2,454,329, in GB patent 953,454, in JP patent applications 69,624/77, 122,335/74 and 16,141/76.

In addition to DIR couplers, some other compounds which release development inhibitors upon development can also be present in the light-sensitive material. Such kind of DIR compounds is described for example in US patents 3,297,445 and 3,379,529, in DE patent application 2,417,914, in JP patent applications 15,271/77 and 9,116/78.

Two or more kinds of the couplers described above can be incorporated in the same layer, or the same coupler can also be present in two or more layers.

The layers of the photographic material can contain various colloids, alone or in combination, such as binding materials, as for example described in Research Disclosure 17643, IX, December 1978.

The above described emulsions can be coated onto several support bases (cellulose triacetate, paper, resincoated paper, polyester, and the like) by adopting various methods, as described in Research Disclosure 17643, XV and XVI, December 1978.

The present invention is not limited to photographic materials with a particular type of emulsion or silver halides. It can therefore find an application with photographic materials containing different types of emulsions or silver halides, such as for example those described in Research Disclosure 17643, I, December 1978.

The silver halide emulsions prepared according to the process of this invention may be used as photosensitive emulsions for various photographic materials, such as high surface sensitivity or high internal sensitivity negative emulsions, surface-fogged or unfogged direct-positive emulsions, print-out emulsions, reversal emulsions, emulsions for black-and-white materials, for color materials, radiographic materials, transfer color materials, and the like.

The photographic elements, including a silver halide emulsion prepared according to this invention, may be processed to form a visible image upon association of the silver halides with an alkaline aqueous medium in the presence of a developing agent contained in the medium or in the material, as known in the art. Suitable developing compounds are in particular the p-phenylenediamine derivatives, for example 2-amino-5-diethylamino-toluene chlorydrate (called CD2), 2-amino-N-ethyl-N-(β-methanesulfonamido)-m-toluidine sesquisulfate monohydrate (called CD3), 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate (called CD4).

In the case of color photographic materials, the processing comprises at least a color developing bath and, optionally, a prehardening bath, a neutralizing bath, a first (black and white) developing bath, etc. These baths are well known in the art and are described for instance in Research Disclosure 17643, 1978.

After color development, the image-wise developed metallic silver and the remaining silver salts generally must be removed from the photographic element. This is performed in separate bleaching and fixing baths or in a single bath, called blix, which bleaches and fixes the image in a single step. The bleaching bath is a water solution having a pH equal to 5.60 and containing an oxidizing agent, normally a complex salt on an alkali metal or of ammonium and of trivalent iron with an organic acid, e. g., EDTA.Fe.NH_4, wherein EDTA is the ethylenediaminotetracetic acid. While processing, this bath is continously aired to oxidize the divalent iron which forms while bleaching the silver image and regenerated, as known in the art, to maintain the bleach effectiveness. Poor working of these operations may cause loss of cyan density of the dyes.

Further to the above mentioned oxidizing agents, the blix bath contains known fixing agents, such as for example ammonium or alkali metal thiosulfates. Both bleaching and fixing baths can contain other additives, e. g. polyalkyleneoxide derivatives, as described in GB patent 933,008 in order to increase the effectiveness of the bath, or thioethers known as bleach accelerators.

The present invention will now be illustrated by the following examples, but not limited to them.

EXAMPLE 1. (prior art)

A photographic silver chlorobromoiodide emulsion with 5.13 mol% chloride, 87.7 mol% bromide and 7.17 mol% iodide with an average grain size of 0.43 μm was chemically sensitized with gold, thiocyanate, p-toluensulfonate and p-toluenethiosulfonate and then stabilised with N-ethyl-benzothiazolium iodide.

The above emulsion was then divided into seven parts and each part was finalled at 38°C to give the compositions as follows:

1) A methanolic solution of 0.046 moles/mol Ag of the red sensitizers (S-10) and of 0.286 moles/mol Ag of the red sensitizer (S-11) was added to get a coverage of 0.332 moles of the two dyes per mol Ag; the emulsion was paused 20 minutes under stirring, then added of a water solution of 4-hydroxy-6-methyl tetrazaindene and of cyan coupler (C-1) in an amount of 0.126 moles/mol Ag.

2) The emulsion was optically sensitized and stabilised as above, with the only replacement of cyan coupler (C-1) with non-leuco cyan coupler (I-19), in amount of 0.094 moles/mol Ag.

The compositions 3 to 7 were finalled as the composition 2, with the only replacement of the pair of optical sensitisers (S-10) and (S-11) with the following ones, in the same molar ratio to silver :

3) (S-10)

4) (S-11)

5) (S-5)

6) (S-6)

7) (S-7)

Each of the compositions was coated on a cellulose triacetate base at 30 minutes after the end of finalling; the same compositions were separately coated after 15 hours holding at 40°C under stirring.

A gelatin layer was coated on each film as protective top-coat, containing the monochloro-dihydroxy-triazine hardener. The films were kept 7 days at room condition to let them harden, then aged 7 days at 38°C and 75% relative humidity. Each of the film samples was exposed through a continuous wedge at 5500°K, processed in a standard Kodak EP-2 processing color chemistry as described in US patent No. 4,346,873, then read at an automatic densitometer.

Table 1 compares the speed values of the sample films obtained by coating the compositions 1 to 7 30 minutes after the end of finalling with the speed values of the same sample films obtained by coating the same compositions after 15 hours holding at 40°C under stirring. The speed values were measured at a value of optical density of 0.20+Fog.

TABLE 1

Film	30 minutes	5 hours
1 (control)	19.9	20.1
2 (control)	19.0	15.3
3 (control)	16.2	12.3
4 (control)	19.0	14.8
5 (invention)	17.5	17.2
6 (invention)	17.7	16.5
7 (invention)	16.7	17.1

It can be clearly seen the loss of speed of the film 2, containing the same pair of red spectral sensitizers (S-10) and (S-11) of film 1 and the non-leuco cyan coupler (I-19) in place of the coupler (C-1). Each of these sensitizers (S-10) and (S-11), both of a cationic type, show the similar problem, when they are singularly combined with the non-leuco cyan coupler (I-19) (films Nos. 3 and 4).

On the contrary, it can be seen (films Nos. 5, 6 and 7) that no substantial desensitization occurs when the sulfo substituted red sensitizers of anionic type (S-5), (S-6) and (S-7) have been used in combination with the non-leuco cyan coupler (I-19).

EXAMPLE 2

A photographic silver iodobromide emulsion with 91 mol% bromide and 9 mol% iodide with an average grain size of 1.13 μm was prepared by double jetting $AgNO_3$ and KBr plus KCl in presence of a gelatin water solution containing KI plus KCl. At the end of the precipitation, the obtained emulsion was fed to an ultrafiltration unit fitted with four polysulfone semipermeable membranes, type PTHK000C5, (commercially available from Millipore Co., USA), having a total working surface of 1.84 m^2 and a NMWL (Nominal Molecular Weight Limit) of 100,000 and washed by diafiltration while continously adding makeup water to the emulsion to get a concentrate of ionic conductivity 1000 S, then chilled and stored.

Part of the concentrate was then used to reconstitute an emulsion (control) of silver to gelatin ratio of 1.2.

Another part (a) of the same concentrate was added of a methanol solution of the sensitizing dye (S-5), in amount of 0.334 mmoles/mol Ag. A third part (b) of the same concentrate was added with 0.028 mmoles/mol Ag of sensitizing dye (S-8), 0.293 mmoles/mol Ag of sensitizing dye (S-5) and 0.016 mmoles/mol Ag of sensitizing dye (S-9). A fourth part (c) of the same concentrate was added with 0.028 mmoles/mol Ag of sensitizing dye (S-8), 0.293 mmoles/mol Ag of sensitizing dye (S-1) and 0.016 mmoles/mol Ag of sensitizing dye (S-9).

Compositions (a), (b) and (c) were then added of the same amount of gelatin as the control emulsion, before starting the chemical ripening with gold, thiocyanate, p-toluensulfonate and p-toluene-thiosulfonate, and N-ethyl-benzothiazolium iodide.

Control emulsion was divided into three parts, that were optically sensitized during the finalling step before coating, using the same amounts of the dyes as in the respective emulsions sensitized according to the present invention obtaining composition (a′) with sensitizing dye (S-5), composition (b′) with sensitizing dyes (S-8)+(S-5)+(S-9) and composition (c′) with sensitizing dyes (S-8)+(S-1)+(S-9).

The three compositions for use in the present invention (a), (b) and (c) and the three control compositions (a′), (b′) and (c′) were then added of the stabilizer 4-hydroxy-6-methyl tetrazaindene, antifoggants, surfactants and an amount of 0.094 moles/mol Ag of the cyan coupler (I-19), and coated on a triacetate base, at a silver coverage of 2 g Ag/sqm, with a gelatin layer as a top-coat, containing the hardener monochloro dihydroxy-triazine, obtaining, respectively, the films Nos. 1, 2 and 3 of the present invention and the control films Nos. 4, 5 and 6.

Another set of films, respectively, films Nos.7, 8 and 9 of the present invention and control films Nos. 10, 11 and 12 were each coated using the compositions (a), (b), (c), (a′), (b′) and (c′) as cyan layers, then each overcoated with the same magenta layer. This was obtained from a silver bromoiodide emulsion prepared as above, chemically and optically sensitisied in a conventional way, using the (S-12) sensitizing dye, then added of the (C-2) colour coupler; films 7 to 12 were overlayered with a gelatin top-coat, as above.

Samples of films Nos.1 to 12 were stored for 7 days at room condition to let them harden, then aged 7 days at 38°C and 75% relative humidity. Each of the film samples was exposed through a continuous wedge at 5500°K, then processed in a standard Kodak EP-2 processing color chemistry with conditions similar to those stated in US Pat. No. 4,346,873.

After processing, status D densitometry was measured. Table 2 reports the sensitometric values of the cyan coatings, after 15 days on shelf life :

TABLE 2

Film n.	Fog	Dmax	Sensitivity (0,20+Fog)	Sensitivity (1,00+Fog)
1 invention	0.11	1.77	19.9	9.3
4 control	0.10	1.76	18.7	8.4
2 invention	0.11	1.75	20.5	10.3
5 control	0.10	1.67	18.9	8.6
3 invention	0.12	1.76	19.8	9.5
6 control	0.14	1.72	18.0	8.1

It can be seen the increase of speed obtained by optically sensitizing the emulsion concentrate after the ultrafiltration process (films Nos. 1, 2 and 3), versus the speed obtained by optically sensitizing the reconstituted and chemically ripened emulsions, as it is common practice (control films Nos. 4, 5 and 6).

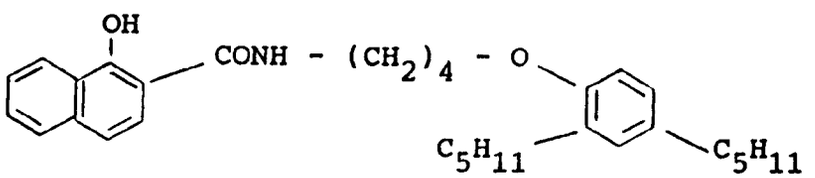
Figs. 1 and 2 show the sensitization spectra of samples exposed to a Jarrel-Ash Spectrometer and processed as above.

Fig.1 shows the comparison between the magenta and cyan spectra of the films 7 (invention: continuous line) and 10 (control: dashed line), whose cyan layers were sensitized with the same sensitizing dye (S-5), respectively, after the desalting step process (according to the present invention) and before coating (control).

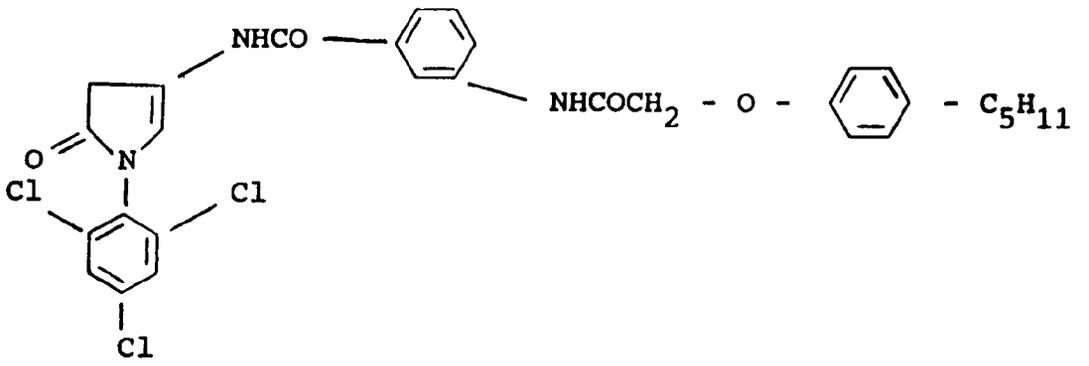
Fig.2 shows the comparison between the magenta and cyan spectra of the the films 9 (invention: continuous line) and 12 (control: dashed line), whose cyan layers were sensitized with the same sensitizing dyes (S-8)+(S-1)+(S-9), respectively, after the desalting step process (according to the present invention) and before coating (control).

Looking at both graphs, it can be appreciated the increase of magenta optical density in the red region (550-600 nm), shown by the dashed area occurring in the control films Nos. 10 and 12 whose cyan layers were sensitized in the conventional way: that proves the migration of the red sensitizers into the green sensitive layers, so that a magenta color is formed upon exposure of red light affecting the color purity of the element.

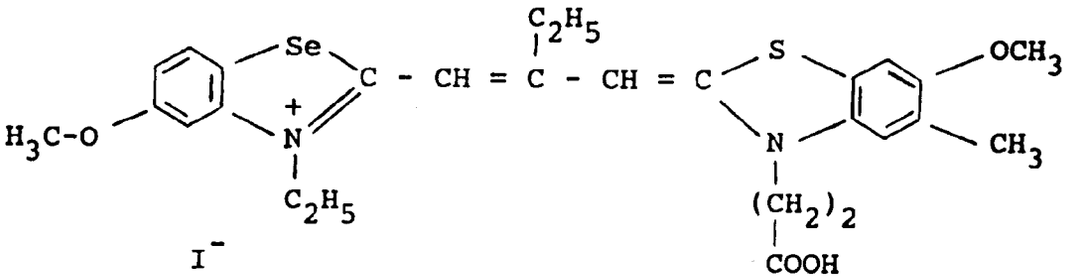
(C-1)



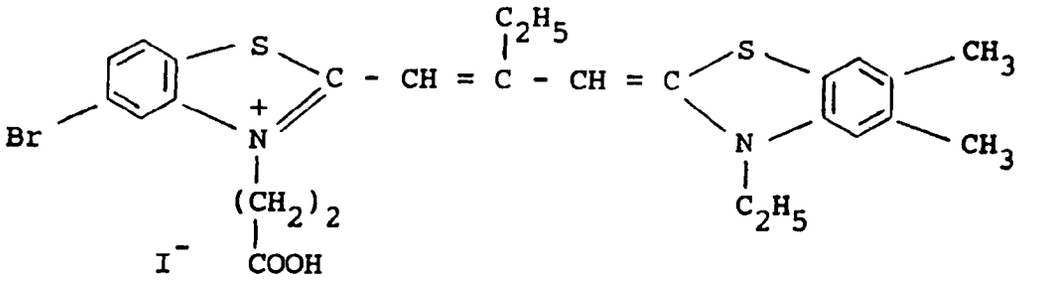
(C-2)



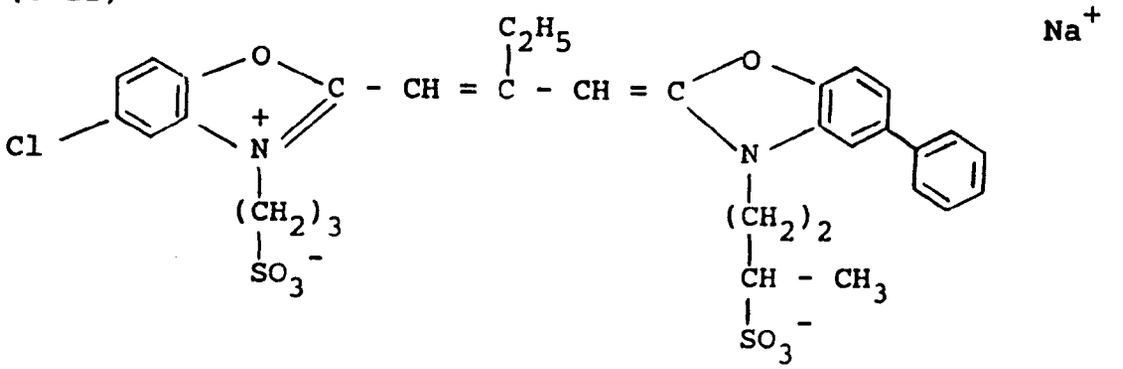
(S-10)



(S-11)



(S-12)

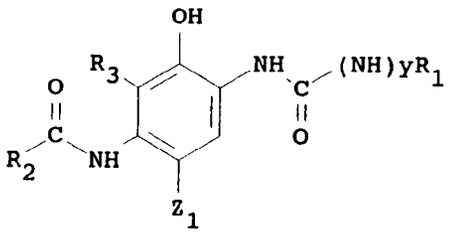


Claims

1. A multilayer light-sensitive silver halide color photographic element having at least one layer comprising

a red-sensitive silver halide photographic emulsion containing at least one 2,5-diacylamino phenol cyan coupler and at least one sulfo-substituted thiacarbocyanine spectral sensitizing dye, characterized in that said red-sensitive silver halide emulsion has been spectrally sensitized by addition of said spectral sensitizing dye after the desalting step in the preparation of said emulsion and before the addition of dispersing medium to reconstitute the emulsion to provide substantially no migration of said spectral sensitizing dye into adjacent layers.

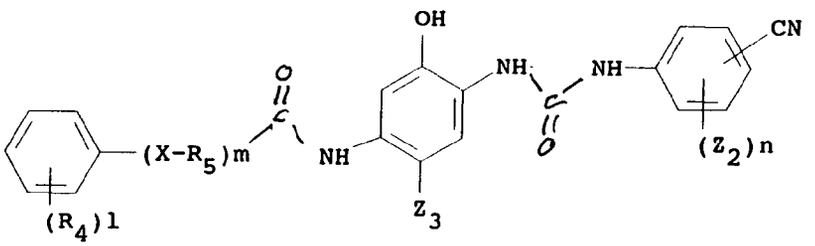
2. A light-sensitive silver halide color photographic element of claim 1 wherein said phenol cyan coupler is represented by the formula (I):



(I)

wherein R_1 is an aryl group, R_2 is an alkyl group or an aryl group, R_3 is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group, and Z_1 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent and y is 0 or 1.

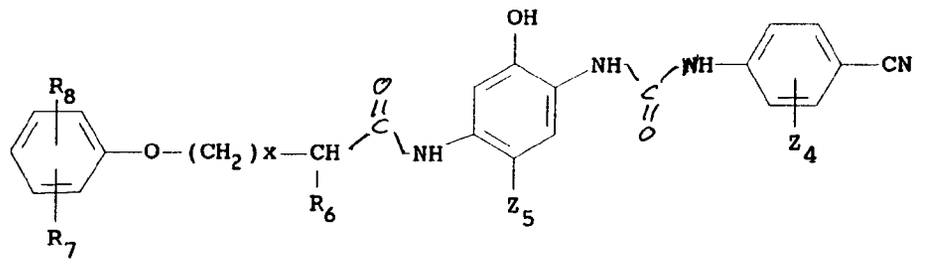
3. A light-sensitive silver halide color photographic element of claim 1 wherein said phenol cyan coupler is represented by the formula (II):



(II)

wherein Z_2 is a hydrogen atom, a halogen atom or a monovalent organic group, R_4 is a hydrogen atom, a halogen atom, a hydroxyl group, a nitro group, an alkyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxy group, an aryloxy group, an alkylcarbonyl group, an arylcarbonyl group, an acyloxy group, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfonamido group, a sulfamoyl group, X is an oxygen atom or a sulfur atom, R_5 is a straight-chain or a branched-chain alkylene group, n is an integer of 0 to 3, m is an integer of 0 to 4 and l is an integer of 1 to 4, and Z_3 is a hydrogen atom, a halogen atom or a group which can be splitt off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.

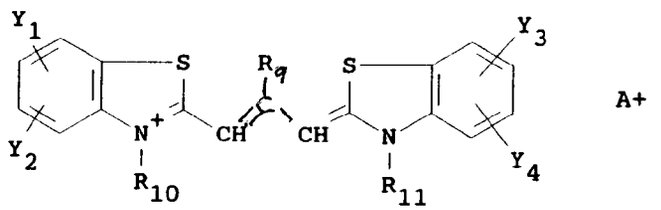
4. A light-sensitive silver halide color photographic element of claim 1 wherein said phenol cyan coupler is represented by the formula (III):



(III)

wherein Z_4 is a hydrogen atom or a halogen atom, Z_5 is a hydrogen atom or a chlorine atom, R_6 is a hydrogen atom or an alkyl group, R_7 and R_8 may be either the same or different and each is a hydrogen atom, an alkyl group or an alkoxy group, provided that the sum of carbon atoms of R_6, R_7 and R_8 is from 8 to 20, and x is an integer of 0 to 2.

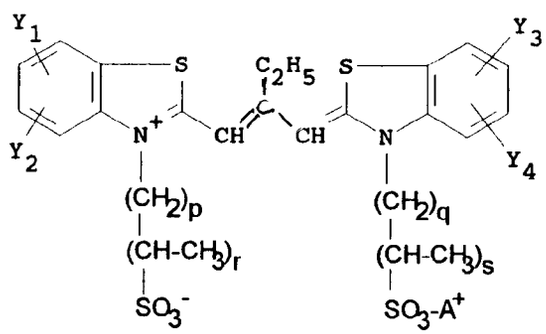
5. A light-sensitive silver halide color photographic element of claim 1, wherein said spectral sensitizing dye is represented by the formula (IV):



(IV)

wherein Y_1, Y_2, Y_3 and Y_4 represent a hydrogen atom, a halogen atom, a hydroxy group, an alkoxy group, an amino group, an acylamino group, an alkoxycarbonyl group, an alkyl group, an alkoxycarbonylamino group, or an aryl group, or, together, Y_1 and Y_2 and, respectively Y_3 and Y_4, form the atoms necessary to complete a benzene ring, R_9 is hydrogen or a low alkyl group having 1 to 3 carbon atoms, R_{10} and R_{11} may be either the same or different and each is a sulfo group-containing straight- or branched-alkyl group having 1 to 5 carbon atoms, one of said sulfo groups forming an inner salt with the quaternary nitrogen atom, and A is a hydrogen atom or cationic group.

6. A light-sensitive silver halide color photographic element of claim 1, wherein said spectral sensitizing dye is represented by the formula (V):



(V)

wherein Y_1, Y_2, Y_3 and Y_4 represent a hydrogen atom, a halogen atom, a hydroxy group, an alkoxy group, an amino group, an acylamino group, an alkoxycarbonyl group, an alkyl group, an alkoxycarbonylamino group, or an aryl group, or, together, Y_1 and Y_2 and, respectively Y_3 and Y_4, form the atoms necessary to complete a benzene ring, p and q are integers of 1 to 4, r and s are integers of 0 to 1, and A is a hydrogen atom or a cationic group.

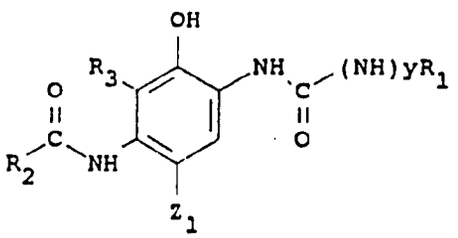
7. Process for chemically and spectrally sensitizing a silver halide photographic emulsion containing at least one 2,5-diacylamino phenol cyan coupler and at least one sulfo-substituted thiacarbocyanine dye, characterized by the steps of desalting the silver halide emulsion, spectrally sensitizing said emulsion by addition of said dye, reconstituting the silver halide emulsion by the addition of dispersing medium, chemically sensitizing said emulsion and then adding at least one 2,5-diacylamino phenol cyan coupler to said emulsion.

8. Process for chemically and spectrally sensitizing a silver halide photographic emulsion of claim 7, wherein said desalting step comprises an ultrafiltration process.

Patentansprüche

1. Mehrschichtiges, lichtempfindliches farbphotographisches Silberhalogenid-Element mit mindestens einer Schicht, umfassend ein rotempfindliche photographische Silberhalogenid-Emulsion, die mindestens einen 2,5-Diacylaminophenol-Cyan-Kuppler und mindestens einen Sulfo-substituierten spektralen Thiocarbocyanin-Sensibiliserungsfarbstoff enthält, dadurch gekennzeichnet, daß die rotempfindliche Silberhalogenid-Emulsion durch Zusatz des spektralen Sensibilisierungsfarbstoffes bei der Herstellung der Emulsion nach dem Entsalzungsschritt und vor dem Zusatz des Dispersionsmittels zum Rekonstituieren der Emulsion spektral sensibilisiert wurde, um im wesentlichen keine Migration des spektralen Sensibilisierungsfarbstoffes in die benachbarten Schichten zu gewähren.

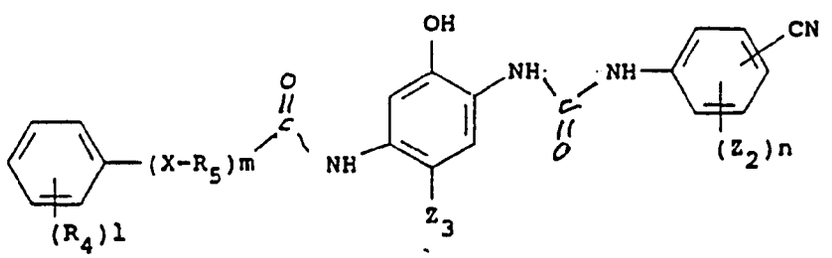
2. Lichtempfindliches farbphotographisches Silberhalogenid-Element nach Anspruch 1, bei welchem der Phenol-Cyan-Kuppler durch die Formel (I) dargestellt wird:



(I)

worin R_1 eine Aryl-Gruppe, R_2 eine Alkyl-Gruppe oder eine Aryl-Gruppe, R_3 ein Wasserstoffatom, ein Halogenatom, eine Alkyl-Gruppe oder eine Alkoxy-Gruppe sind und Z_1 ein Wasserstoffatom, ein Halogenatom oder eine Gruppe ist, die durch Umsetzen des Kupplers mit dem oxidierten Produkt eines aromatischen Farbentwicklungsmittels vom primären Amin-Typ abgespalten werden kann, und Y Null oder 1 ist.

3. Lichtempfindliches farbphotographisches Silberhalogenid-Element nach Anspruch 1 bei welchem der Phenol-Cyan-Kuppler dargestellt wird durch die Formel (II):

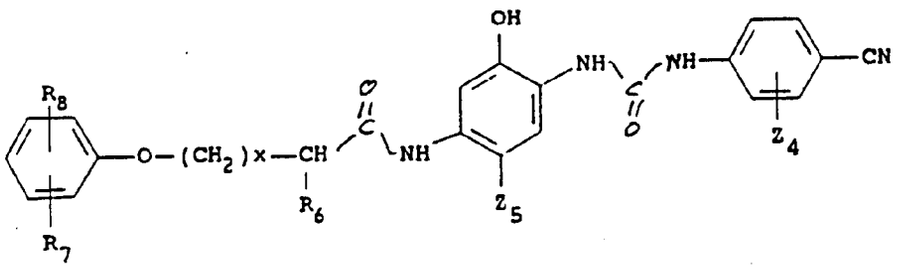


(II)

worin Z_2 ein Wasserstoffatom, ein Halogenatom oder eine einwertige organische Gruppe, R_4 ein Wasserstoffatom, ein Halogenatom, eine Hydroxyl-Gruppe, eine Nitro-Gruppe, eine Alkyl-Gruppe, eine Alkoxycarbonyl-Gruppe, eine Aryloxycarbonyl-Gruppe, eine Alkoxy-Gruppe, eine Aryloxy-Gruppe, eine Alkylcarbonyl-Gruppe, eine Arylcarbonyl-Gruppe, eine Acyloxy-Gruppe, eine Alkylsulfonyl-Gruppe, eine Arylsulfonyl-Gruppe, eine Acyl-Gruppe, eine Acylamino-Gruppe, eine Sulfonamido-Gruppe, eine

Sulfamoyl-Gruppe sind, X ein Sauerstoffatom oder ein Schwefelatom ist, R_5 ein geradkettige oder verzweigtkettige Alkylen-Gruppe ist, n eine ganze Zahl von 0 bis 3, m eine ganze von 0 bis 4 und *l* eine ganze Zahl von 1 bis 4 sowie Z_3 ein Wasserstoffatom, ein Halogenatom oder eine Gruppe ist, die durch Umsetzen des Kupplers mit dem oxidierten Produkt eines aromatischen Farbentwicklungsmittels vom primären Amin-Typ abgespalten werden kann.

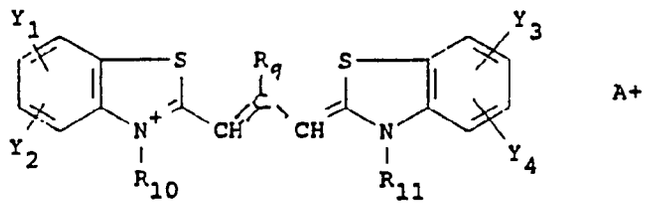
4. Lichtempfindliches farbphotographisches Silberhalogenid-Element nach Anspruch 1, bei welchem der Phenol-Cyan-Kuppler dargestellt wird durch die Formel (III):



(III)

worin Z_4 ein Wasserstoffatom oder Halogenatom, Z_5 ein Wasserstoffatom oder ein Chloratom, R_5 ein Wasserstoffatom oder eine Alkyl-Gruppe sind, R_7 und R_5 entweder gleich oder verschieden sein können und jeweils ein Wasserstoffatom, eine- Alkyl-Gruppe oder eine Alkoxy-Gruppe unter der Voraussetzung, daß die Summe der Kohlenstoffatome von R_5, R_7 und R_5 8 bis 20 beträgt und x eine ganze Zahl von 0 bis 2 ist.

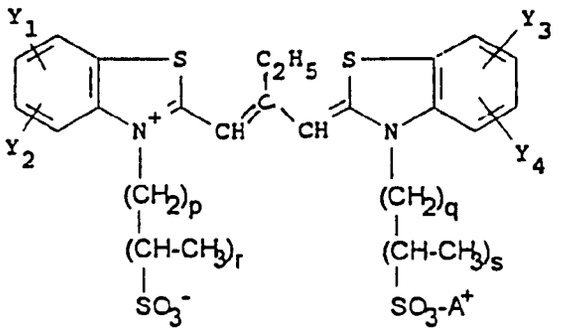
5. Lichtempfindliches farbphotographisches Silberhalogenid-Element nach Anspruch 1, bei welchem der spektrale Sensibilisierungsfarbstoff dargestellt wird durch die Formel (IV):



(IV)

worin Y_1, Y_2, Y_3 und Y_4 ein Wasserstoffatom, ein Halogenatom, eine Hydroxy-Gruppe, eine Alkoxy-Gruppe, eine Amino-Gruppe, eine Acylamino-Gruppe, eine Alkoxycarbonyl-Gruppe, eine Alkyl-Gruppe, eine Alkoxycarbonylamino-Gruppe oder eine Aryl-Gruppe darstellen oder zusammen Y_1 und Y_2 bzw. Y_3 und Y_4 die Atome bilden, die zum Vervollständigen eines Benzol-Rings notwendig sind, R_9 Wasserstoff oder eine niedere Alkyl-Gruppe mit 1 bis 3 Kohlenstoffatomen ist, R_{10} und R_{11} entweder gleich oder verschieden sein können und jeweils eine Sulfo-Gruppe enthaltende geradkettige oder verzweigtkettige Alkyl-Gruppe mit 1 bis 5 Kohlenstoffatomen sind, von denen eine der Sulfo-Gruppen ein inneres Salz mit dem quaternären Stickstoffatom bildet, und A ein Wasserstoff oder eine kationische Gruppe ist.

6. Lichtempfindliches farbphotographisches Silberhalogenid-Element nach Anspruch 1, bei welchem der spektrale Sensibilisierungsfarbstoff dargestellt wird durch die Formel (V):



(V)

worin Y_1, Y_2, Y_3 und Y_4 ein Wasserstoffatom, ein Halogenatom, eine Hydroxy-Gruppe, eine Alkoxy-Gruppe, eine Amino-Gruppe, eine Acylamino-Gruppe, eine Alkoxycarbonyl-Gruppe, eine Alkyl-Gruppe, eine Alkoxycarbonylamino-Gruppe oder eine Aryl-Gruppe darstellen oder zusammen Y_1 und Y_2 bzw. Y_3 und Y_4 die Atome bilden, die zur Vervollständigung eines Benzol-Ringes erforderlich sind, p und q ganze Zahlen von 1 bis 4 sind, r und s ganze Zahlen von 0 bis 1 und A ein Wasserstoffatom oder eine kationische Gruppe sind.

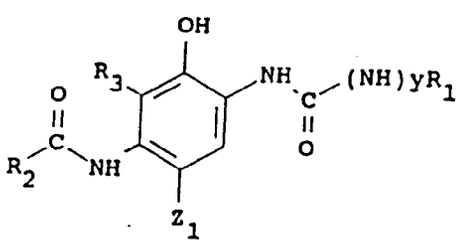
7. Verfahren zum chemischen oder spektralen Sensibilisieren einer photographischen Silberhalogenid-Emulsion enthaltend mindestens einen 2,5-Diacylaminophenol-Cyan-Kuppler und mindestens einen Sulfo-substituierten Thiacarbocyanin-Farbstoff, gekennzeichnet durch die Schritte des Entsalzens der Silberhalogenid-Emulsion, spektralen Sensibilisierens der Emulsion durch Zusatz des Farbstoffes, Rekonstituieren der Silberhalogenid-Emulsion durch Zusatz von Dispersionsmittel, chemisches Sensibilisieren der Emulsion und nachfolgendes Zusetzen von mindestens einem 2,5-Diacylaminophenol-Cyan-Kuppler zu der Emulsion.

8. Verfahren zum chemischen und spektralen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 7, bei welchem der Entsalzungsschritt einen Ultrafiltrationsprozeß umfaßt.

Revendications

1. Elément photographique en couleurs à halogénure d'argent photosensible multicouche comportant au moins une couche comprenant une émulsion photographique d'halogénure d'argent sensible au rouge contenant au moins un copulant de cyan de 2,5-diacylamino phénol et au moins un colorant de sensibilisation spectrale de thiacarbocyanine sulfo-substituée, caractérisé en ce que l'émulsion d'halogénure d'argent sensible au rouge a été spectralement sensibilisée par l'addition dudit colorant de sensibilisation spectrale après l'étape d'élimination des sels lors de préparation de ladite émulsion et avant l'addition de milieu dispersant pour reconstituer l'émulsion de manière à ce qu'il n'y ait pratiquement aucune migration du colorant de sensibilisation spectrale dans des couches adjacentes.

2. Elément photographique en couleurs à halogénure d'argent photosensible suivant la revendication 1, dans lequel le copulant de cyan de phénol est représente par la formule (I) :

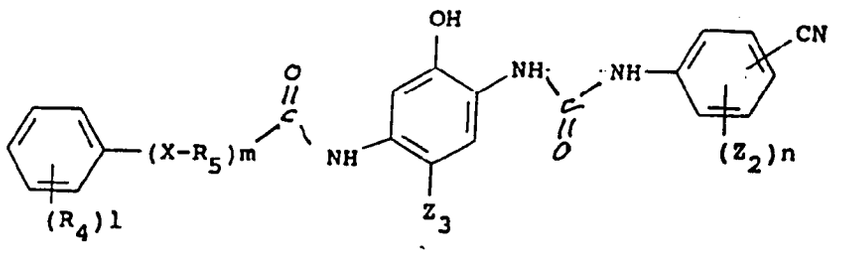


(I)

dans laquelle R_1 représente un groupe aryle, R_2 représente un groupe alkyle ou un groupe aryle, R_3 représente un atome d'hydrogène, un atome d'halogène, un groupe alkyle ou un groupe alcoxy et Z_1 repré-

sente un atome d'hydrogène, un atome d'halogène ou un groupe qui peut être séparé par la réaction dudit copulant avec le produit oxyde d'un agent de développement chromogène du type amine primaire aromatique et y est égal à 0 ou 1.

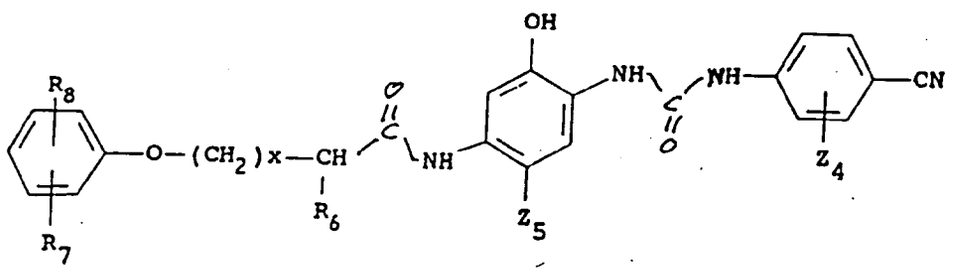
3. Elément photographique en couleurs à halogénure d'argent photosensible suivant la revendication 1, dans lequel le copulant de cyan de phénol est représenté par la formule (II) :



(II)

dans laquelle Z_2 représente un atome d'hydrogène, un atome d'halogène ou un groupe organique monovalent, R_4 représente un atome d'hydrogène, un atome d'halogène, un groupe hydroxyle, un groupe nitro, un groupe alkyle, un groupe alcoxycarbonyle, un groupe aryloxycarbonyle, un groupe alcoxy, un groupe aryloxy, un groupe alkylcarbonyle, un groupe arylcarbonyle, un groupe acyloxy, un groupe alkylsulfonyle, un groupe arylsulfonyle, un groupe acyle, un groupe acylamino, un groupe sulfonamido, un groupe sulfamoyle, X représente un atome d'oxygène ou un atome de soufre, R_5 représente un groupe alkylène à chaîne droite ou à chaîne ramifiée, n est un nombre entier de 0 à 3, m est un nombre entier de 0 à 4 et l est un nombre entier de 1 à 4 et Z_3 représente un atome d'hydrogène, un atome d'halogène ou un groupe qui peut être séparé par la réaction du copulant avec le produit oxydé d'un agent de développement chromogène du type amine primaire aromatique.

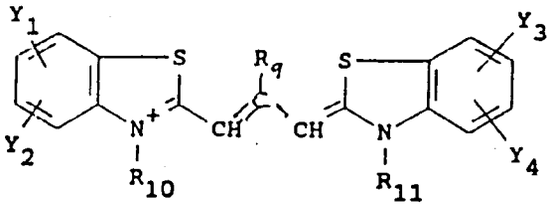
4. Elément photographique en couleurs à halogénure d'argent photosensible suivant la revendication 1, dans lequel le copulant de cyan de phénol est représenté par la formule (III) :



(III)

dans laquelle Z_4 représente un atome d'hydrogène ou un atome d'halogène, Z_5 représente un atome d'hydrogène ou un atome de chlore, R_6 représente un atome d'hydrogène ou un groupe alkyle, R_7 et R_8 peuvent être identiques ou différents et représentent chacun un atome d'hydrogène, un groupe alkyle ou un groupe alcoxy, pour autant que la somme des atomes de carbone de R_5, R_7 et R_5 soit de 8 à 20 et x est un nombre entier de 0 à 2.

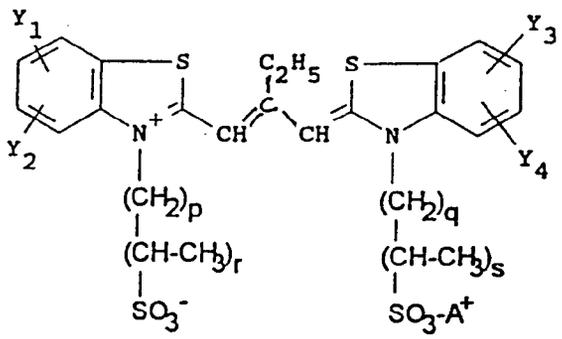
5. Elément photographique en couleurs à halogénure d'argent photosensible suivant la revendication 1, dans lequel le colorant de sensibilisation spectrale est représenté par la formule (IV) :



(IV)

dans laquelle Y_1, Y_2, Y_3 et Y_4 représentent un atome d'hydrogène, un atome d'halogène, un groupe hydroxy, un groupe alcoxy, un groupe amino, un groupe acylamino, un groupe alcoxycarbonyle, un groupe alkyle, un groupe alcoxycarbonylamino ou un groupe aryle ou bien, ensemble, Y_1 et Y_2 et, respectivement Y_3 et Y_4, forment les atomes nécessaires pour réaliser un noyau benzénique, R_9 représente de l'hydrogène ou un groupe alkyle inférieur comportant 1 à 3 atomes de carbone, R_{10} et R_{11} peuvent être identiques ou différents et représentent chacun un groupe alkyle droit ou ramifié contenant des groupes sulfo comportant 1 à 5 atomes de carbone, l'une de ces groupes sulfo formant un sel interne avec l'atome d'azote quaternaire et A représente un atome d'hydrogène ou un groupe cationique.

6. Elément photographique en couleurs à halogénure d'argent photosensible suivant la revendication 1, dans lequel le colorant de sensibilisation spectrale est représenté par la formule (V)



(V)

dans laquelle Y_1, Y_2, Y_3 et Y_4 représentent un atome d'hydrogène, un atome d'halogène, un groupe hydroxy, un groupe alcoxy, un groupe amino, un groupe acylamino, un groupe alcoxycarbonyle, un groupe alkyle, un groupe alcoxycarbonylamino ou un groupe aryle ou bien, ensemble, Y_1 et Y_2 et, respectivement Y_3 et Y_4, forment les atomes nécessaires pour réaliser un noyau benzénique , p et q sont des nombres entiers de 1 à 4, r et s sont des nombres entiers de 0 à 1 et A représente un atome d'hydrogène ou un groupe cationique.

7. Procédé de sensibilisation chimique et spectrale d'une émulsion photographique d'halogène d'argent contenant au moins un copulant de cyan de 2,5-diacylamino phénol et au moins un colorant de thiacarbocyanine sulfo-substituée, caractérisé par les étapes d'élimination des sels de l'émulsion d'halogénure d'argent, de sensibilisation spectrale de ladite émulsion par l'addition dudit colorant, de reconstitution de l'émulsion d'halogénure d'argent par l'addition de milieu dispersant, de sensibilisation chimique de l'émulsion susdite et ensuite d'addition d'au moins un copulant de cyan de 2,5-diacylamino phénol à l'émulsion.

8. Procédé de sensibilisation chimique et spectrale d'une émulsion photographique d'halogénure d'argent suivant la revendication 7, dans lequel l'étape d'élimination des sels comprend un procédé d'ultrafiltration.

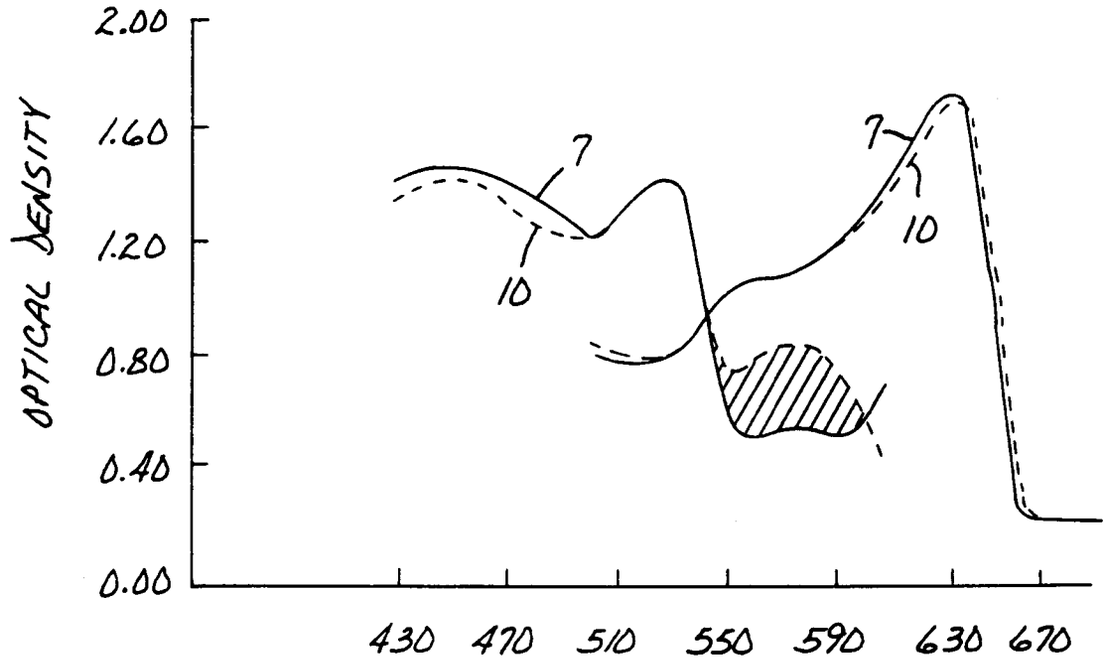

2.00
1.60
1.20
0.80
0.40
0.00
OPTICAL DENSITY
7
10
7
10
430
470
510
550
590
630
670
WAVE LENGTH (nm)

Fig. 1

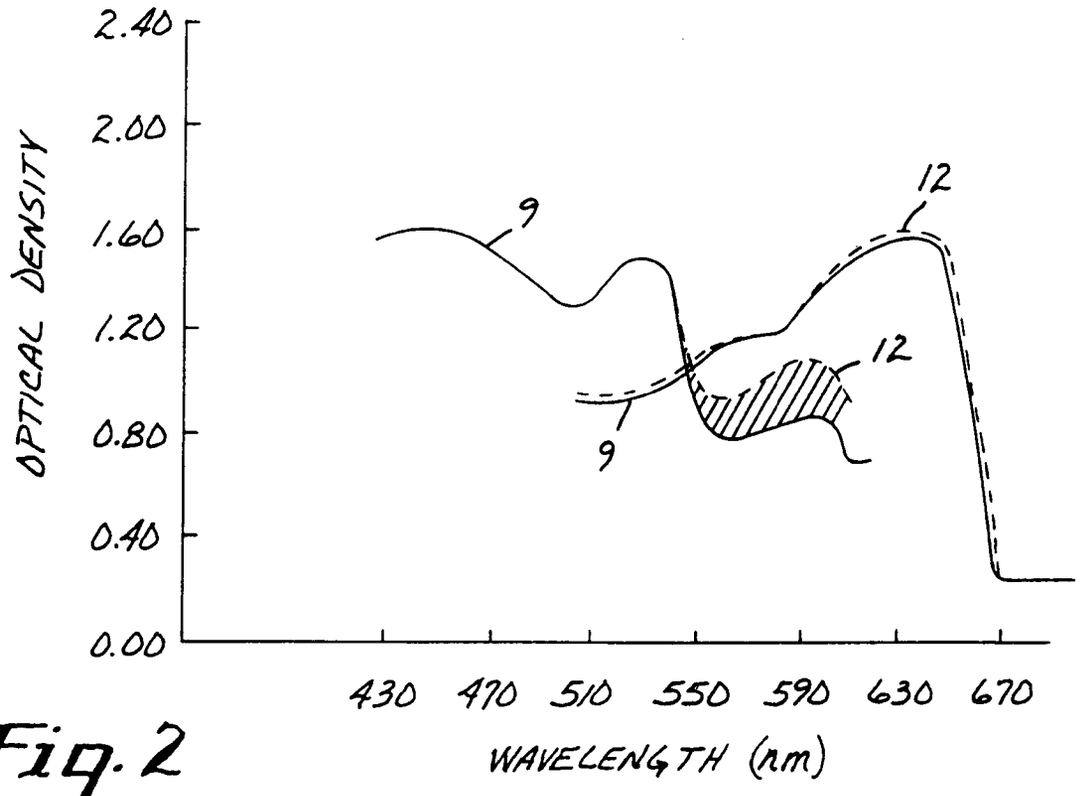

2.40
2.00
1.60
1.20
0.80
0.40
0.00
OPTICAL DENSITY
9
12
12
9
430
470
510
550
590
630
670
WAVELENGTH (nm)

Fig. 2