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(54) **Method for processing silver halide color photosensitive materials.**

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EP-A- 0 128 720
EP-A- 0 178 539
EP-A- 0 289 008
FR-A- 2 388 308
JOURNAL OF THE SOCIETY OF MOTION PICTURE AND TELEVISION ENGINEERS, vol. 88, no.3, March 1979, pages 165-167, Society of Motion Picture and Television Engineers,Scardale, US; L.E. ALLEN: "Ion-exchange recovery techniques for the reuse of color developers"

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EP 0 368 340 B1

Description

Background of the Invention

This invention relates to a method for processing silver halide color photosensitive (photographic) materials. In particular, this invention relates to a method for processing silver halide color photosensitive materials wherein the color developer is regenerated and reused to reduce the amount of the waste solution. By this method, the silver halide color photosensitive materials have their stable finish and excellent images.

As environmental pollution by industrial waste waters poses problems recently, various efforts are made to reduce the amount of waste solutions for reducing the pollution load on the environment in the processing of photosensitive materials. Among these efforts the most important is that toward the reduction of the amount of waste color developer having a high BOD (biochemical oxygen demand) and COD (chemical oxygen demand). Methods proposed heretofore for solving this problem fall is into categories: (1) a method wherein the amount of the color developer to be replenished is reduced while lowering of the color developing activity is prevented by enhancing the color development temperature and (2) a regeneration processing method wherein halogen accumulated in the used color developer is removed to restore the developability thereof.

In the former method, restoration of the activity of the developer reduced due to the accumulation of halogen ions such as iodine, bromine and chlorine ions released from the photosensitive material in the development step is achieved by elevating the temperature or by increasing the pH or the amount of the color developing agent. Although the operation is easy in this method, degree of compensation obtainable is limited and it is difficult to markably reduce the amount of the replenisher to minimize the amount of the waste solution.

In the latter regeneration processing method, the accumulated halogen ions are removed by an anion exchange resin method described in the Journal of the SMPTE, 65, 478-484 (September, 1956) or an electrodialysis method as described in Japanese Patent Unexamined Published Application (hereinafter referred to as 'J. P. KOKAI') No. 52-119934. Although these methods have a demerit in that they require a special apparatus, they ahve a merit in that they can be conducted without discharging the waste color developer. In view of these circumstances, further studies are being made into these methods.

In particular, the anion exchange resin method is employed relatively widely, since the cost of the apparatus in this method is lower than that in the electrodialysis method. Studies are being made for further improving this method. The improved methods developed so for include, for example, a method for preventing deterioration of the effect of the anion exchange resin by pretreating the color developer with an adsorbent before processing it with the anion exchange resin as described in the Journal of Applied Photographic Engineering, Vol. 5, No. 4, 216-219 (Autumn, 1979) and a method for improving a miniaturized system wherein a disposable anion exchange resin is used as described in the Journal of Image Technology Vol. 13, No. 3, 85 to 89 (June, 1987).

However, when a color developer is used repeatedly by regeneration with an anion exchange resin, oxidation products of the color developing agent, oxidation and decomposition products of a preservative and substances dissolved out of a silver halide color photosensitive material accumulate in the color developer to change the finishing effect of the silver halide color photographic material and particularly the sensitivity is changed and the fog is increased. Another problem is that the image-maintaining effect of the color photosensitive material after the processing is impaired and particularly yellow stain increases during the storage at a high temperature and a high humidity. It is thus difficult to reuse the color developer over a long period of time. Therefore, the color developer must be controlled by a complicated method such as a method wherein a part thereof is replaced with fresh color developer at a given time interval, a method wherein the used color developer is partially discarded while a given amount of fresh color developer is continuously replenished or a method wherein the pH and the composition of the color developer are adjusted in order to compensate for change in the performacne thereof.

EP-A-0 128 720 discloses a process for regenerating a colour developer which includes the step of contacting it with an anion exchanger. The anion exchanger can include quaternary ammonium salt-type exchange groups which remove bromide ions from the used colour developer.

EP-A-0 252 288 teaches that pyrazoloazole dyes are superior to pyrazolone dyes due to their possessing superior storage stability with respect to fading or yellow stains.

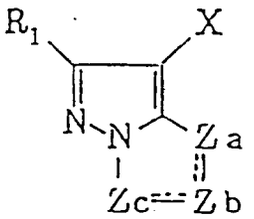
Summary of the Invention

Therefore, a primary object of the present invention is to provide a method for processing silver halide color photosensitive materials by repeatedly regenerating and reusing (hereinafter referred to as 'regenerating') a color developer with an anion exchanger in such that changes in the sensitivity and fog, and deterioration of

the shelf stability of the image are inhibited, no complicated control is required and discharge of the color developer is substantially unnecessary.

Other objects of the present invention will be clear from the following description and Examples.

The present invention has been accomplished on the basis of a finding that the above-described object of the present invention is attained by incorporating at least one pyrazoloazole magenta coupler of the following general formula (I) into a silver halide color photosensitive material to be processed with a color developer which is to be regenerated with an anion exchanger:

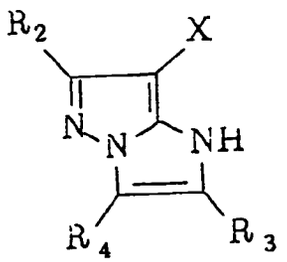


(I)

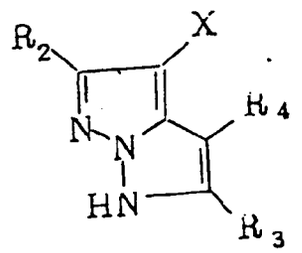
wherein R_1 represents a hydrogen atom or a substituent, X represents a hydrogen atom or a group capable of being eliminated by a coupling reaction with an oxidized product of an aromatic primary amine developing agent, and Za, Zb and Zc each represent methine, substituted methine, =N- or -NH- with the provisos that one of the Za ⎓ Zb bond and Zb-Zc bond is a double bond and the other is a single bond, that when the Zb ⎓ Zc bond is a carbon-to-carbon double bond, it may constitute a part of an aromatic ring, that R_1 or X may form a polymer (at least a dimer) by acting as a bridging group to one or more other groups of general formula (I) and that when Za, Zb or Zc is a substituted methine, the substituted methine may form a polymer (at least a dimer) by acting as a bridging group to one or more other groups of general formula (I).

In the general formula (I), the term 'polymers' indicates those having two or more groups of the general formual (I) in the molecule including bis-compounds and polymer couplers. The polymer couplers herein may be homopolymers comprising only a monomer having a moiety represented by the general formula (I) (preferably having a vinyl group; hereinafter referred to as 'vinyl monomer') or they may form copolymers with a non-color-developing ethylenic monomer which does not couple with an oxidized product of an aromatic primary amine developing agent.

The compounds of the general formula (I) are nitrogen-containing heterocyclic couplers of five-membered ring / five-membered ring condensation type. The color-developing mother nucleus thereof has isoelectronic aromatic properties like those of naphthalene and a chemical structure generally called 'azapentalenes'. Among the couplers represented by the general formula (I), preferred are 1H-imidazo[1,2-b]pyrazoles, 1H-pyrazolo[1,5-b]pyrazoles, 1H-pyrazolo[5,1-c][1,2,4]triazoles, 1H-pyrazolo[1,5-b][1,2,4]triazoles, 1H-pyrazolo[1,5-d]tetrazoles and 1H-pyrazolo[1,5-a]benzimidazoles represented by the following general formulae (II), (III), (IV), (V), (VI) and (VII). Among them, those of the formulae (II), (IV) and (V) are particularly preferred. The most preferred are the compounds of the general formula (V).



(II)



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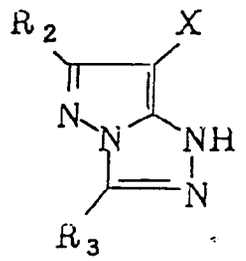

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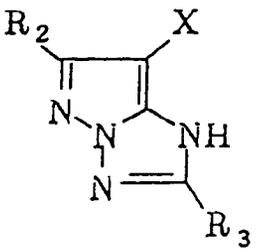

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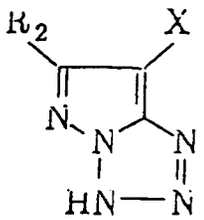

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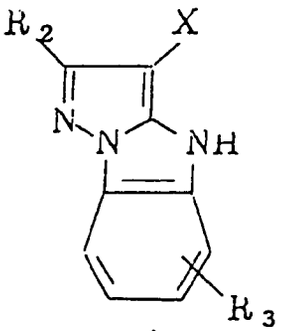


(VII)

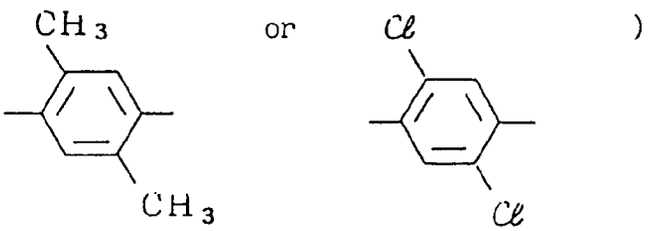
In the general formulae (II) to (VII), R_2, R_3 and R_4 each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonyl group or an aryloxycarbonyl group, and X represents a hydrogen atom, a halogen atom, a carboxy group or a group bonded with the carbon atom at the coupling site through an oxygen atom, a nitrogen atom or a sulfur atom and capable of being coupled off.

R_2, R_3, R_4 or X may be a divalent group to form a bis-compound. When the part represented by any of the general formulae (II) to (VII) is a part of a vinyl monomer, R_2, R_3 or R_4 represents a single bond or a connecting group through which this part is bonded to the vinyl group.

Examples of R_2, R_3 and R_4 include a hydrogen atom, a halogen atom (such as chlorine or bromine atom), an alkyl group [such as methyl, propyl, i-propyl, t-butyl, trifluoromethyl, tridecyl, 3-(2,4-di-t-amylphenoxy)propyl, 2-dodecyloxyethyl, 3-phenoxypropyl, 2-hexylsulfonylethyl, cyclopentyl or benzyl group], an aryl group (such as phenyl, 4-t-butylphenyl, 2-4-di-t-amylphenyl or 4-tetradecanamidophenyl group), a heterocyclic group (such as 2-furyl, 2-thienyl, 2-pyrimidinyl or 2-benzothiazolyl group), a cyano group, an alkoxy group (such as methoxy, ethoxy, 2-methoxyethoxy, 2-dodecyloxyethoxy, 2-phenoxyethoxy or 2-methanesulfonylethoxy group), an aryloxy group (such as phenoxy, 2-methylphenoxy or 4-t-butylphenoxy group), a heterocyclic oxy group (such as 2-benzimidazolyloxy group), an acyloxy group (such as acetoxy or hexadecanoyloxy group), a carbamoyloxy group (such as N-phenylcarbamoyloxy or N-ethylcarbamoyloxy group), silyloxy group (such as trimethylsilyloxy group), a sulfonyloxy group (such as dodecylsulfonyloxy group), an acylamino group [such as acetamido, benzamido, tetradecanamido, α - (2,4-di-t-amylphenoxy)butylamido, γ -(3-t-butyl-4-hydroxyphenoxy)butylamido, or α - {4-(4-hydroxyphenylsulfonyl)phenoxy} decanamido group], an anilino group [such as phenylamino, 2-chloroanilino, 2-chloro-5-tetradecanamidoanilino, 2-chloro-5-dodecyloxycarbonylanilino, N-acetylanilino or 2-chloro-5- { α -(3-t-butyl-4-hydroxyphenoxy)dodecanamido } anilino group], a ureido group (such as phenylureido, N-butyl-N'-methylureido, methylureido or N,N-dibutylureido group), an imido group [such as N-succinimido, 3-benzylhydantoinyl or 4-(2-ethylhexanoylamino)phthalimido group], a sulfamoylamino group (such as N,N-dipropylsulfamoylamino or N-methyl-N-decylsulfamoylamino group), an alkylthio group [such as methylthio, octylthio, tetradecylthio, 2-phenoxyethylthio, 3-phenoxypropylthio or 3-(4-t-butylphe-

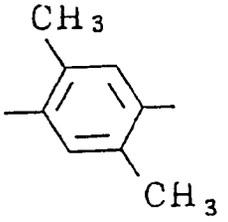
noxy)propylthio group], an arylthio group (such as phenylthio, 2-butoxy-5-t-octylphenylthio, 3-pentadecylphenylthio, 2-carboxyphenylthio or 4-tetradecaneamidophenylthio group), a heterocyclic thio group (such as 2-benzothiazolylthio group), an alkoxycarbonylamino group (such as methoxycarbonylamino or tetradecyloxycarbonylamino group), an aryloxycarbonylamino group (such as phenoxycarbonylamino or 2,4-di-tert-butylphenoxycarbonylamino group), a sulfonamido group (such as methanesulfonamido, hexadecanesulfonamido, benzenesulfonamido, p-toluenesulfonamido, octadecanesulfonamido or 2-methyloxy-5-t-butylbenzenesulfonamido group), a carbamoyl group [such as N-ethylcarbamoyl, N-N-dibutylcarbamoyl, N-(2-dodecyloxyethyl)carbamoyl, N-methyl-N-dodecylcarbamoyl or N-{3-(2,4-di-tert-amylphenoxy)propyl} carbamoyl group], an acyl group [such as acetyl, (2,4-di-tert-amylphenoxy)acetyl or benzoyl group], a sulfamoyl group [such as N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-(2-dodecyloxyethyl)sulfamoyl, N-ethyl-N-dodecylsulfamoyl or N,N-diethylsulfamoyl group], a sulfonyl group (such as methanesulfonyl, octanesulfonyl, benzenesulfonyl or toluenesulfonyl group), a sulfinyl group (such as octanesulfinyl, dodecylsulfinyl or phenylsulfinyl group), an alkoxycarbonyl group (such as methoxycarbonyl, butyloxycarbonyl, dodecylcarbonyl or octadecylcarbonyl group) or an aryloxycarbonyl group (such as phenyloxycarbonyl or 3-pentadecyloxycarbonyl group). X represents a hydrogen atom, a halogen atom (such as chlorine, bromine or iodine atom), a carboxyl group or a group connecting through an oxygen atom (such as acetoxy, propanoyloxy, benzoyloxy, 2,4-dichlorobenzoyloxy, ethoxyoxaloyloxy, pyruvoyloxy, cinnamoyloxy, phenoxy, 4-cyanophenoxy, 4-methanesulfonamidophenoxy, 4-methanesulfonylphenoxy, α -naphthoxy, 3-pentadecylphenoxy, benzyloxycarbonyloxy, ethoxy, 2-cyanoethoxy, benzyloxy, 2-phenethyloxy, 2-phenoxyethoxy, 5-phenyltetrazolyloxy or 2-benzothiazolyloxy group), a group connecting through a nitrogen atom [such as benzenesulfonamido, N-ethyltoluenesulfonamido, heptafluorobutanamido, 2,3,4,5,6-pentafluorobenzamido, octanesulfonamido, p-cyanophenylureido, N,N-diethylsulfamoylamino, 1-piperidyl, 5,5-dimethyl-2,4-dioxo-3-oxazolidinyl, 1-benzylethoxy-3-hydantoinyl, 2N-1,1-dioxo-3(2H)-oxo-1,2-benzoisothiazolyl, 2-oxo-1,2-dihydro-1-pyridinyl, imidazolyl, pyrazolyl, 3,5-diethyl-1,2,4-triazol-1-yl, 5- or 6-bromobenzotriazol-1-yl, 5-methyl-1,2,3,4-triazol-1-yl, benzimidazolyl, 3-benzyl-1-hydantoinyl, 1-benzyl-5-hexadecyloxy-3-hydantoinyl, 5-methyl-1-tetrazolyl, 4-methoxyphenylazo, 4-pivaloylaminophenylazo or 2-hydroxy-4-propanoylphenylazo group), or a group connecting through a sulfur atom (such as phenylthio, 2-carboxyphenylthio, 2-butoxy-5-t-octylphenylthio, 4-methanesulfonamidophenylthio, 2,5-dibutoxyphenylthio, 4-methanesulfonylphenylthio, 4-octanesulfonamidophenylthio, 2-butoxyphenylthio, 4-dodecyloxyphenylthio, 2-(2-hexanesulfonylethyl)-5-tert-octylphenylthio, benzylthio, 2-cyanoethylthio, 1-ethoxycarbonyltridecylthio, 5-phenyl-2,3,4,5-tetrazolylthio, 2-benzothiazolylthio, 2-dodecylthio, 2-dodecylthio-5-thiophenylthio or 2-phenyl-3-dodecyl-1,2,4-triazolyl-5-thio group).

When R_2, R_3, R_4 or X is a divalent group to form a bis compound, the divalent group is a substituted or unsubstituted alkylene group (such as methylene, ethylene, 1,10-decylene or $-CH_2CH_2-O-CH_2CH_2-$ group), a substituted or unsubstituted phenylene group (such as 1,4-phenylene, 1,3-phenylene,



or a $-NHCO-R_2-CONH-$ group in which R_2 represents a substituted or unsubstituted alkylene or phenylene group.

When the part represented by one of the general formulae (II) to (VII) is a part of the vinyl monomer, the connecting group represented by R_2, R_3 or R_4 includes a group comprising a combination of groups selected from the group consisting of substituted or unsubstituted alkylene groups (such as methylene, ethylene, 1,10-decylene and $-CH_2CH_2OCH_2CH_2-$), substituted or unsubstituted phenylene groups (such as 1,4-phenylene, 1,3-phenylene,



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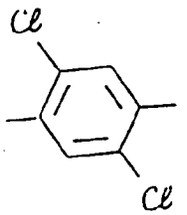
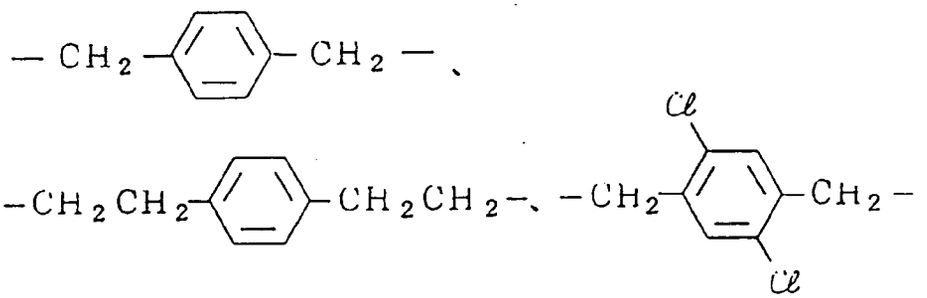


),

-NHCO-, -CONH-, -O-, -OCO- and aralkylene groups such as



The vinyl group of the vinyl monomer includes those having a substituent in addition to these represented by the general formulae (II) to (VII). The preferred substituents are hydrogen atom, chlorine atom and lower alkyl groups having 1 to 4 carbon atoms.

Examples of the uncoupling ethylenic monomer which does not couple with the oxidized products of the aromatic primary amine developing agent include acrylic acid, α -chloroacrylic acid, α -alkylacrylic acids (such as methacrylic acid), esters and amides derived from these acrylic acids (such as acrylamide, n-butylacrylamide, t-butylacrylamide, diacetoneacrylamide, methacrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and β -hydroxymethacrylate), methylenedibisacrylamide, vinyl esters (such as vinyl acetate, vinyl propionate and vinyl laurate), acrylonitrile, methacrylonitrile, aromatic vinyl compounds (such as styrene and its derivatives, vinyltoluene, divinylbenzene, vinylacetophenone and sulfostyrene), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, vinyl alkyl ethers (such as vinyl ethyl ether), maleic acid, maleic anhydride, maleic esters, N-vinyl-2-pyrrolidone, N-vinylpyridine and 2- and 4-vinylpyridines. Two or more kinds of the uncoupling ethylenically unsaturated monomers may be used in combination.

Examples of the coupler compounds of the general formulae (II) to (VII) and methods for synthesizing them are disclosed, for example in the literature shown below.

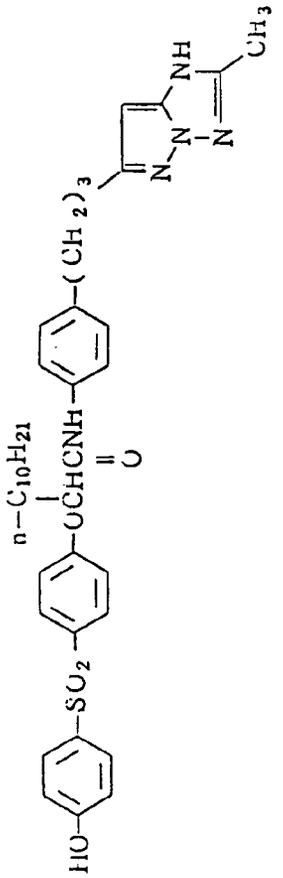
The compounds of the general formula (II) are described in J. P. KOKAI No. 59-162348. The compounds of the general formula (III) are described in J. P. KOKAI No. 60-43659. Those of the general formula (IV) are described in Japanese Patent Publication for Opposition Purpose (hereinafter referred to as 'J. P. KOKOKU) No. 47-27411. Those of the general formula (V) are described in J. P. KOKAI Nos. 59-171956 and 60-172982. Those of the general formula (VI) are described in J. P. KOKAI No. 60-33552. Those of the general formula (VII) are described in U. S. Patent No. 3,061,432.

High color developing ballast groups described in J. P. KOKAI Nos. 58-42045, 59-214854, 59-177553, 59-

177544 and 59-177557 can be applied to all of the compounds of the above general formulae (II) to (VII).

Examples of the pyrazoloazole couplers usable in the present invention will be given below. They by no means limit the pyrazoloazole couplers usable herein:

(M − 1)



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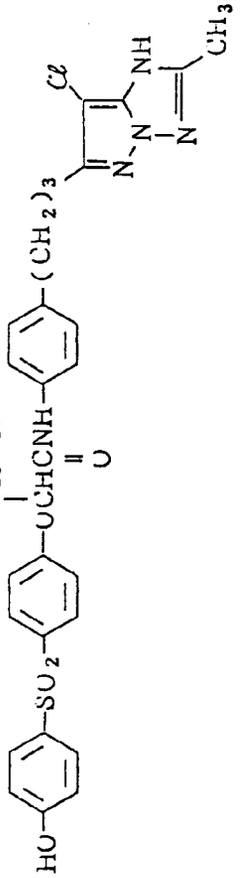

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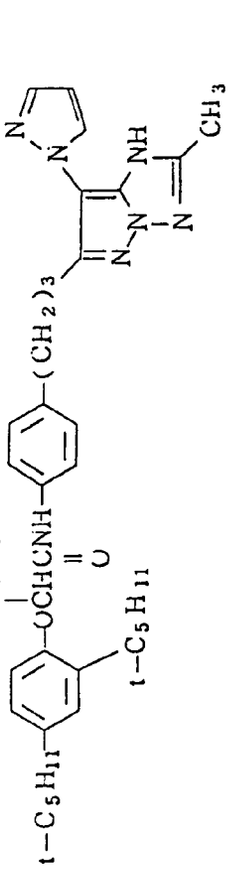

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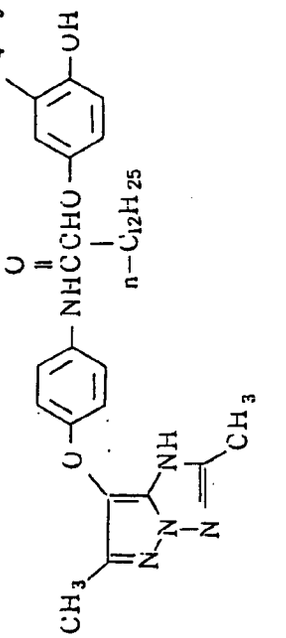

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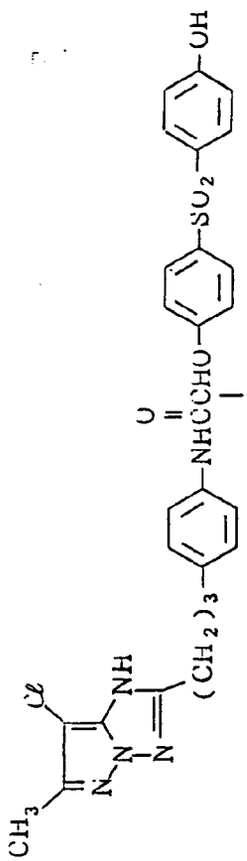

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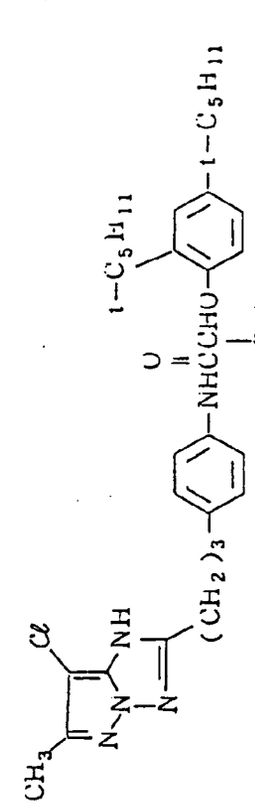

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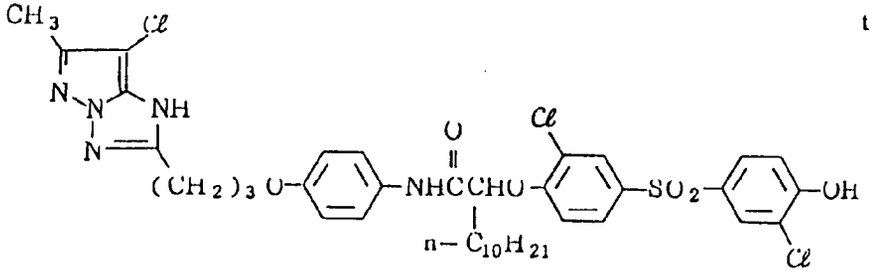

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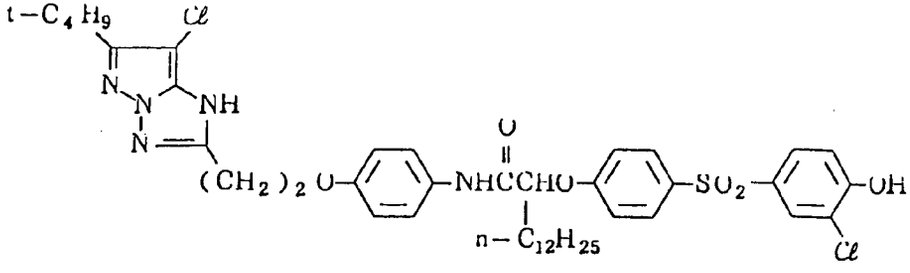
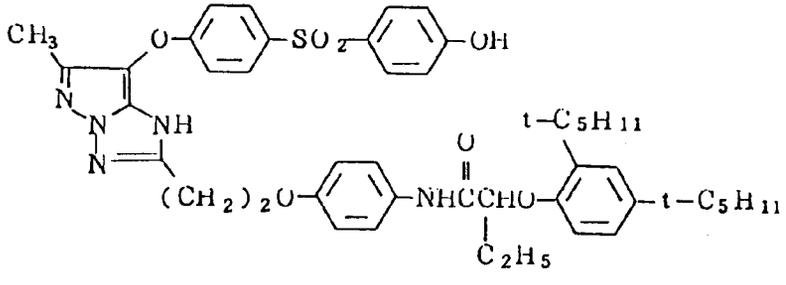
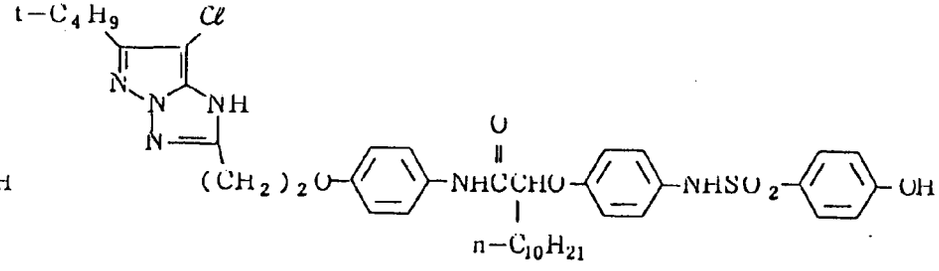


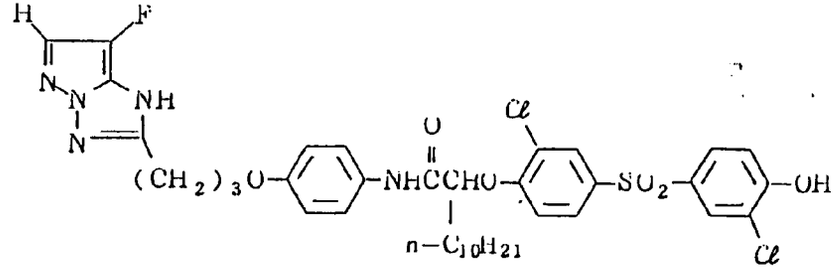
(M − 9)



(M − 10)



(M − 11)



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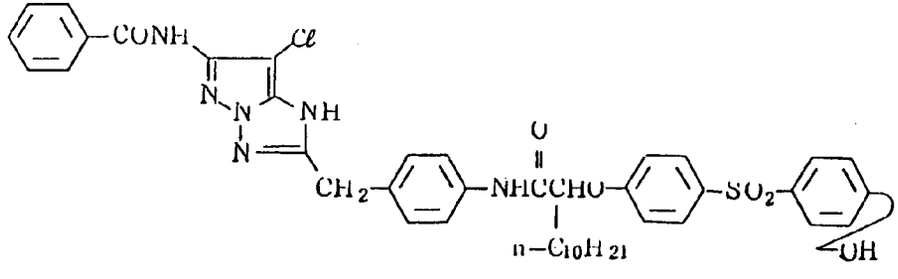

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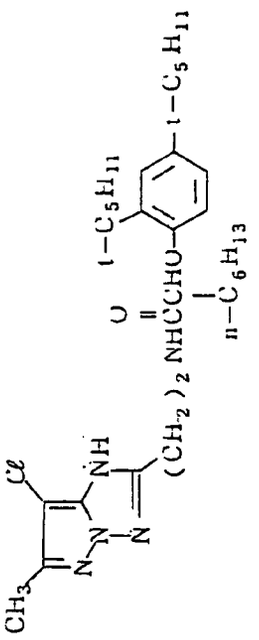

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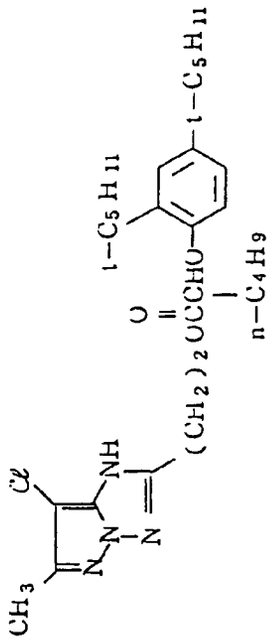

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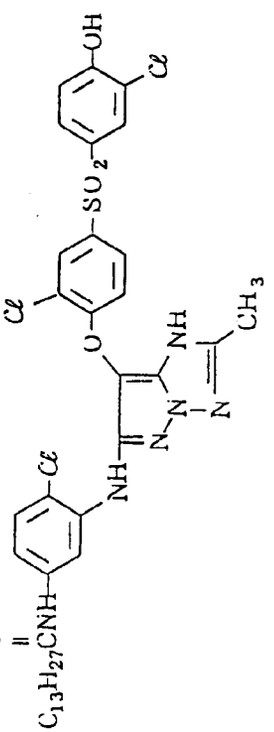

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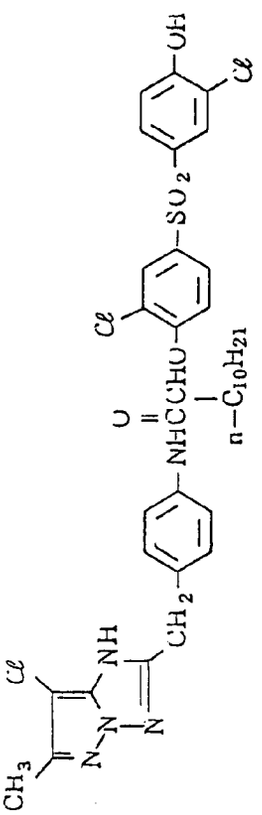

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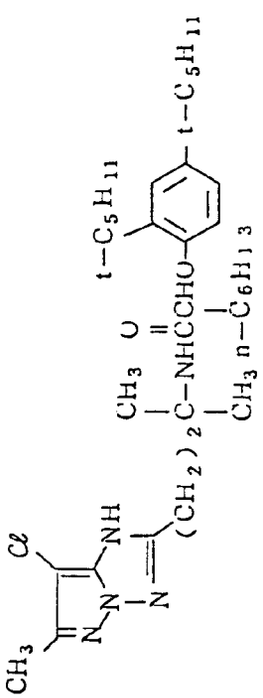

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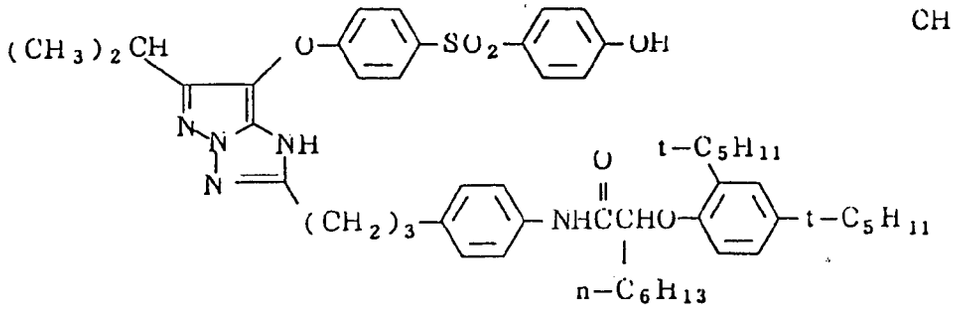
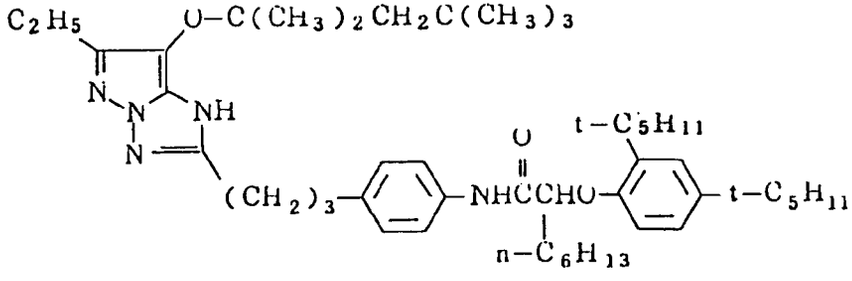


(M − 1 9)



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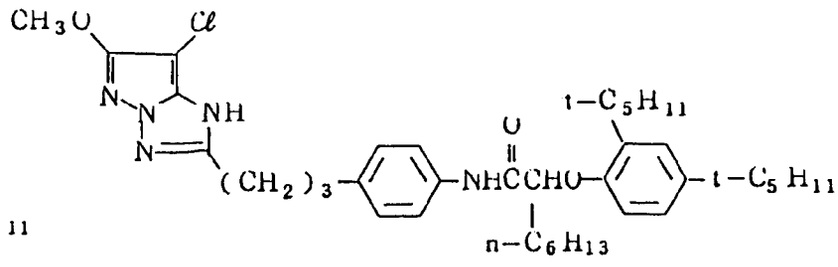

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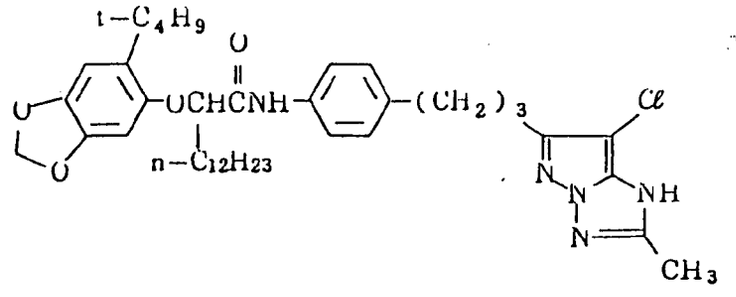

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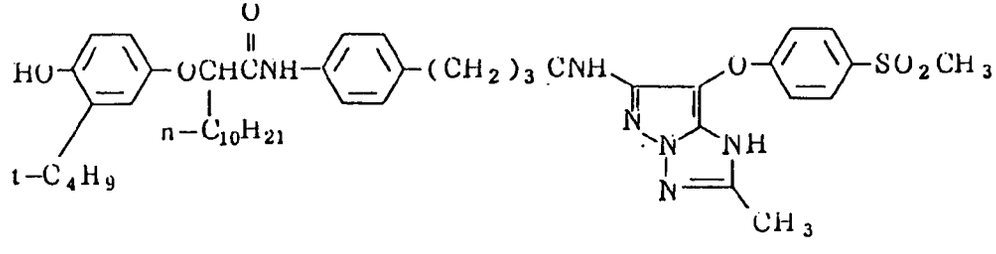

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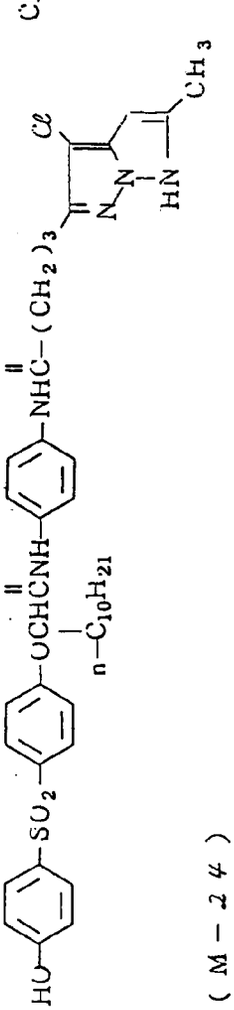

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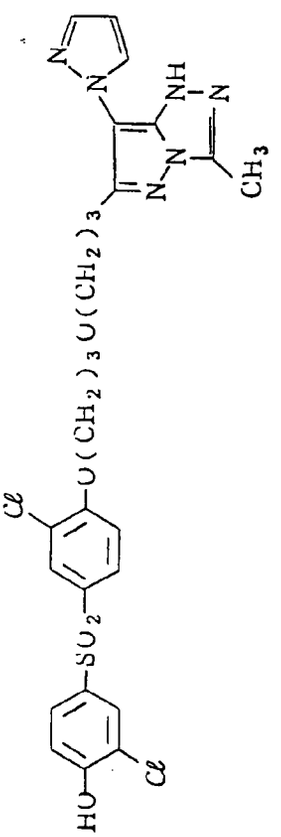

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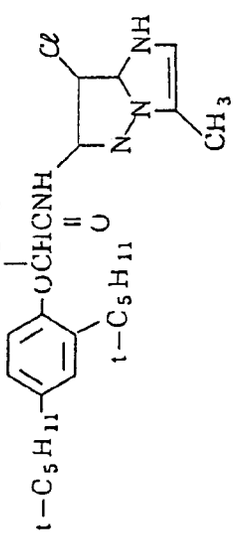

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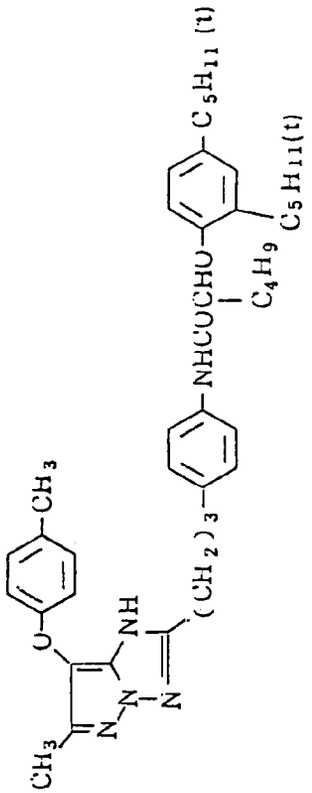

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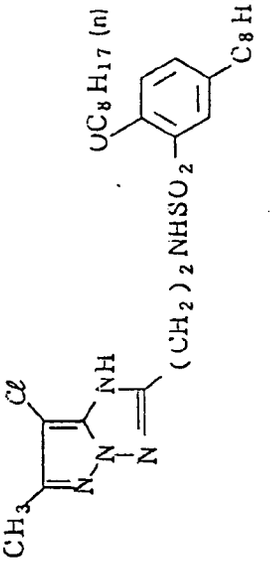

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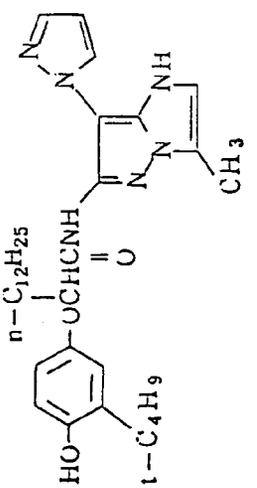

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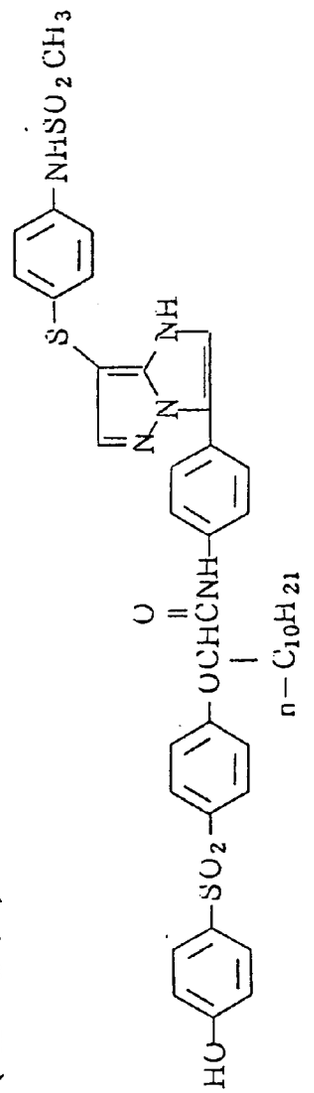
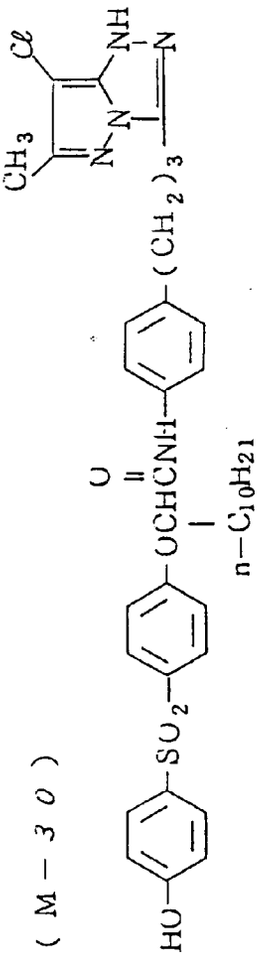


(M − 30)



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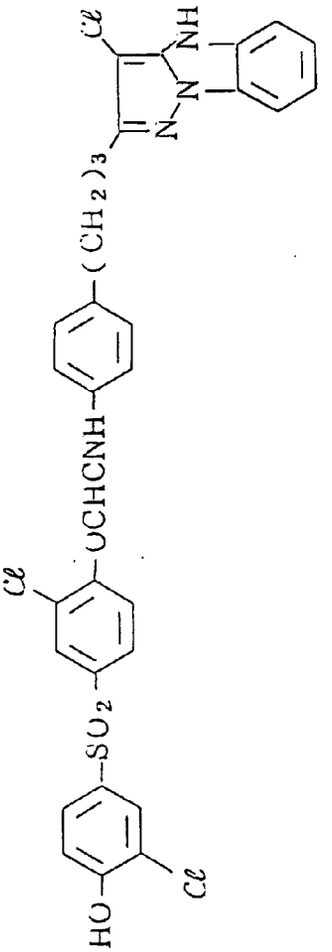

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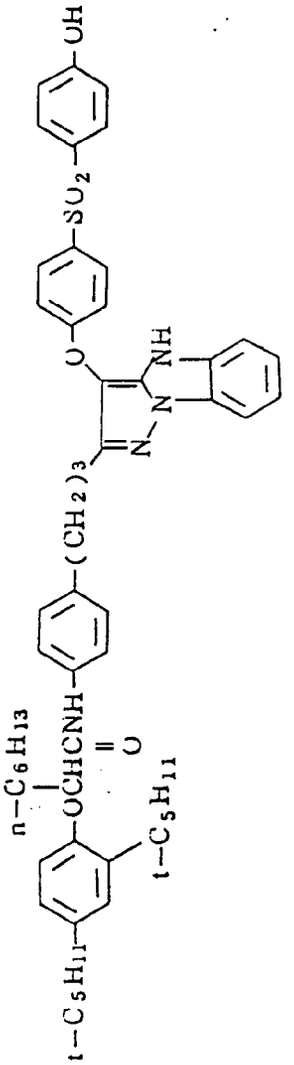

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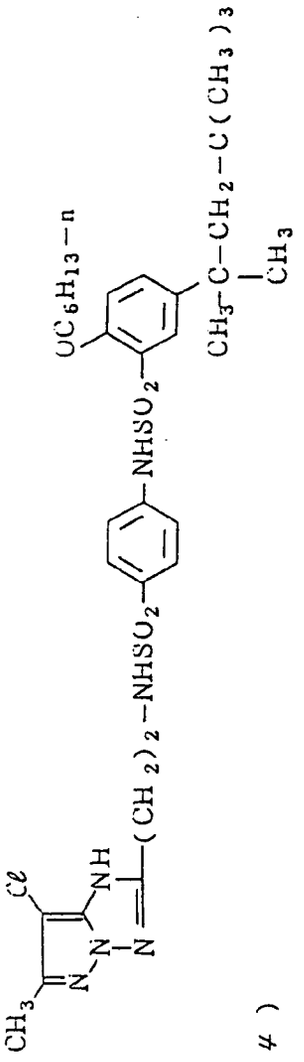

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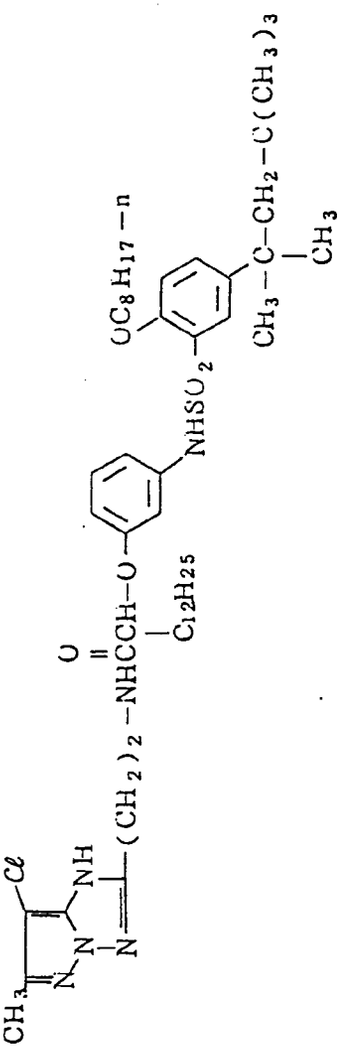

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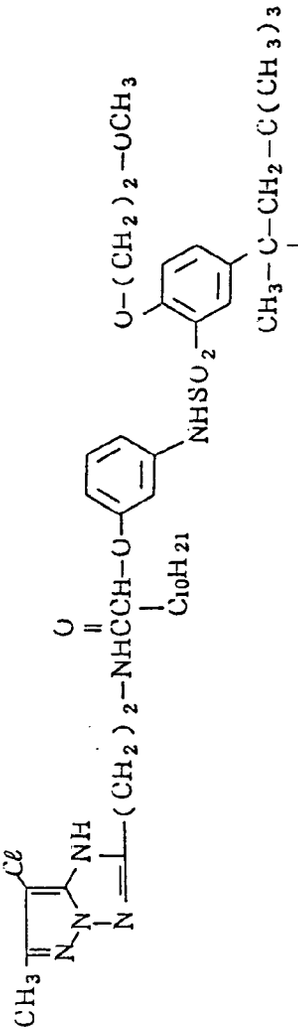

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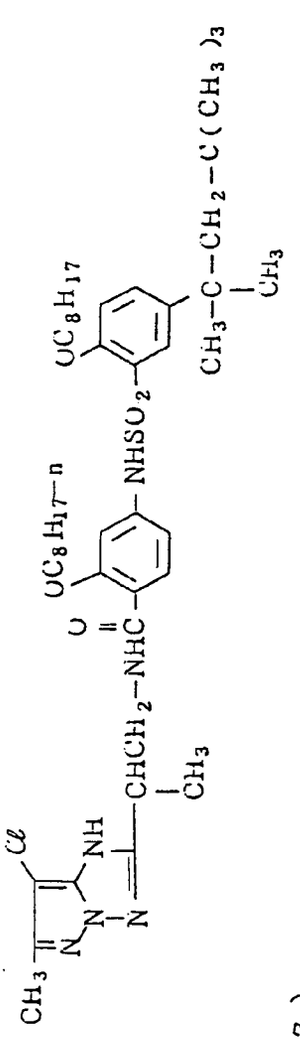

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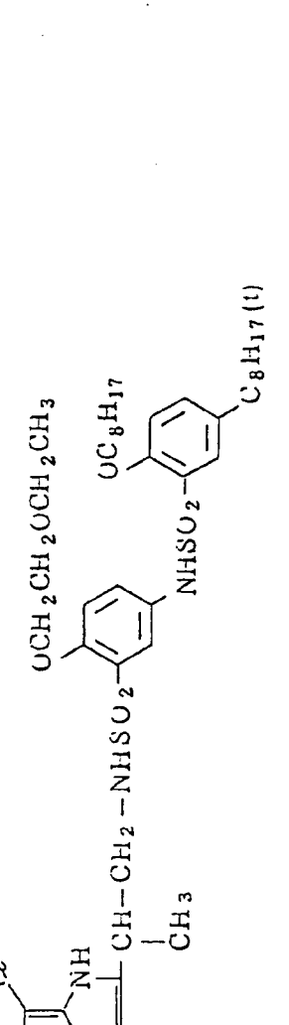

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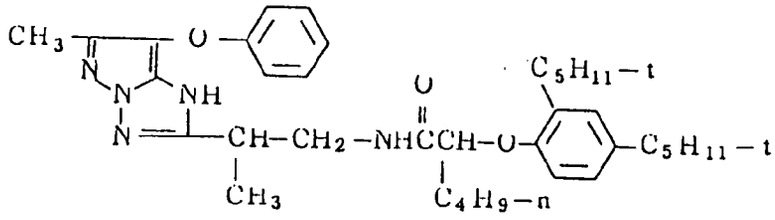

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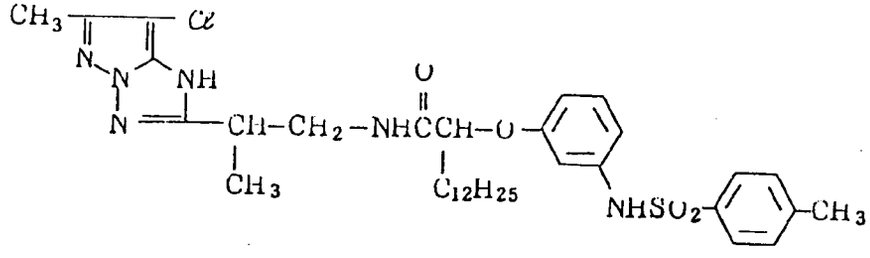

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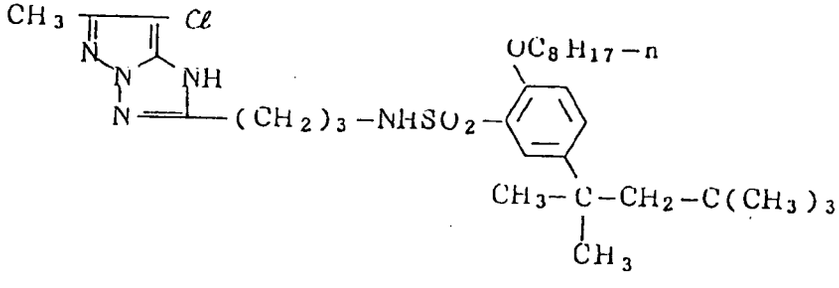

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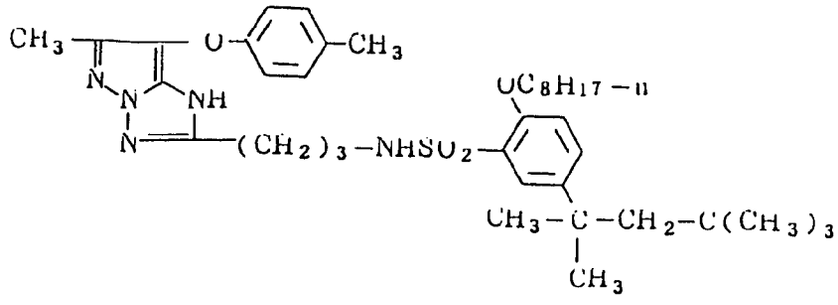

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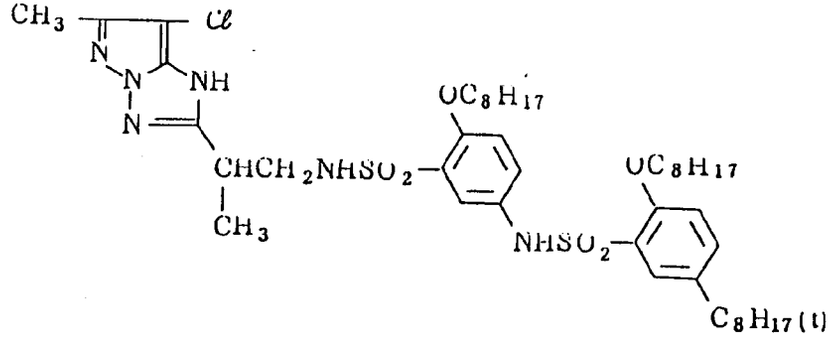

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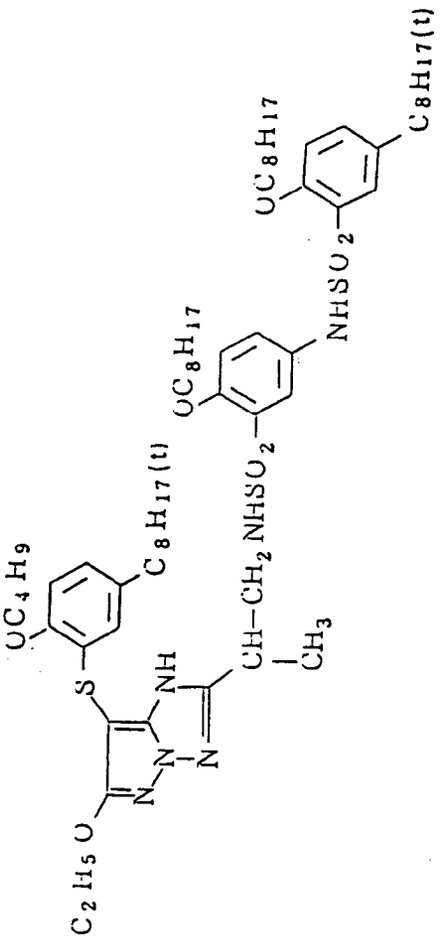

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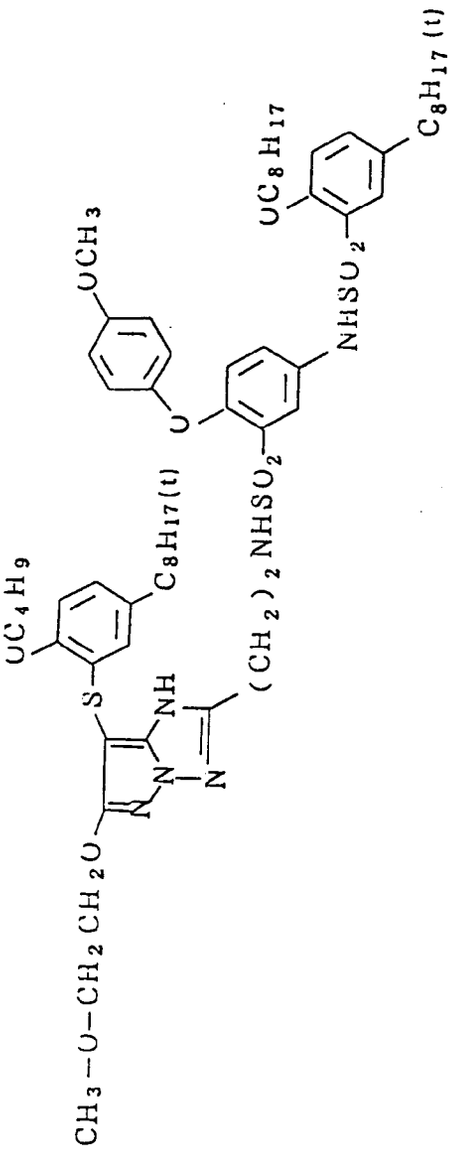

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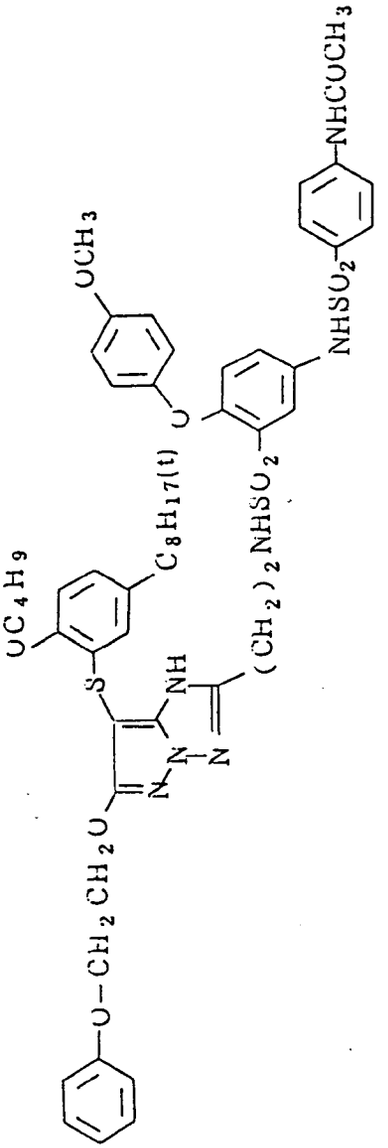

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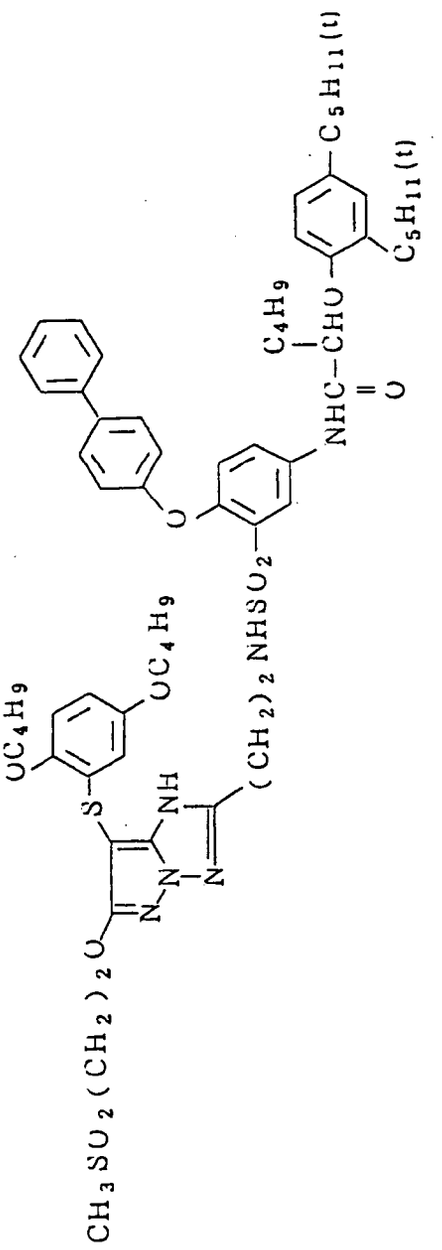

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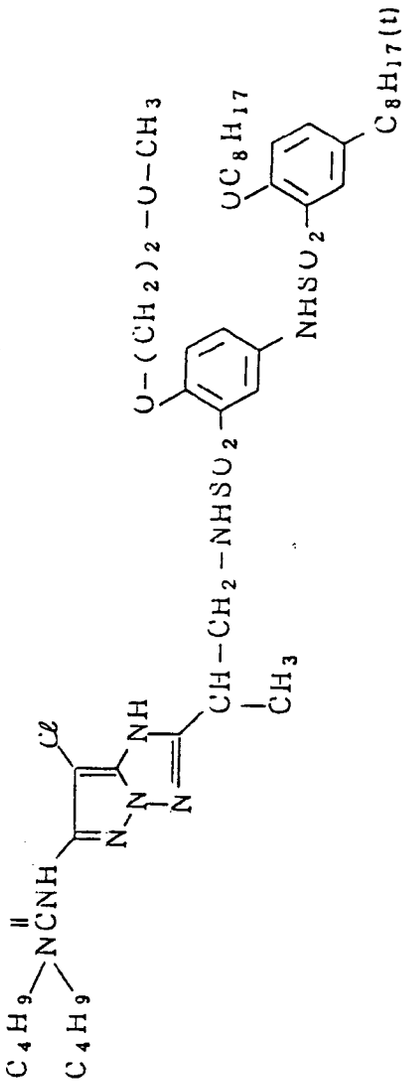

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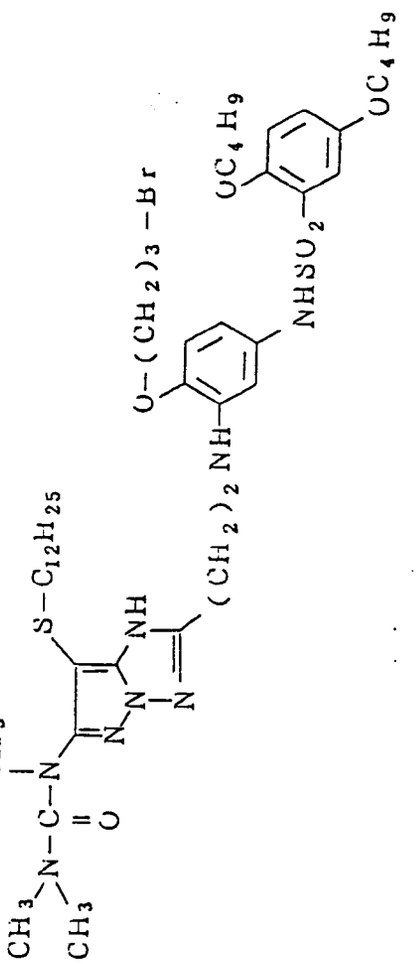

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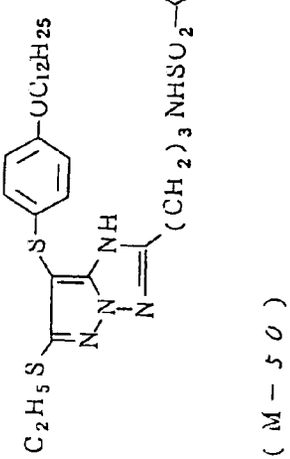

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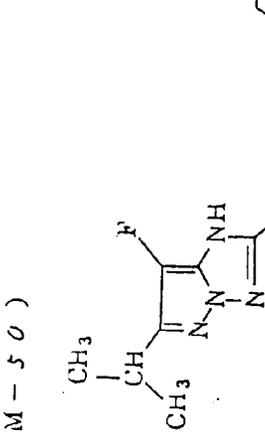

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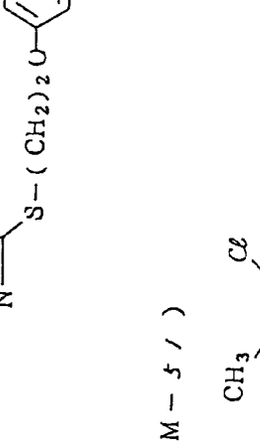

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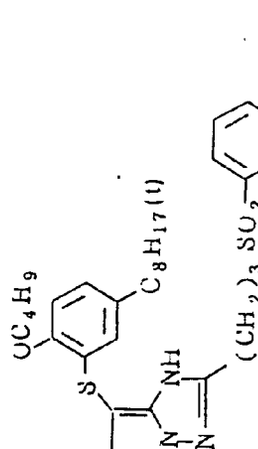

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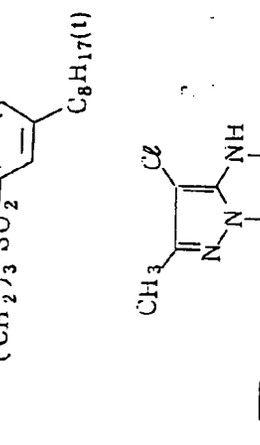

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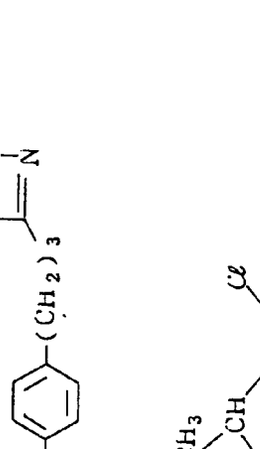

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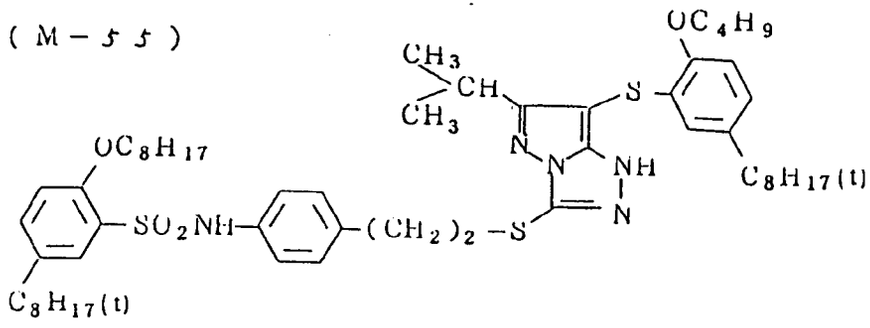

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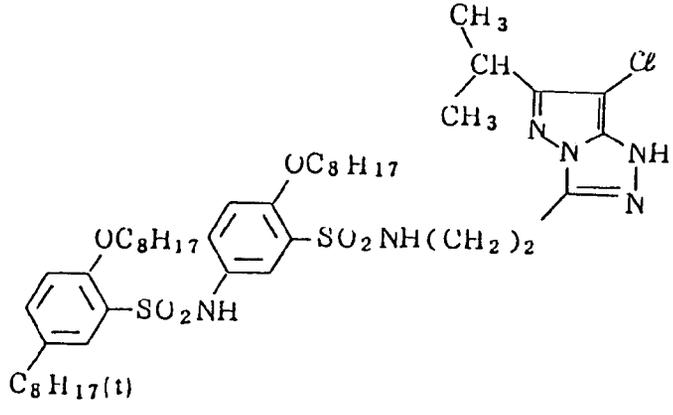

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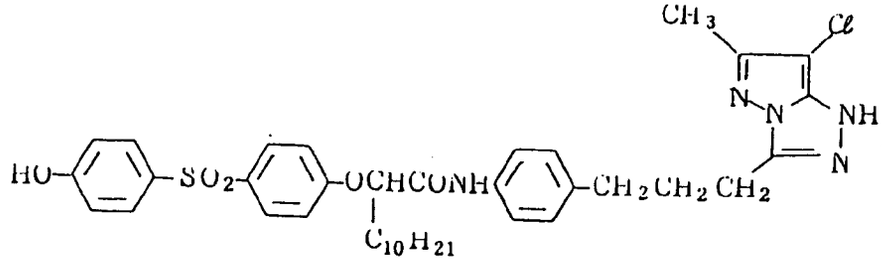

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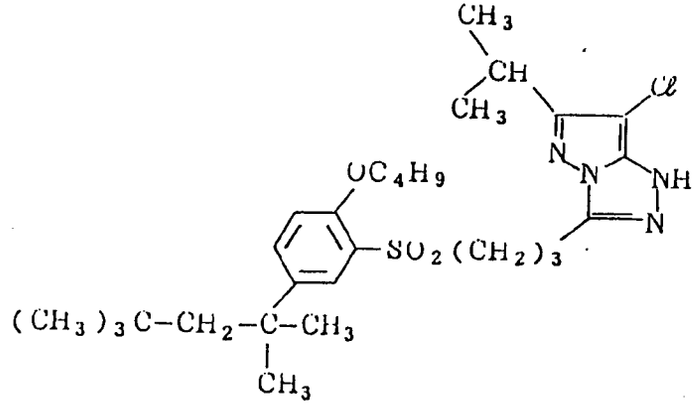

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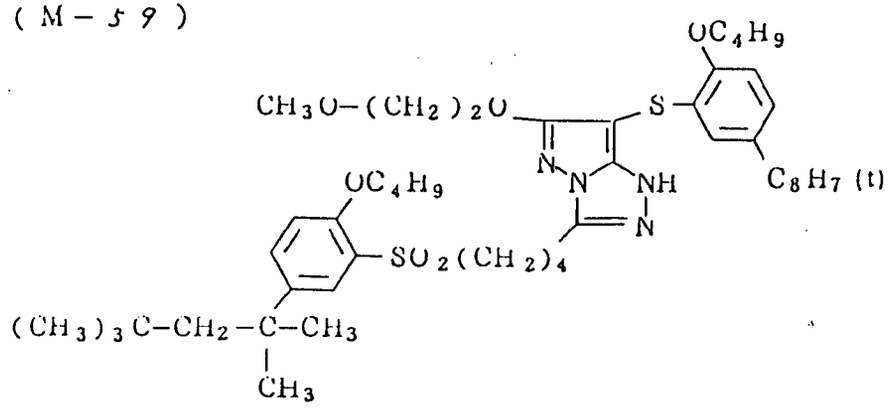

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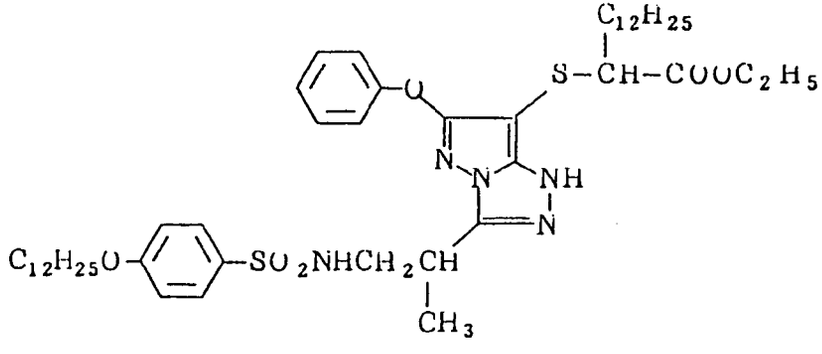

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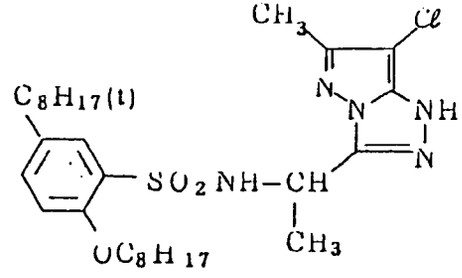

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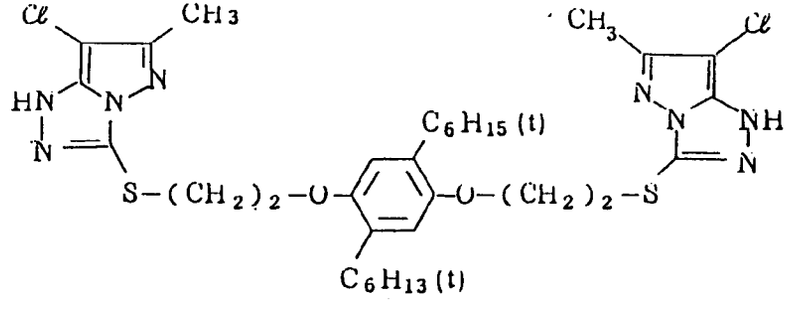

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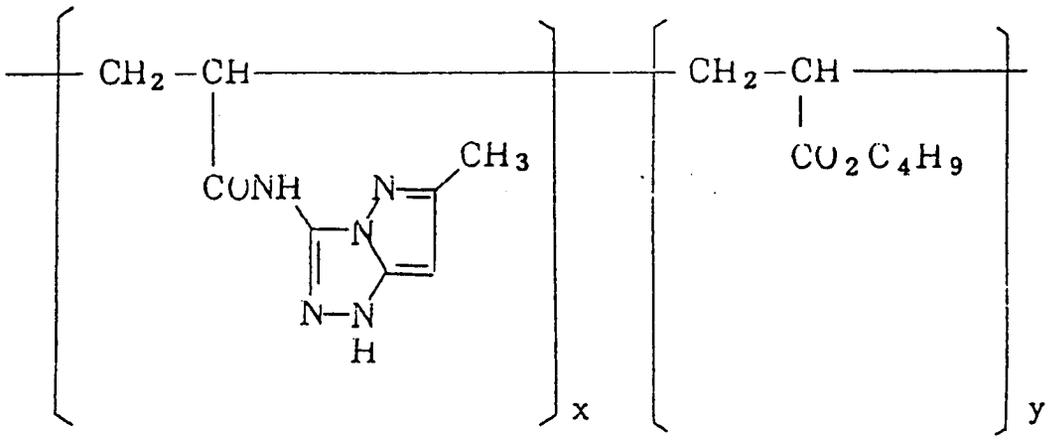
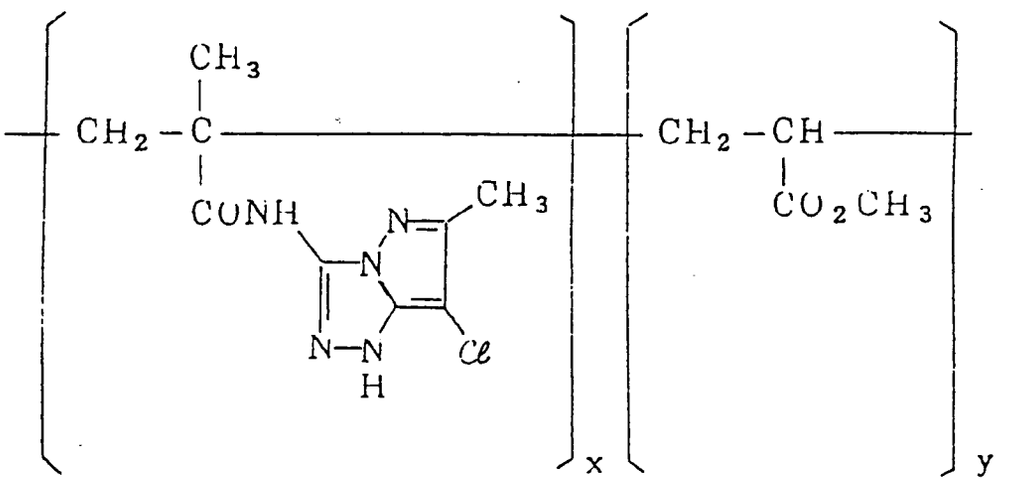


x : y = 5 0 : 5 0

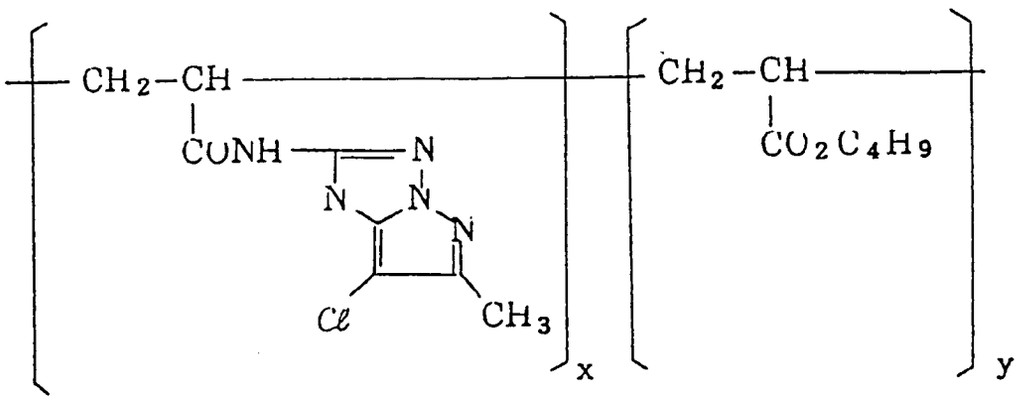
(weight ratio; the same shall apply hereinafter)

(M − 6 4)



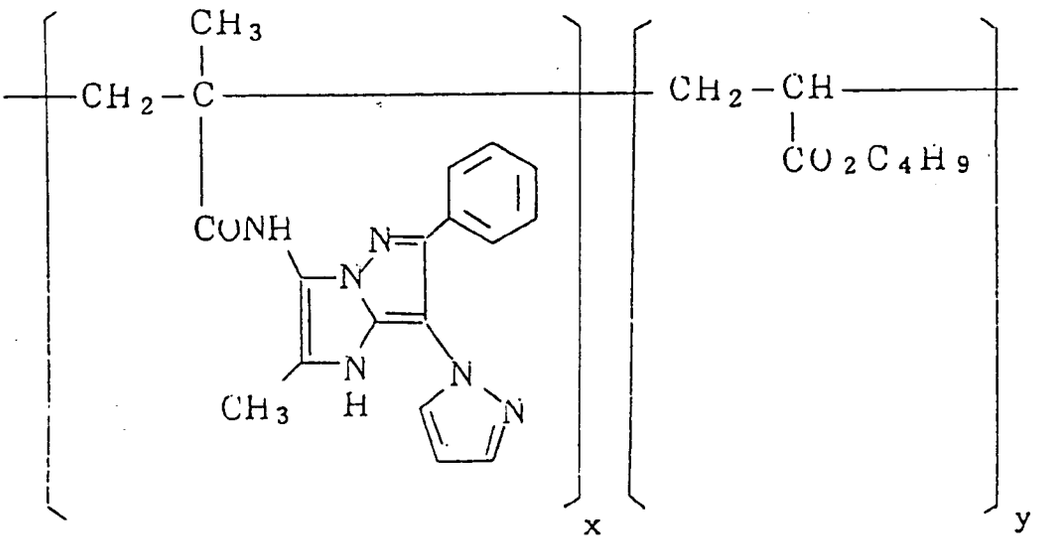
x : y = 4 0 : 6 0

(M − 6 5)



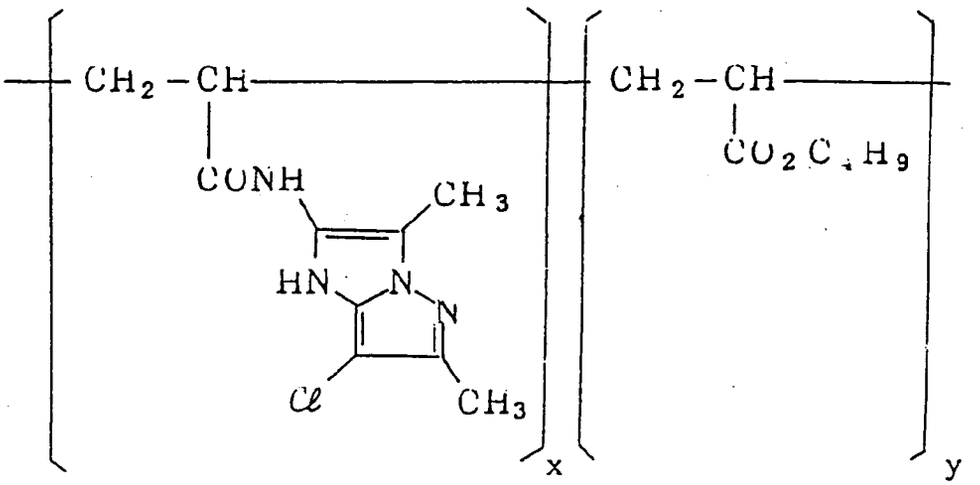
x : y = 5 0 : 5 0

(M − 6 6)



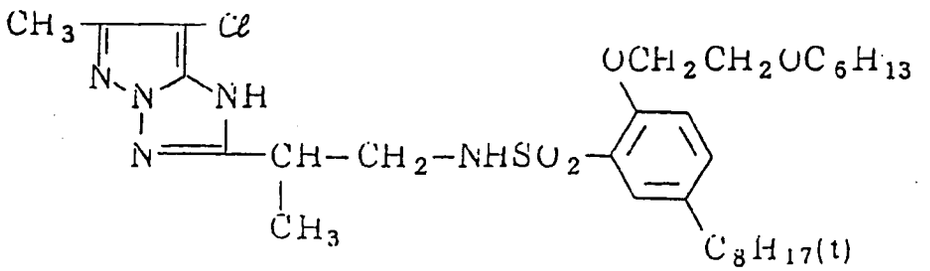
x : y = 5 5 : 4 5

(M − 6 7)



x : y = 5 0 : 5 0

(M − 6 8)



These couplers are used in an amount of 2×10^{-3} mol to 5×10^{-1} mol, preferably 1×10^{-2} mol to 5×10^{-1} mol, per mol of silver in the emulsion layer.

Two or more couplers can be contained in the same layer or the same coupler can be contained in two or more layers in order to obtain satisfactory characteristic properties required of the photosensitive material.

The coupler can be introduced into the silver halide emulsion layer by a known method such as that described in U. S. Patent No. 2,322,027. The coupler may be dissolved, for example, in one of the following solvents: alkyl phthalates (such as dibutyl phthalate and dioctyl phthalate), phosphoric esters (such as diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and dioctylbutyl phosphate), citric esters (such as tributyl acetylcitrate), benzoic esters (such as octyl benzoate), alkylamides (such as diethyllaurylamide), fatty acid esters (such as dibutoxyethyl succinate and diethyl azelate), and trimesic esters (such as tributyl trimesate). Also the coupler may be dissolved in an organic solvent having a boiling point of about 30 °C to 150 °C such as a lower alkyl acetate, e.g. ethyl acetate or butyl acetate, ethyl propionate, sec-butyl alcohol, methyl isobutyl ketone, β-ethoxyethyl acetate or methyl cellosolve acetate and then the solution is dispersed in a hydrophilic colloid. The above-described organic solvents of high and low boiling points may be mixed together.

Now description will be made on the regeneration method for the color developer with the anion exchanger according to the present invention.

In the method of the present invention, a silver halide color photosensitive material is continuously processed with a color developer while a replenisher is added thereto.

The regeneration method comprises the following steps:

Used color developer → Contact with anion exchanger →

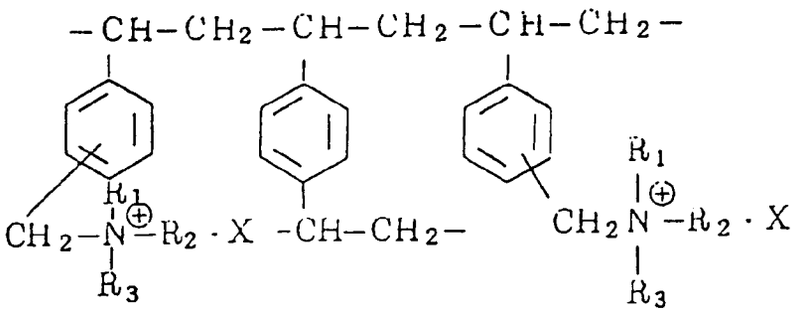
Replenishment of consumed components and correction of pH →

Color developing replenisher

Namely, the used color developer is processed as described above and reused as the replenisher. The used color developer which overflows from the color development tank upon the feeding of the replenisher is taken and subjected to the processing.

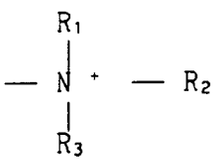
Various anion exchange resins can be used as the an ion exchangers. Among them, strongly basic anion exchange resins having a quaternary ammonium salt-type exchange group are preferred, since their halogen ion-exchange capacity is high. The anion exchange resins mainly comprise a styrene/divinylbenzene copolymer and particularly preferably have a divinylbenzene content of 3 to 12%. The quaternary ammonium salt-type exchange groups will be further described below.

The basic structure of the anion exchange resin is as follows:



wherein X is a counter ion.

R_1, R_2 and R_3 are each preferably an alkyl group having 1 to 8 carbon atoms. The groups of the formula:



include trimethylammonium, tributylammonium, trihexylammonium and trioctylammonium type groups. Among them, trimethylammonium type resins are preferred, since they are readily available on the market. They are available under trade names of, for example, Amberlite IRA-400 and IRA-410 (products of Rohm & Haas Co.), LEWATIT M 600 (a product of Bayer Co.) and Diaion SA-10A and PA-418 (products of Mitsubishi Chemical Industries, Ltd.).

The counter ion of the ion exchange group can be exchanged with various ions by bringing a solution of a salt of the ion into contact with another ion. The ion must be exchangeable with the halogen ion in the color developer and must not exert any influence on the processing capacity in the solution. From this viewpoint, the counter ion is, for example, a carbonate ion, bicarbonate ion, hydroxyl ion, sulfate ion, nitrate ion, phosphate ion, hydrogenphosphate ion or oxalate ion. Among these, the carbonate ion, bicarbonate ion, hydroxyl ion or phosphate ion is preferred, since it is easily exchangeable with the halogen ion and it has an effect of replenishing the necessary components when the ion exchanger is used in the color developer.

The counter ion is carried by the resin by bringing the resin into contact with a 0.1 to 4 N solution of sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium hydroxide, potassium hydroxide, sodium phosphate or potassium phosphate.

The anion exchange resin having the counter ion can be brought into contact with the used color developer by any method. In view of ease of the operation and the efficiency of the ion exchange, a method wherein the color developer is passed through a column containing the resin to continuously bringing them to contact with

each other is preferred. For increasing the efficiency of the ion exchange reaction, the rate of passing the color developer is preferably in the range of 0.3 to 10 parts by volume, more preferably 0.5 to 5 parts by volume and particularly 0.5 to 3 parts by volume, per part by volume of the resin layer per hour. After completion of the processing with the anion exchange resin, necessary components are supplemented to the color developer in order to compensate for their consumption by the processing or for their reduction by adsorption on the anion exchange resin. The amounts of the components to be supplemented can be determined by chemical analysis.

The components which are to be indispensably supplemented include the color developing agent and a preservative such as hydroxylamine sulfite. If necessary, a chelating agent; a buffering agent such as a carbonate, phosphate, potassium hydroxide or sodium hydroxide; and an alkali are also replenished.

After the supplement of the components, the color developing replenisher thus prepared has concentrations of the components higher than those to be kept in the color developing tank. The ratio of concentrations of the components of the replenisher to those of the color developer in the color development tank is usually 1.0/1 to 2.0/1. This ratio varies depending on the amount of the replenisher to be added. The smaller the amount of the replenisher, the higher the ratio. When the amount of the replenisher is 100 $m\ell$ or larger per m^2 of the photosensitive material, the ratio is preferably in the range of 1.0 to 1.5. The same applies to pH. The pH of the replenisher is usually higher than that of the color developer in the color developing tank by 0.1 to 1.0. The relationship between pH and the amount of the replenisher is the same as that between the concentration and the amount as described above.

When the photosensitive material is a printing material such as a color paper in the regeneration processing method according to the present invention, the amount of the color developer to be replenished is 50 to 300$m\ell$, preferably 100 to 250 $m\ell$ and most preferably 130 to 220 $m\ell$ per m^2 of the photosensitive material. When the photosensitive material is a photographic material such as a color negative film or color reversal film, the amount is 300 to 3000 $m\ell$, preferably 400 to 1500$m\ell$ and most preferably 500 to 1200$m\ell$ per m^2 of the material. As the amount of the replenisher is increased, the stabilization of the performance becomes easier but, on the other hand, the regeneration process must be conducted more frequently. Therefore, the preferred amounts of them the limited in the above-described ranges to well balance them.

It is preferred for further increasing the effect of minimizing the change of the sensitivity according to the present invention that the color developer be brought into contact with an adsorbent described in the Journal of Applied Photographic Engineering, Vol. 5, 216 to 219 (Autumn, 1979) prior to the step of bringing the color developer into contact with the anion exchange resin.

The adsorbents usable in the present invention include, for example, phenol/formaldehyde-type adsorbent resins, active carbon and surface-modified active carbon described in J. P. KOKAI No. 53-132343 and polystyrene-type adsorbent resins described in Diaion Manual (II) (the eighth edition, 1985) published by Mitsubishi Chemical Industries. Ltd.

The anion exchange resin having a reduced exchange capacity is subjected to the regeneration in the present invention. The regeneration can be conducted by a known method such as a method described on pages 19 to 21 of Diaion Manual (I) (the 14th Edition, 1986) published by Mitsubishi Chemical Industries, Ltd.

The solution used for the regeneration of the anion exchange resin can be the same as that used for keeping the preferred counter ion.

To increase the regeneration efficiency, for example, a sodium chloride solution can be used for dissolving out the iodine ion and bromine ion accumulated on the resin and then a solution of sodium carbonate, sodium hydrogencarbonate, sodium hydroxide or the like can be used for exchanging with the preferred counter ion.

The halogen ions accumulated in the color developer are removed by the above-described process and the developing activity is recovered by the suplement of the consumed components. However, only anions are thoroughly removed by this process, leaving or partially leaving various components, e.g. oxides and polymers of the color developing agent; oxides and decomposition products of the preservative such as hydroxylamine or the chelating agent such as aminopolyphosphonic acid or aminopolycarboxylic acid; anti-irradiation dye, sensitizing dye, surfactant, antifoggant, and the like dissolved out of the silver halide color photosensitive material. These components are accumulated in the color developer after repetition of the regeneration. The amount of the accumulated components varies depending on the degree of fatigue of the anion exchange resin, velocity of passing the color developer, method of the regeneration of the anion exchange resin and whether or not the adsorbent is used in the pretreatment step. It further exerts influences on the sensitivity of the magenta-forming layer in the finished photosensitive material in the color developing step, the fog density of the magenta dye and degree of a yellow stain formed during the storage at a high temperature at a high humidity. The inventors have found unexpected effects of the particular magenta couplers of the general formula (I). Specifically, these couplers greatly reduce the effects of the complicated influences of the accumulated components on the color photosensitive material and, therefore, enable the color developer to be regenerated and reused semipermanently. The present invention has been completed on the basis of this finding.

Although the regenerated color developer of the present invention contains a large amount of the accumulated components, it is characterized in that the accumulation of halogen ions is only slight, unlike a color developer used in a low replenishing process in which merely the amount of the replenisher is reduced.

The effect of the present invention is obtained when the halogen ion concentration in the color developer is below a certain level. Namely, this effect is obtained when bromine ion concentration is $2x10^{-2}$ mol/ ℓ or less, particularly $1.5x10^{-2}$ mol/ℓ or less and more particularly $1.2x10^{-2}$ mol/ ℓ or less and chlorine ion concentration is $4x10^{-2}$ mol/ ℓ or less, particularly $3x10^{-3}$ mol/ ℓ or less and more particularly $2.7x10^{-3}$ mol/ℓ or less.

Now description will be made on the color developer used in the present invention.

The color developer used in the present invention contains a known aromatic primary amine color developing agent. Preferred examples include p-phenylenediamine derivatives such as those listed below, which by no means limit the color developing agent usable in the present invention:

D-1 N,N-Diethyl-p-phenylenediamine
D-2 2-Amino-5-diethylaminotoluene
D-3 2-Amino-5-(N-ethyl-N-laurylamino)toluene
D-4 4-[N-Ethyl-N-(β-hydroxyethyl)amino]aniline
D-5 2-Methyl-4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline
D-6 4-Amino-3-methyl-N-ethyl-N- [β-(methanesulfonamido)ethyl] aniline
D-7 N-(2-Amino-5-diethylaminophenylethyl)methanesulfonamide
D-8 N,N-Dimethyl-p-phenylenediamine
D-9 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline
D-10 4-Amino-3-methyl-N-ethyl-N- β -ethoxyethylaniline
D-11 4-Amino-3-methyl-N-ethyl-N- β -butoxyethylaniline.

Among the p-phenylenediamine derivatives described above, Compounds D-5 and D-6 are preferred and Compound D-6 is particularly preferred from the viewpoint of the coloring, stability of the formed dye, stability of the compound per se and safety in handling.

These p-phenylenediamine derivatives may be in the form of sulfate, hydrochloride, sulfite or p-toluenesulfonate thereof. The amount of the aromatic primary amine developing agent used is preferably 1 to 20 g, and more preferably 3 to 10 g, per liter of the developer.

If necessary, the color developer may contain a preservative such as a sulfite, e.g. sodium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite or a carbonyl sulfite adduct.

The amount of the preservative used is 0.5 to 10 g, more preferably 1 to 5 g, per liter of the color developer.

Preferred compounds usable for directly preserving the color developing agent include, for example, hydroxylamine, dialkylhydroxylamines (particularly diethylhydroxylamine) described on pages 7 and 8 of WO 87/04534, hydrazines described in J. P. KOKAI No. 63-170642 (particularly a compound of Example I-11), phenols described in J. P. KOKAI Nos. 63-44656 and 63-58443, α -hydroxyketones and α -aminoketones described in J. P. KOKAI No. 63-44656, and/or saccharides described in J. P. KOKAI No. 63-36244. It is particularly preferred to use an alkanolamine (particularly triethanolamine) described on pages 13 and 14 of WO 87/04534 in combination with the above-described compounds in order to further improve the preservability of the color developing agent.

If necessary, other preservatives may also be used, such as metals described in J. P. KOKAI Nos. 57-44148 and 57-53749, salicylic acids described in J. P. KOKAI No. 59-180588, alkanolamines described in J. P. KOKAI No. 54-3532, polyethyleneimines described in J. P. KOKAI No. 56-94349 and aromatic polyhydroxy compounds described in U. S. Patent No. 3,746,544. Among these, the aromatic polyhydroxy compounds have a marked effect of inhibiting the deterioration of the developing agent or hydroxylamine due to an oxidative catalytic effect of the metal ion and, therefore, they are preferably used in the present invention.

The color developer used in the present invention has a pH of preferably 9 to 12, more preferably 9.5 to 11. It can further contain other compounds known as constituents of the developer.

The pH is kept in this range preferably by using a buffering agent.

Examples of the buffering agents include sodium carbonate, potassium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium tertiary phosphate, disodium hydrogenphosphate, dipotassium hydrogenphosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate) and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate). However, these compounds by no means limit the buffering agents of the present invention.

The amount of the buffering agent to be added to the color developer is preferably at least 0.1 mol/ℓ, particularly 0.1 to 0.4 mol/ℓ.

The color developer may contain a chelating agent for inhibiting the precipitation of calcium or magnesium or for improving the stability thereof.

The chelating agent is preferably an organic acid compound such as an aminopolycarboxylic acid, an organic phosphonic acid or a phosphonocarboxylic acid.

Examples of the chelating agents include nitrilotriacetic acid, diethylenetriamine pentaacetate, ethylenediamine tetraacetate, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N′-N′-tetramethylenephosphonic acid, trans-cyclohexanediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, hydroxyethyliminodiacetic acid, glycol ether diaminetetraacetic acid, ethylenediamine-o-hydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid and N,N′-bis(2-hydroxybenzyl)ethylenediamine-N,N′-diacetic acid. Two or more of these chelating agents can be used in combination, if necessary.

Among these chelating agents, particularly preferred are 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine-N,N,N′-N′-tetramethylenephosphonic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid and nitrilo-N,N,N-trimethylenephosphonic acid, since they are not adsorbed on the anion exchange resin in the course of the regeneration of the developer, their function is stable during the regeneration and reuse over a long period of time and they have a remarkable effect of preserving the developing agent, hydroxylamine or dialkylhydroxylamine. The chelating agent is used in an amount sufficient for sequestering calcium, magnesium and other metal ions in the color developer.

The amount of the chelating agent is usually $1x10^{-3}$ to $1x10^{-1}$ mol, preferably $3x10^{-3}$ to $3x10^{-2}$ mol, per liter of the color developer.

The color developer of the present invention may contain, if necessary, an antifoggant such as an alkali metal halide, e. g. sodium chloride, potassium bromide or potassium iodide or an organic antifoggant. Examples of the organic antifoggants include nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolybenzimidazole, 2-thiazolylmethylbenzimidazole, indazole, hydroxyazaindolizine and adenine.

The color developer used in the present invention may contain a fluorescent brightening agent, preferably a 4,4′-diamino-2,2′-disulfostilbene compound, in an amount of 0 to 5g/ℓ, preferably 0.1 to 4 g/ℓ.

The color developer may if necessary, contain, also a surfactant such as an alkylsulfonic acid, arylphosphonic acid, aliphatic carboxylic acid or aromatic carboxylic acid.

The processing temperature for the color developer of the present invention is 20 to 50 °C , preferably 30 to 40 °C . The processing time is in the range of 20 sec to 5 min. The processing time for the silver chloride color photosensitive material having a silver chloride content of as high as 95 molar % or higher is preferably 30 sec to 1 min and that for the silver chlorobromide or silver iodobromide color photosensitive material having a silver chloride content of less than 95 molar % is preferably 1 min to 3.5 min.

The developing bath may comprise, if necessary, two or more baths. In such a case, the color developing replenisher is added to the first bath or the last bath in order to reduce the developing time or to reduce the amount of the replenisher.

The processing method of the present invention is usable also for the color reversal process. In this case, a known black-and-white first developer usually used in the reversal process for the color photographic photosensitive material or a developer usually used for processing the black-and-white photosensitive material can be used as the black-and-white developer in the present invention. Further known additives usually added to the black-and-white developer can also be used.

Typical examples of the additives include developing agents such as 1-phenyl-3-pyrazolidone, Metol and hydroquinone; preservatives such as sulfites; alkaline accelerators such as sodium hydroxide, sodium carbonate and potassium carbonate; inorganic or organic inhibitors such as potassium bromide, 2-methylbenzimidazole and methylbenzothiazole; softeners for hard water such as polyphosphates; and development inhibitors comprising a very small amount of an iodide or mercapto compound.

In the method of the present invention, it is preferred not to use benzylalcohol which is widely used as a coloring accelerator. Benzyl alcohol is physically adsorbed on the anion exchange resin to reduce the ion exchange reaction velocity. Thus benzyl alcohol is preferably not used in order to positively capture the halogen ions in the color developer and to maintain the stable processing capacity. The method of the present invention is particularly preferred for processing a color photographic photosensitive material having a high chloride content which can be sufficiently color-developed without using benzyl alcohol.

Now description will be made on the steps following the color development step.

After the color development, the silver halide color photographic photosensitive material can be processed by the following steps:

1. color development - bleach-fixing - washing with water (stabilization)
2. color development - washing with water (termination) bleach-fixing- washing with water (stabilization)
3. color development - bleaching - fixing - washing with water (stabilization)
4. color development - washing with water (termination) - bleaching - fixing - washing with water (stabili-

zation)

5. color development - washing with water (termination) - bleaching - washing with water (stabilization) - fixing - washing with water (stabilization)

The steps in parentheses are interchangeable ones. Now, description will be made on the bleach-fixing solution.

The bleaching agents used for preparing the bleach-fixing solution include ferric complex salts of organic acids such as aminopolycarboxylic acids and aminopolyphosphonic acids. They are, for example, ferric complex salts of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid and cyclohexanediaminetetraacetic acid.

The amount of the bleaching agent used is 0.05 to 0.5 mol per liter of the bleach-fixing solution. In view of ease of desilverization, color restoration of the cyan dye and antistaining properties, it is particularly preferably 0.1 to 0.3 mol. In using the ferric complex salt of the organic acid, a free organic acid is usually added thereto in a molar ratio of about 1/10.

Known fixing agents such as ammonium thiosulfate and sodium thiosulfate can be used. The preservatives usable herein include sulfites such as sodium sulfite and ammonium sulfite. They can be used in combination with or replaced with an aromatic sulfinic acid such as benzenesulfinic acid or p-toluenesulfinic acid in order to improve the preserving effect.

Further bleaching accelerators described in J. P. KOKAI No. 62-222252 and bromides such as ammonium bromide are usable.

The pH of the bleach-fixer ranges from 3 to 8.5. From the viewpoint of the acceleration of the desilverization, improvement of the color restoration and antistaining properties, preferred pH ranges from 4.5 to 8.0, particularly from 5.0 to 7.5. The bleach-fixing temperature ranges from 25 to 45 °C . From the viewpoint of the processing speed and maintenance of the preserving effect, the temperature is preferably 30 to 40 °C, particularly 33 to 38 °C.

The bleach-fixing can be conducted in two steps, i.e. bleaching step and fixing step. The separation of the bleaching step from the fixing step is described on page 4 of Technical Data Agfa Color Process 94 for Agfa Color Paper Type 9 published by Agfa Gevart Co. in 1988. This technique can be combined with the present invention.

The bleaching solution comprises the same bleaching agent, ferric(III) 1,3-diaminopropane tetraacetate and bleaching accelerator as those of the above-described bleach-fixer, ammonium bromide and a known corrosion inhibitor for metals such as ammonium nitrate. The pH of the bleaching solution is 3.0 to 8.0, preferably 4.0 to 7.0 and particularly preferably 4.5 to 6.5. When the pH is within 4.5 to 6.5, the balance between the desilverization and the color restoration is the best.

The fixer may also contain the fixing components of the above-described bleach-fixer. The pH of the fixer is 5.0 to 8.0, preferably 6.0 to 7.5.

The description on bleaching solutions, bleach-fixers and fixing solutions given from the left lower column, page 28 to the right lower column, page 30 of J. P. KOKAI No. 63-144353 can be applied to the bleaching solution, bleach-fixer and fixing solution of the present invention.

The bleach-fixing time ranges from 30 sec to 2 min, the bleaching time ranges from 30 sec to 2 min and the fixing time ranges from 30 sec to 1 min 30 sec. The bleach-fixing time or bleaching time can be reduced by lowering the pH of the solution.

The amounts of the bleaching solution, bleach-fixing solution and fixing solution to be replenished range from 30 to 300 $m\ell$ per m^2 of the color photosensitive material. From the viewpoint of the balance between the securing of the qualities such as the desilverization properties and the need of the reduction of the amount of the waste, the preferred amount of the replenisher is 50 to 250 $m\ell$. These solutions can be regenerated by a known process such as a process described in J. P. KOKOKU No. 56-33697 wherein deficient components in an overflow are supplied or a process wherein an electrolytic silver recovery apparatus described in J. P. KOKOKU No. 57-16345 is used.

Now description will be made on the steps of washing with water and termination step after the color development step. These steps are provided in order to prevent the drag-in of the color developer into the next step so as to facilitate the regeneration of the solution in the next step when it is to be regenerated. The washing with water is conducted by a known method and a known terminating solution such as an acetic acid solution is used. A typical example of the terminating acetic acid solution is 1.5% aqueous glacial acetic acid solution.

The processing method of the present invention comprises the above-described color development, bleaching, bleach-fixing and fixing steps. Usually the bleach-fixing step or fixing step is followed by a step of washing with water or a stabilization step. However, the stabilization step can be conducted after the processing with a bath having a fixing ability substantially without washing with water.

Water used in the washing step may contain, if necessary, known additives such as softeners for hard

water, e.g. inorganic phosphoric acids, aminopolycarboxylic acids and organic phosphoric acids; germicides and antifungal agents for inhibiting the proliferation of bacteria and algae, e.g. isothiazolone, organic chlorine-containing germicides and benzotriazole; and surfactants for inhibiting the formation of drying marks or drying load. Further compounds described on pages 344 to 359 of L. E. West, 'Water Quality Criteria', Phot. Sci. and Eng., Vol. 9, No. 6 (1965) are also usable.

In the stabilization step, a stabilizer capable of stabilizing the color image is used. The stabilizer is, for example, a solution having a buffering effect in the pH range of 3 to 6 or a solution containing an aldehyde (such as formalin). The stabilizer may contain, if necessary, an ammonium compound, a metal compound such as Bi or Al compound, a fluorescent brightener, a chelating agent (such as 1-hydroxyethylidene-1,1-diphosphonic acid), a germicide, an antifungal agent, a hardener and a surfactant.

In the step of washing with water and the stabilization step, a multistage countercurrent system is preferably employed. The number of the stages is preferably 2 to 4. The amount of the replenisher is 1 to 50 parts, preferably 2 to 30 parts, more preferably 2 to 15 parts, per part of the carryover from the preceding bath per a unit area of the processed photographic material.

Water used in the washing step or stabilization step is city water or preferably water deionized with an ion exchange resin to reduce the concentrations of Ca and Mg to 5 mg/ℓ or less or water sterilized with a halogen or U. V. sterilization lamp.

When the above-described processing steps of the photosensitive material are conducted continuously with an automatic developing machine, the processing solutions might be concentrated due to the evaporation. The concentration is serious particularly when the quantity of the photosensitive material to be processed is small or the opening area of a vessel for the solution is large. A suitable amount of water or replenisher is preferably supplied to normalize the concentration thereof.

The overflow in the step of washing with water or stabilization step can be introduced into the preceding bath having a fixing ability to reduce the amount of the waste.

All the techniques relating to the water for washing or stabilizer described from the right lower column to the left lower column, page 30 of J. P. KOKAI No. 63-144353 can be employed in the present invention.

Now description will be made on the silver halide color photographic photosensitive material used in the present invention.

The method of the present invention can be employed for processing various photosensitive materials such as color papers, color reversal papers, color negative films, color reversal films and color autopositive papers. Among them, the color papers are most suitable.

The silver halide emulsion of the photosensitive material to be processed by the method of the present invention contains at least one of silver chloride, silver bromide and silver iodide. However, in the color papers, silver chlorobromide substantially free from silver iodide is preferred. The term 'substantially free from silver iodide' indicates that the amount of silver iodide is 1 molar % or less, preferably 0.3 molar % or less and more preferably 0.1 molar % or less, based on the total silver halides. Most preferably the silver chlorobromide is utterly free from silver iodide in such a case.

The emulsion preferably used for the color paper in the present invention is a silver chlorobromide emulsion having a silver bromide content of at least 10 molar %. Particularly to obtain an emulsion having a sufficient sensitivity without increasing the fog density, the silver bromide content is preferably at least 20 molar %. On the contrary, in a rapid processing method wherein the development time is reduced, a silver chlorobromide emulsion having a silver bromide content of 10 molar % or less is preferred, that having a silver bromide content of 3 molar % or less is more preferred and that substantially free from silver bromide (silver bromide content: 1 molar % or less) is most preferred.

When the silver bromide content is reduced, not only is the developing velocity increased but also the amount of bromine ion dissolved out in the developer is reduced in the development of the photosensitive material containing it and, therefore, the developing effect can be maintained with a smaller amount of the replenisher.

The silver halide grains in the photographic emulsion may be so-called regular grains having a regular crystal shape such as cubic, octahedral, tetradecahedral or polydodecahedral crystalline grains, or irregular crystalline grains such as spherical grains. Further those having a crystalline deficiency such as a twinning place and complexes of them are also usable.

The grain diameter of the silver halide may be as small as about 0.1μ or less or the diameter of its projected surface area may be as large as about 10μ . The silver halide emulsion may be either a monodisperse emulsion having a narrow distribution or a polydisperse emulsion having a wide distribution.

The siver halide photographic emulsion usable in the present invention can be prepared by a known method such as that described on pages 22 to 23 of Research Disclosure (RD), No. 17643 (December, 1978) (I. Emulsion preparation and types) or that described on page 648 of RD, No. 18716 (November, 1979).

The photographic emulsion usable in the present invention can be prepared by a method described in Glafkides, 'Chimie et Physique Photographique Paul Montel' (1967), a method described in G. F. Duffin, 'Photographic Emulsion Chemistry' (Focal Press) (1966) or a method described in V. L. Zelikman et al., 'Making and Coating Photographic Emulsion' (Focal Press) (1964).

The monodisperse emulsion is preferably used in the present invention.

A typical example of the monodisperse emulsion is an emulsion comprising silver halide grains having an average grain diameter of not less than about 0.1 μ in which at least about 95 wt.% of the grains have a grain diameter within the average grain diameter± 40%. Emulsions havig an average grain diameter of about 0.25 to 2 μ in which at least about 95 wt.%, or at least about 95% of the number of the grains have a grain diameter within the average grain diameter ± 20% can be used in the present invention.

Tabular grains having an aspect ratio of at least about 5 are also usable in the present invention. The tabular grains can be easily prepared by a method described on pages 248 to 257 of Gutoff, 'Photographic Science and Engineering', Vol. 14 (1970) or a method described in U. S. Patent No. 4,434,226, 4,414,310, 4,433,048 or 4,439, 520 or British Patent No. 2,112,157. When the tabular grains are used, advantages such as an improvement in the spectral sensitization efficiency with a sensitizing dye, improvement in the graininess and increase of the sharpness are obtained as described in detail in the above-mentioned U. S. Patent No. 4,434,226, etc.

The crystal structure may be uniform or each of the crystalline grains may comprise a core and shell having different compositions. A typical example of such grains is those of a core/shell type or a double structure type in which the halogen composition of the core is different from that of the shell. In these grains, the shape of the core may be the same as or different from that of the whole grain including the shell.

For example, the core may be cubic and the whole grain including the shell be cubic or octahedral or vice versa. Not only the double structure but also triple or multilayer structure is possible. The surface of the grain having the core/shell double structure may have a thin coating of a different silver halide.

The halogen composition of the grain constituting the photosensitive material to be processed by the method of the present invention is preferably not homogeneous. Namely, the grains constituting the emulsion preferably have a heterogeneous structure. In a silver chlorobromide emulsion used for the color papers, the shell of each core/shell type grain preferably contains silver bromide in an amount smaller than that of the core. A typical example thereof is an emulsion of core/shell-type grains in which the silver bromide content of the core is higher than that of the shell. The difference in the silver bromide content between the core and the shell is preferably 3 to 95 molar % and the molar ratio of silver in the core to that in the shell is 5:95 to 95:5, preferably 7:93 to 90:10.

In a silver bromoiodide emulsion for, for example, color negative films, the silver iodide content of the core is higher than that of the shell. The core has a silver iodide content of preferably 10 to 45 molar %, more preferably 15 to 40 molar %. The shell has a silver iodide content of preferably not more than 5 molar %, more preferably 2 molar % or less. The ratio of silver in the core to that in the shell is 15:85 to 85:15, preferably 15:85 to 75:25.

These grains are in the emulsions described in, for example, British Patent No. 1,027,146, U. S. Patent Nos. 3,505,068 and 4,444,877 and Japanese Patent Application No. 58-24846.

The silver halide photographic emulsion used in the present invention can be spectrally sensitized with, for example, a methine dye. The dyes usable for this purpose include cyanine dye, merocyanine dye, complex cyanine dye, complex merocyanine dye, holopolar cyanine dye, hemicyanine dye, styryl dye and hemioxonol dye. Among them, the cyanine dye, merocyanine dye and complex merocyanine dye are particularly preferred.

The sensitizing dyes usable in the present invention are those described on page 23 of Research Disclosure, Vol. 176, Item 17643 IV (December, 1978).

The sensitizing dye can be used in any step of producing the photographic emulsion and can be present in any stage after the production of the emulsion and immediately before the coating. The steps of producing the photographic emulsion are, for example, silver halide grain-forming step, physical aging step and chemical aging step.

Particularly, it is described in U. S. Patent Nos. 4,183,756 and 4,225,666 that when the spectrally sensitizing dye is added to the emulsion after formation of a stable core for forming the silver halide grain, the photographic sensitivity is increased and the adsorption of the spectral sensitizing dye on the silver halide grains is improved advantageously.

The silver halide photographic emulsion used in the present invention can contain various compounds in order to prevent the fogging during the steps of producing the photosensitive material, during the storage thereof or during processing the photographs or to stabilize the photographic properties. The compounds are those known as antifoggants or stabilizers, for example, azoles such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothia-

zoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles and mercaptotetrazoles (particularly 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; thioketo compounds such as oxazolinethion; azaindenes such as triazaindenes, tetraazaindenes [particularly 4-hydroxy-substituted (1,3,3n,7)tetraazaindenes] and pentaazaindenes; benzenethiosulfonic acid; benzenesulfinic acid; and benzenesulfonic acid amide. They are disclosed in Research Disclosure (RD), Nos. 17643 and 18716 at the locations shown in the following table.

Kind of Additive	RD 17643	RD 18716
1. Chemical sensitizing agent	Page 23	Page 648, right column
2. Sensitivity-increasing agent		ditto
3. Spectral sensitizing agent and supersensitizing agent	Pages 23 to 24	Page 648, right column to page 649, right column
4. Brightening agent	Page 24	
5. Anti-fogging agent and stabilizer	Pages 24 to 25	Page 649, right column
6. Light-absorbing agent, filter and color ultraviolet absorbing agent	Pages 25 to 26	Page 649, right column
7. Anti-stain agent	Page 25	Page 650, left column to right column
8. Color image stabilizer	Page 25	
9. Hardener	Page 26	Page 651, left column
10. Binder	Page 26	ditto
11. Plasticizer and lubricant	Page 27	Page 650, right column
12. Coating assistant and surfactant	Pages 26 to 27	ditto
13. Antistatic agent	Page 27	ditto

The silver halide color photosensitive material to be processed by the method of the present invention may contain various color couplers. Typical examples of them are cyan, magenta and yellow dye-forming couplers described in patents referred to in Research Disclosure 17643 VII-D (December, 1978) and 18717 (November 1979). These couplers are preferably made diffusion-resistant by the introduction of a ballast group or by polymerization (including dimerization). They may be 4- or 2-equivalent couplers. Couplers capable of diffusing the formed dye to improve the graininess and DIR couplers capable of releasing the development inhibitor, etc. upon the coupling reaction to exhibit an edge effect or interlayer effect are also usable.

Further compounds which release a group capable of accelerating the development or a group capable of fogging the silver halide as the coupling reaction proceeds can also be used. These compounds are described in, for example, J. P. KOKAI Nos. 57-150845, 59-50439, 59-157638 and 59-170840 and Japanese Patent Application No. 58-146097.

As for the color couplers, the effect of the compound of the present invention can be obtained more easily as the relative amount of the 4-equivalent coupler is reduced. The amount of the 4-equivalent coupler is preferably 50 molar % or less, more preferably 40 molar % or less and particularly 30 molar % or less, based on the total couplers contained in the photosensitive material.

Preferred yellow couplers are oxygen-linked coupling-off type or nitrogen-linked coupling-off type α -pivaloyl- or α -benzoyl acetoanilide couplers. Particularly preferred examples of the 2-equivalent couplers include oxygen-linked coupling-off type yellow couplers described in U. S. Patent Nos. 3,408,194, 3,447,928, 3,933,501 and 4,022,620 and nitrogen-linked coupling-off type yellow couplers described in U. S. Patent Nos. 3,973,968 and 4,314,023, J. P. KOKOKU No. 58-10739, J. P. KOKAI No. 50-132926 and West German Patent Unexamined Publication Nos. 2,219,917, 2,261,361, 2,329,587 and 2,433,812.

Other components of the processing solutions and photosensitive material preferably usable in the present invention substantially without exerting influence on the photographic properties include, for example, fluorescent brighteners of general formula (I) given in J. P. KOKAI No. 63-204257, yellow couplers of general formula (I), magenta couplers of general formula (II) and cyan couplers of general formulae (IV) and (V) given in J. P. KOKAI No. 63-229456, sensitizing dyes of general formulae (I) and (II) given in J. P. KOKAI No. 63-184954 and anti-irradiation dyes of general formulae (AI-1) to (AI-IV) given in J. P. KOKAI No. 63-48550. Among these couplers, those used in Examples are preferred.

The cyan couplers preferably used herein are those having fastness to humidity and temeprature. Typical examples include phenol couplers described in U. S. Patent No. 3,772,002; 2,5-diacylaminophenol couplers described in J. P. KOKAI No. 59-31953, Japanese Patent Application No. 58-42671 and J. P. KOKAI No. 58-133293; phenol couplers having a phenylureido group at the 2-position and an acylamino group at the 5-position described in U. S. Patent No. 4,333,999; and naphthol couplers described in Japanese Patent Application No. 59-93605.

A yellow or magenta-colored coupler can be used in order to correct an unnecessary sub-absorption on the short wave-side of the main absorption of the coloring dye. These couplers are usually dissolved in a high-boiling organic solvent such as a phthalic ester or phosphoric ester having 16 to 32 carbon atoms combined with, if necessary, another organic solvent such as ethyl acetate and the solution is dispersed in an aqueous medium to form an emulsion. The standard amount of the color coupler is preferably 0.01 to 0.5 mol (yellow coupler) or 0.002 to 0.3 mol (cyan coupler) per mol of the photosensitive silver halide.

According to the method of the present invention, the photographic properties of the color photosensitive material are quite stable even when the color developer is regenerated with the anion exchanger and used over a long period of time and an excellent image can be maintained over a long period of time.

Therefore, it is unnecessary to discard a part of the used color developer or to replace it with a fresh color developer. The waste load can be greatly reduced and the control operation can be dramatically facilitated.

Examples

The present invention will be further illustrated in connection with the following non-limitative Examples.

Example 1

Multilayer photographic Printing Paper 101 which was composed of layers of the following compositions on a paper support laminated with polyethylene on both surfaces, was prepared. The coating solutions were prepared as described below.

(Preparation of the coating solution for forming the first layer)

27.2 *mℓ* of ethyl acetate and 7.7 *mℓ* (8.0 g) of a high-boiling solvent (Solv-1) were added to a mixture of 10.2 g of a yellow coupler (ExY-1), 9.1 g of yellow coupler (ExY-2) and 4.4 g of a color image stabilizer (Cpd-1) to dissolve the mixture. The solution was dispersed in 185 *mℓ* of 10% aqueous solution of gelatin containing 8 *mℓ* of 10 % sodium dodecylbenzenesulfonate to form an emulsion. The product was mixed with Emulsions EM 1 and EM 2 to control the gelatin concentration as will be described below, thereby to form the first layer-forming coating solution. The coating solutions for forming the second to the seventh layers were prepared in the same manner as above. Sodium 1-oxy-3,5-dichloro-s-triazine was used as the gelatin hardener in each layer.

The thickening agent used was Cpd-2.

(Layer construction)

The compositions of the respective layers will be shown below. The numerals indicate the amount (g/m^2) of the applied coating solution. The amount of the silver halide emulsion was given in terms of the amount of applied silver.

Support:

Polyethylene-laminated paper [containing a white pigment (TiO_2) and a blue dye in the polyethylene layer on the first layer side]

The first layer (blue-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM 1) spectrally sensitized with sensitizing dye (ExS-1)	0.13
Monodisperse silver chlorobromide emulsion (EM 2) spectrally sensitized with sensitizing dye (ExS-1)	0.13
Gelatin	1.86
Yellow coupler (ExY-1)	0.44
Yellow coupler (ExY-2)	0.39
Color image stabilizer (Cpd-11)	0.19
Solvent (Solv-1)	0.35

The second layer (color-mixing inhibiting layer)

Gelatin	0.99
Color-mixing inhibitor (Cpd-3)	0.08

The third layer (green-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM 3) spectrally sensitized with sensitizing dye (ExS-2,3)	0.05
Monodisperse silver chlorobromide emulsion (EM 4) spectrally sensitized with sensitizing dye (ExS-2,3)	0.11
Gelatin	1.80
Magenta coupler (ExM-1)	0.39
Color image stabilizer (Cpd-4)	0.20
Color image stabilizer (Cpd-5)	0.02
Color image stabilizer (Cpd-6)	0.03
Solvent (Solv-2)	0.12
Solvent (Solv-3)	0.25

The fourth layer (U.V.-absorbing layer)

Gelatin	1.60
U.V. absorber (weight ratio of Cpd-7/ Cpd-8/Cpd-9 = 3/2/6)	0.70
Color-mixing inhibitor (Cpd-10)	0.05
Solvent (Solv-4)	0.27

The fifth layer (red-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM 5) spectrally sensitized with sensitizing dye (ExS-4, 15)	0.07
Monodisperse silver chlorobromide emulsion (EM 6) spectrally sensitized with sensitizing dye (ExS-4,5)	0.16
Gelatin	0.92
Cyan coupler (ExC-1)	0.32
Color image stabilizer (weight ratio of Cpd-8/Cpd-9/Cpd-12 = 3/4/2	0.17
Polymer for dispersion (Cpd-11)	0.28
Solvent (Solv-2)	0.20

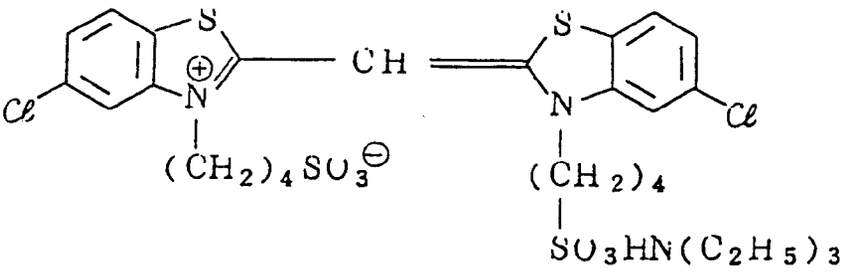
The sixth layer (U.V.-absorbing layer)

Gelatin	0.54
U.V. absorber (weight ratio of Cpd-7/Cpd-9/Cpd-12 = 1/5/3)	0.21
Solvent (Solv-2)	0.08

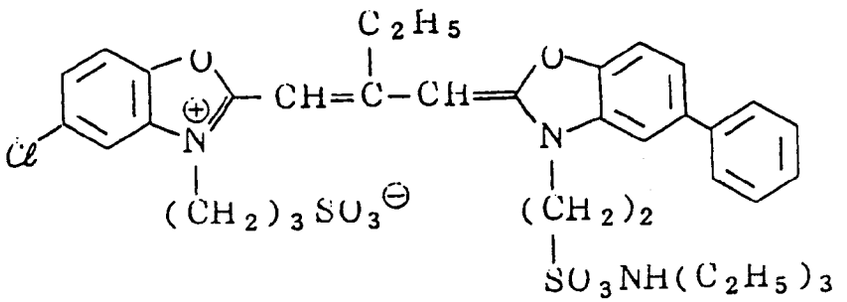
The seventh layer (protective layer)

Gelatin	1.33
Acryl-modified polyvinyl alcohol copolymer (degree of modification: 17%)	0.17
Liquid paraffin	0.03

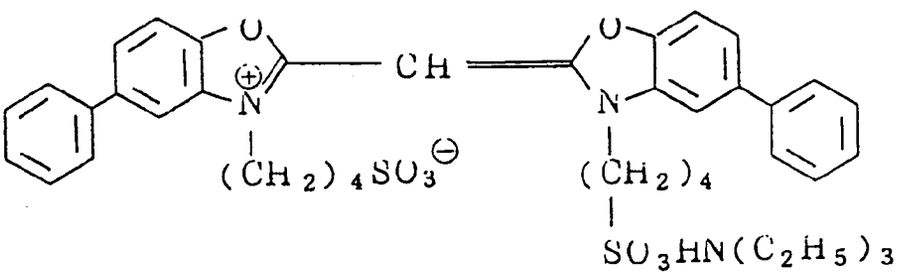
Exs-1



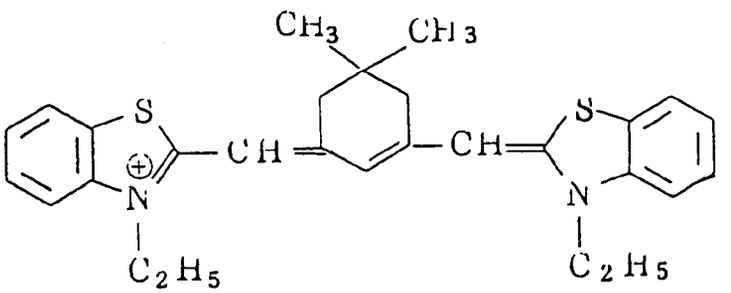
Exs-2



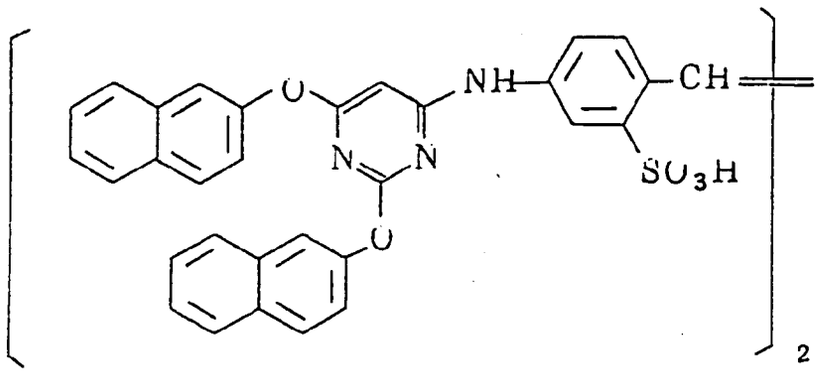
Exs-3



Exs-4



Ex S – 5



Cpd-13 and Cpd-14 were used as the anti-irradiation dye.

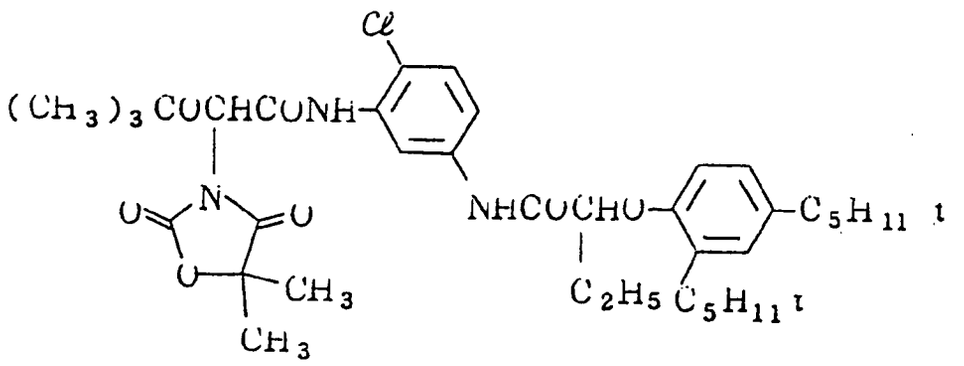
Alkanol B (a product of Du Pont Co.), sodium alkylbenzenesulfonate, succinic esters and Magefacx F-120 (a product of Dainippon Ink & Chemicals, Inc.) were incorporated into the layers as the emulsifying or dispersing agent and coating assistant. Cpd-15 and 16 were used as the stabilizer for the silver halide.

The details of the emulsion used are as follows:

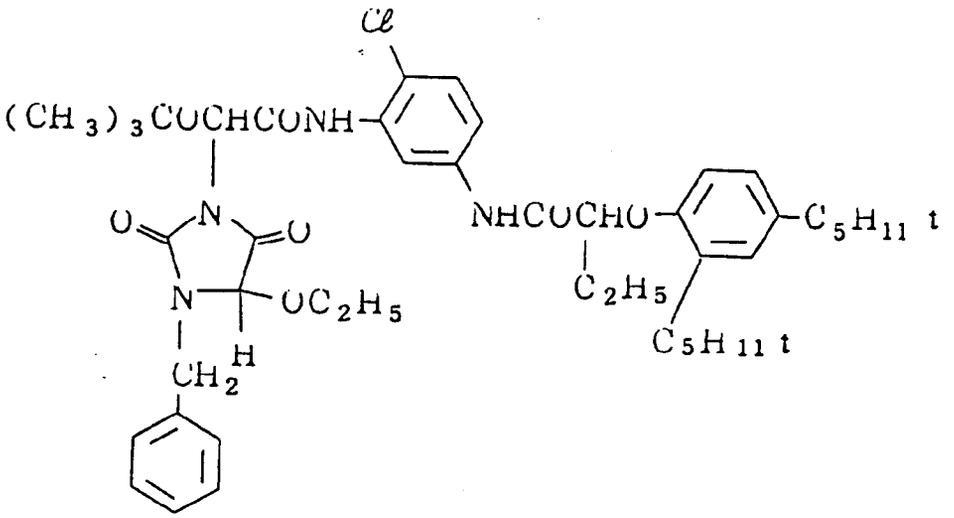
Emulsion	Shape	Grain diameter (μ)	Br content (molar %)	Coefficient of variation
EM 1	Cubic	1.0	80	0.08
EM 2	Cubic	0.75	80	0.07
EM 3	Cubic	0.5	83	0.09
EM 4	Cubic	0.4	83	0.10
EM 5	Cubic	0.5	73	0.09
EM 6	Cubic	0.4	73	0.10

The structural formulae of the compounds used are as follows:

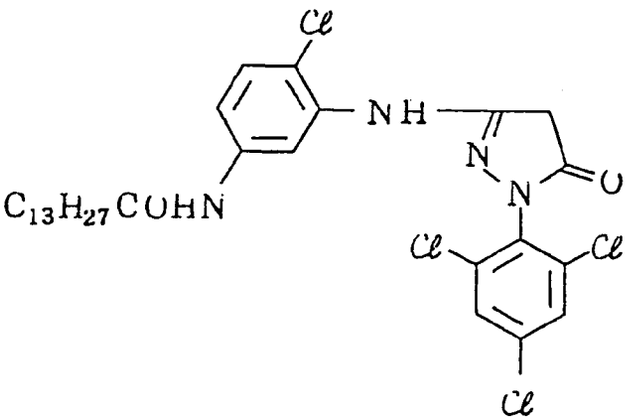
Ex Y – 1



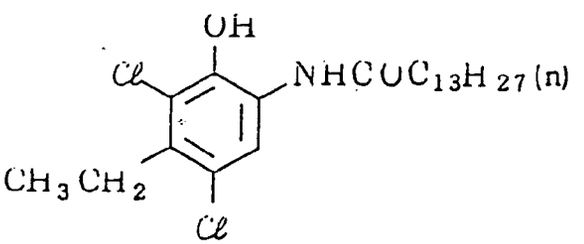
Ex Y – 2



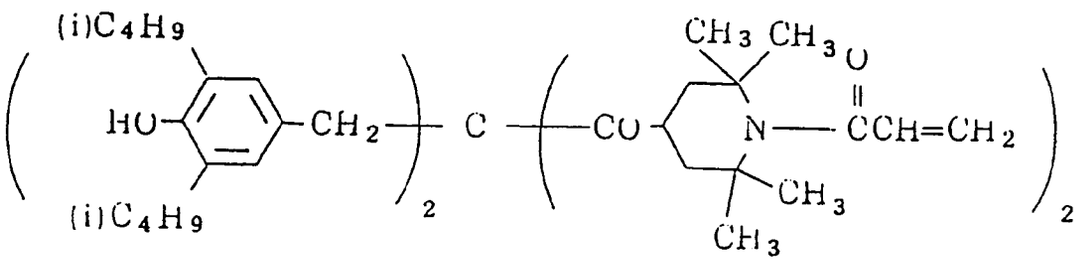
EXM – 1



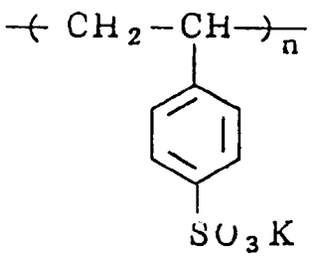
Ex C – 1



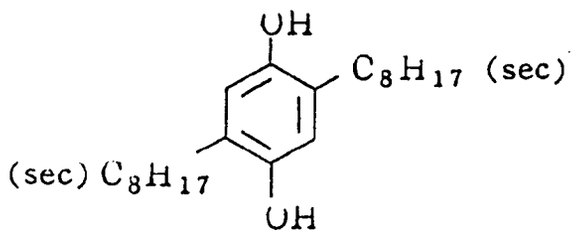
Cpd-1



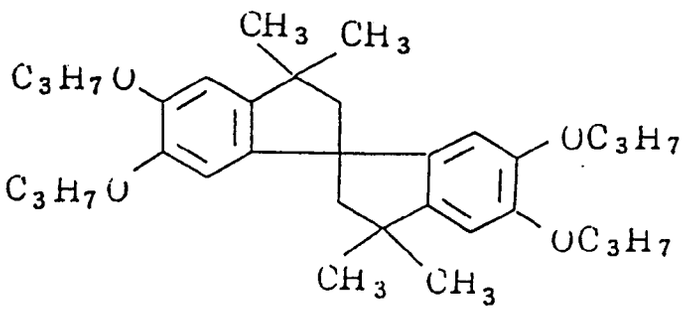
Cpd-2



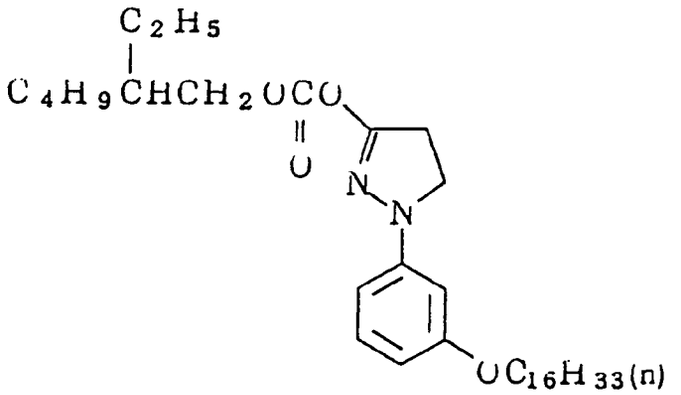
Cpd-3



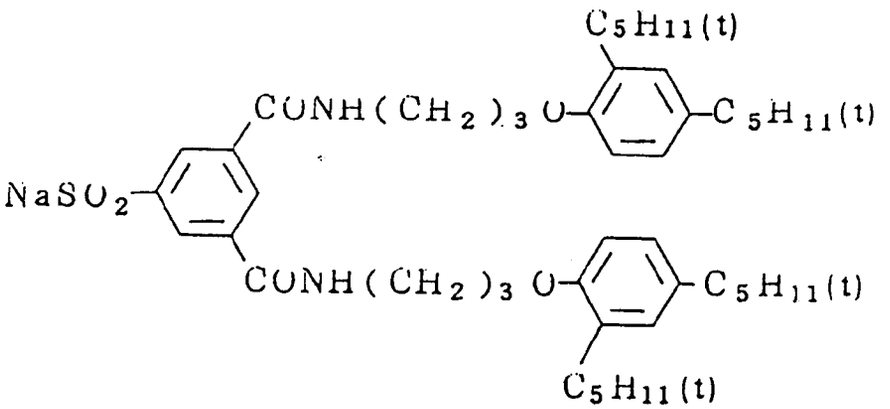
Cpd-4



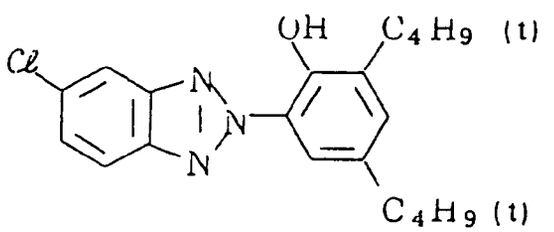
Cpd-5



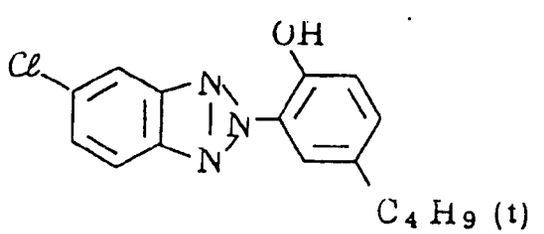
Cpd-6



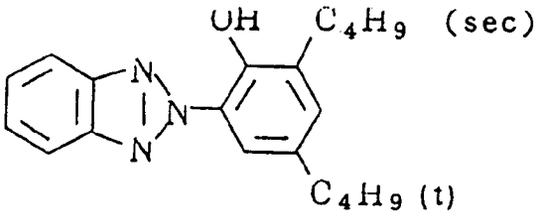
Cpd-7



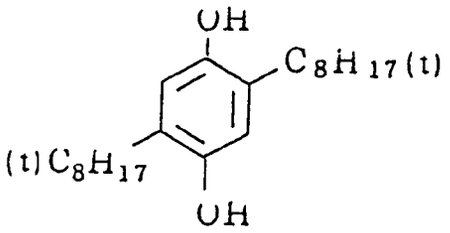
Cpd-8



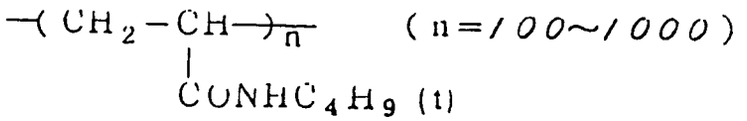
Cpd-9



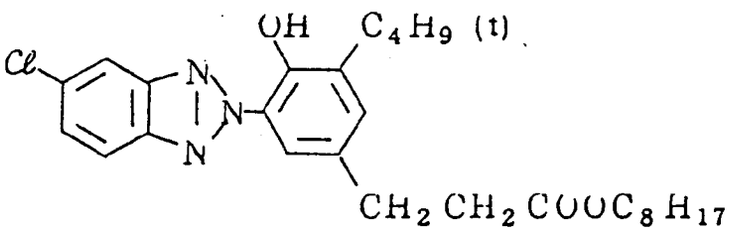
Cpd-10



Cpd-11

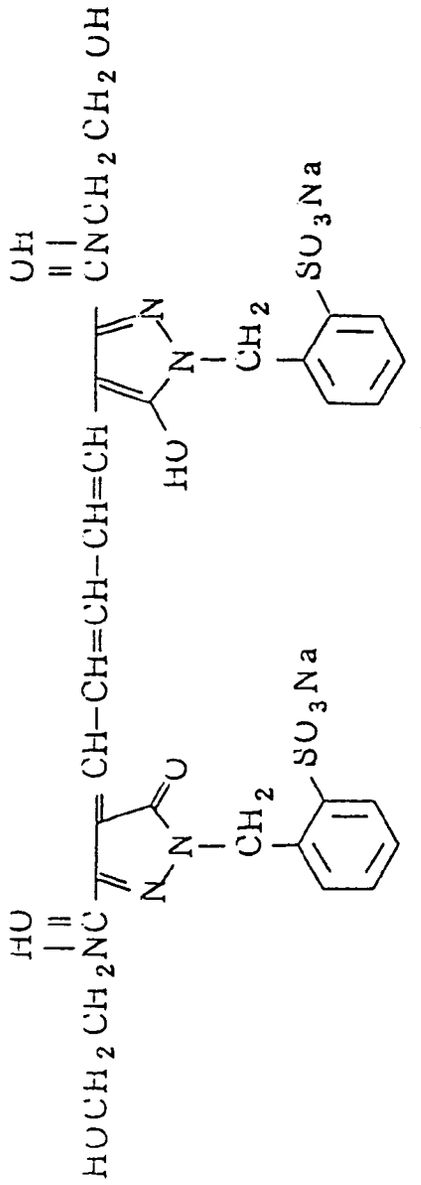


Cpd-12

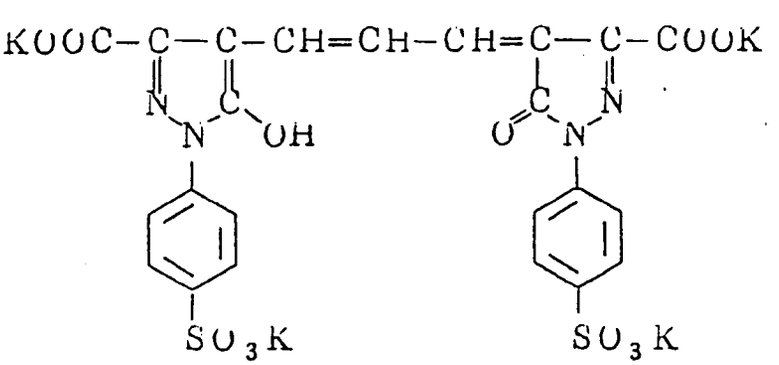


Solv-1	Dubutyl phthalate
Solv-2	Tricresyl phosphate
Solv-3	Trioctyl phosphate
Solv-4	Trinonyl phosphate

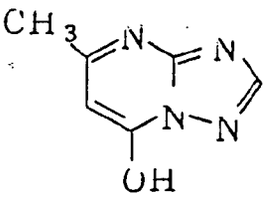
Cpd-13



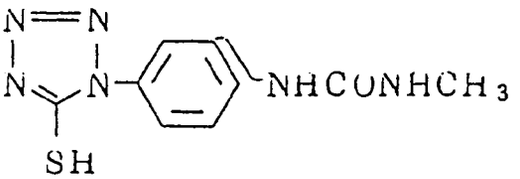
Cpd-14



Cpd-15

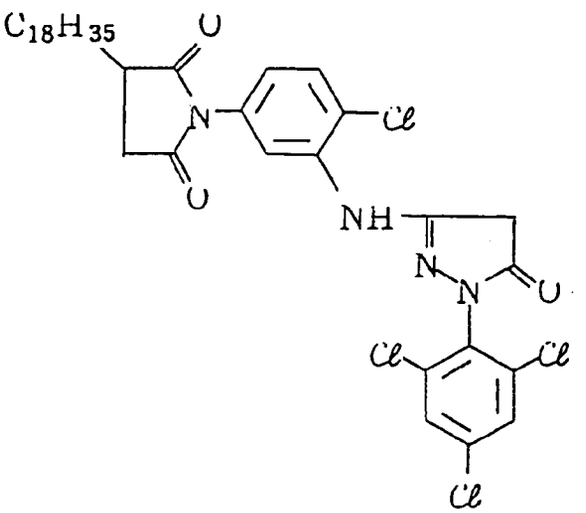


Cpd-16

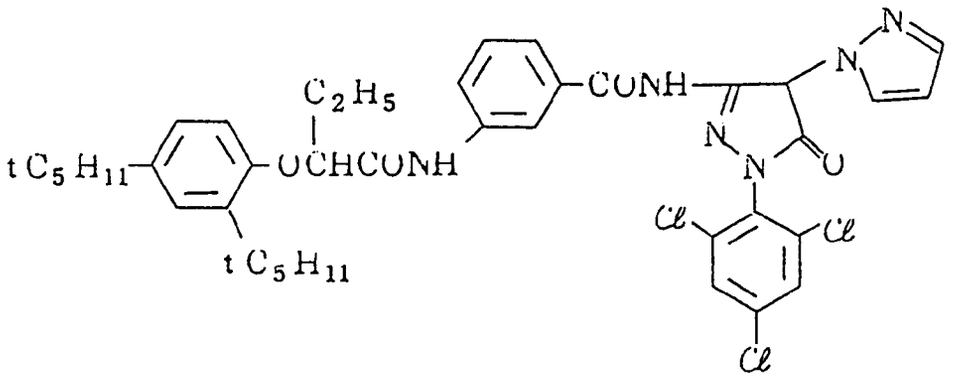


Samples 102 to 106 were prepared in the same manner as above except that Magenta Coupler EXM was replaced with the following coupler.

Sample 102



Sample 103



Sample 104: M-37
Sample 105: M-42
Sample 106: M-68

Samples 101 to 106 prepared as described above were cut into pieces having a width of 82.5 mm and exposed with a printer. Then each sample was processed by a method which will be described below with a miniature automatic developing machine while the color developer was regenerated until the amount of the replenisher became 3 times as much as the capacity of the color developing tank.

The wedge exposure samples having a color temperature of 2854 K and a quantity of exposure of 250 CMS were processed at the start of the process and when the amount of the replenisehr reached 1, 2 and 3 times as much as the capacity of the color developing tank, and magenta sensitivity and change of the minimum density were examined. A change of the minimum yellow density was examined after storage at 60 °C at a relative humidity of 70% for two weeks. The results are shown in Table 1.

Process	Temperature	Time	Amount of replenisher*	Capacity of tank
Color development	37°C	3 min 30 sec	200 ml	6 l
Bleach-fixing	33°C	1 min 30 sec	55 ml	4 l
Washing with water (1)	24 to 34°C	1 min	-	2 l
Washing with water (2)	24 to 34°C	1 min	-	2 l
Washing with water (3)	24 to 34°C	1 min	10 l	2 l
Drying	70 to 80°C	1 min		

* per m^2 of the photosensitive material

[3-tank cascade of washing step (3) → washing step (1)]

The compositions of the processing solutions used are as shown below:

Color developer	Tank	Replenisher
Water	800 ml	800 ml
Diethylenetriaminepentaacetic acid	1.0 g	1.0 g
Nitrilo-N,N,N-trimethylenephosphonic acid	2.0 g	2.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	1.0 ml	1.0 ml
Benzyl alcohol	15 ml	23 ml
Diethylene glycol	10 ml	10 ml
Sodium sulfite	2.0 g	3.0 g
Potassium bromide	1.2 g (1.0×10^{-2} mol)	-
Potassium carbonate	30 g	25 g
N-Ethyl-N-(β -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g	9.0 g
Hydroxylamine sulfate	3.0 g	4.5 g
Fluorescent brightener (WHITEX 4; a product of Sumitomo Chemical Co., Ltd.)	1.0 g	2.0 g
Water	ad 1000 ml	1000 ml
pH (25°C)	10.20	10.80

Bleach-fixing solution	Tank	Replenisher
Water	400 ml	400 ml
Ammonium thiosulfate (700g/ℓ)	150 ml	300 ml
Sodium sulfite	13 g	26 g
Ferric ammonium ethylenediaminetetraacetate · $2H_2O$	55 g	110 g
Disodium ethylenediaminetetraacetate	5 g	10 g
Water	ad 1000 ml	1000 ml
pH (25℃)	6.70	6.30

Regeneration method of color developer

4.8 ℓ of the overflow recovered after replenishing 6 ℓ of the color developer was passed through a plastic column having an inner diameter of 12.5 cm and the resin layer height of about 40 cm which column was filled with 5 ℓ of an anion exchange resin (Amberlite IRA-400, a product of Rohm & Haas Co.). The passing rate was 80 to 100 mℓ/min.

The amounts of benzyl alcohol, diethylene glycol, sodium sulfite, N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate, hydroxylamine sulfate, fluorescent brightener and potassium carbonate in the recovered color developer were determined. Water was added thereto to make the total quantity 6 ℓ. The components were added thereto to obtain the above-described composition of the replenisher. The amounts of diethylenetriaminepentaacetic acid and nitrilo-N,N,N-trimethylenephosphonic acid added were 2.2 g and 4.3 g, respectively, for 6 ℓ of the total quantity. The pH was adjusted to be the same as that of the replenisher with potassium hydroxide and sulfuric acid.

The replenisehr thus prepared was thereafter used. After each 6 ℓ of the replenisher was supplied, the solution was regenerated in the same manner as that described above and used.

Method for processing anion exchange resin:

The first step:

6 ℓ of 0.5 M/ℓ sodium hydrogencarbonate solution was passed through the column at a rate of 80 mℓ/min and then 6 ℓ of distilled water was passed at a rate of 160 mℓ/min to clean the resin to be used for the regeneration of the developer.

The second step and thereafter:

After the resin was used for the regeneration of 4.8 ℓ of the developer, it was washed with 6 ℓ of distilled water passed at a rate of 160 mℓ/min and then 6 ℓ of 0.5 m/ℓ sodium chloride solution was passed through the column at a rate of 80 mℓ/min. 6 ℓ of distilled water was passed through it again at a rate of 160mℓ/min. Then the same process as that of the first step was repeated and the resin was used for the regeneration of the developer.

Table 1

	Test No.	Sample No.	Change in sensitizing of magenta*1	Change in the minimum density of magenta*2	Change in the minimum yellow density after storage at 60°C at 70% relative humidity for 2 weeks	
					Start	After replenishment of 3-fold volume of replenisher
Comparative Example	1	101	0.07	0.03	0.06	0.11
〃	2	102	0.08	0.04	0.07	0.14
〃	3	103	0.07	0.04	0.04	0.09
Present Invention	4	104	0.02	0.01	0.03	0.03
〃	5	105	0.03	0.01	0.03	0.04
〃	6	106	0.03	0.01	0.04	0.05

*1. *2 The difference between the maximum value and minimum value of the sensitivity or the minimum density in the period of from the start to the completion of the replenishment of 3-fold volume of replenisher (the maximum width of variation)

Thus according to the present invention, the variation of the sensitivity or minimum density (fog) was slight and the yellow stain was not increased at a high temperature at a high humidity, while in the tests of the Samples 101 to 103 with the coupler not within the present invention, the variation of magenta sensitivity or the minimum density (which gradually increased after the start; with an increase of fog) was serious and as the regeneration was continued, the yellow stain increased during the storage at a high temperature at a high humidity.

Example 2

A printing color paper which was composed of layers of the following compositions on a paper support laminated with polyethylene on both surfaces, was prepared. The coating solution was prepared as described below. The product will be referred to as Sample 201.

(Preparation of the coatiang solution for forming the first layer)

27.2 *mℓ* of ethyl acetate and 7.7 *mℓ* (8.0 g) of a high-boiling solvent (Solv-1) were added to a mixture of 19.1 g of a yellow coupler (ExY-1) and 4.4 g of a color image stabilizer (Cpd-1) to dissolve the mixture. The solution was dispersed in 185 *mℓ* of 10% aqueous solution of gelatin containing 8 *mℓ* of 10% sodium dodecylbenzenesulfonate to form an emulsion. The product was mixed with Emulsions EM 7 and EM 8 to control the gelatin concentration as will be described below and thereby to form the first layer-forming coating solution. The coating solutions for forming the second to the seventh layers were prepared in the same manner as described above. Sodium 1-oxy-3,5-dichloro-s-triazine was used as the gelatin hardener in each layer.

The thickening agent used was Cpd-2.

(Layer construction)

The compositions of the respective layers will be shown below. The numerals indicate the amount (g/m^2) of the applied coating solution. The amount of the silver halide emulsion was given int erms of the amount of applied silver.

Support:

Polyethylene-laminated paper [containing a white pigment (TiO_2) and a blue dye in the polyethylene layer on the first layer side]

The first layer (blue-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM 7) spectrally sensitized with sensitizing dye (ExS-1)	0.15
Monodisperse silver chlorobromide emulsion (EM 8) spectrally sensitized with sensitizing dye (ExS-1)	0.15
Gelatin	1.86
Yellow coupler (ExY-1)	0.82
Color image stabilizer (Cpd-2)	0.19
Solvent (Solv-1)	0.35

The second layer (color mixing-inhibiting layer)

Gelatin	0.99
Color-mixing inhibitor (Cpd-3)	0.08

The third layer (green-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM 9) spectrally sensitized with sensitizing dye (ExS-2, 3)	0.12
Monodisperse silver chlorobromide emulsion (EM 10) spectrally sensitized with sensitizing dye (ExS-2, 3)	0.24
Gelatin	1.24
Magenta coupler (ExM-1)	0.39
Color image stabilizer (Cpd-4)	0.25
Color image stabilizer (Cpd-5)	0.12
Solvent (Solv-2)	0.25

The fourth layer (U. V. absorbing layer)

Gelatin	1.60
U. V. absorber (weight ratio of Cpd-6/Cpd-7/Cpd-8 = 3/2/6)	0.70
Color-mixing inhibitor (Cpd-9)	0.05
Solvent (Solv-3)	0.42

The fifth layer (red-sensitive layer)

Monodisperse silver chlorobromide emulsion (EM 11) spectrally sensitized with sensitizing dye (ExS-4, 5)	0.70
Monodisperse silver chlorobromide emulsion (EM 12) spectrally sensitized with sensitizing dye (ExS-4, 5)	0.16
Gelatin	0.92
Cyan coupler (ExC-1)	1.46
Color image stabilizer (weight ratio of Cpd-7/Cpd-8/Cpd-10 = 3/4/2)	0.17
Polymer for dispersion (Cpd-11)	0.14
Solvent (Solv-1)	0.20

The sixth layer (U. V.-absorbing layer)

Gelatin	0.54
U. V. absorber (weight ratio of Cpd-6/Cpd-8/Cpd-10 = 1/5/3)	0.21
Solvent (Solv-4)	0.08

The seventh layer (protective layer)

Gelatin	1.33
Acryl-modified polyvinyl alcohol copolymer (degree of modification: 17%)	0.17
Liquid paraffin	0.03

Cpd-12 and Cpd-13 were used as the anti-irradiation dye.

Alkanol XC® (a product of Du Pont Co.), sodium alkylbenzenesulfonate, succinic esters and Magefacx F-120® (a product of Dainippon Ink & Chemicals, Inc.) were incorporated into the layers as the emulsifying or dispersing agent and coating assistant. Cpd-14 and 15 were used as the stabilizer for the silver halide.

The details of the emulsion used are as follows:

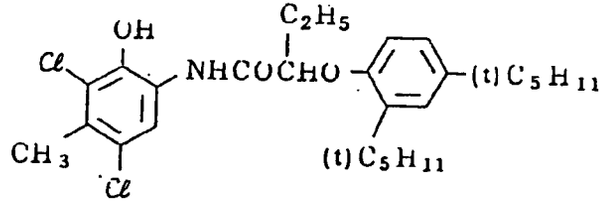
Emulsion	Shape	Grain diameter (μ)	Br content (molar %)	Coefficient of variation*
EM 7	Cubic	1.1	1.0	0.10
EM 8	Cubic	0.8	1.0	0.10
EM 9	Cubic	0.45	1.5	0.09
EM 10	Cubic	0.34	1.5	0.09
EM 11	Cubic	0.45	1.5	0.09
EM 12	Cubic	0.34	1.6	0.10

* Grain size distribution

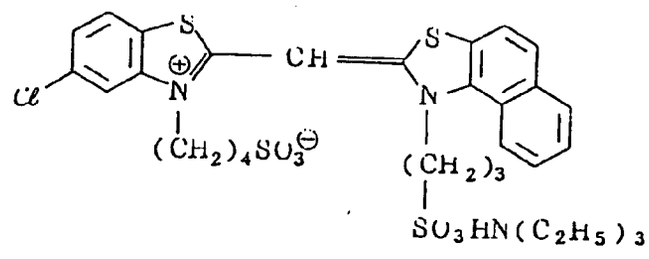
$$= \frac{\text{Standard deviation}}{\text{Average size}}$$

The structural formulae of the compounds used were as follows:

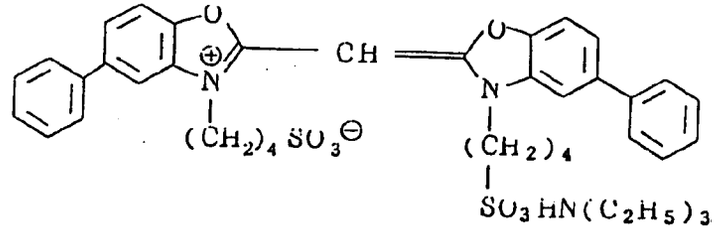
Ex C - 1



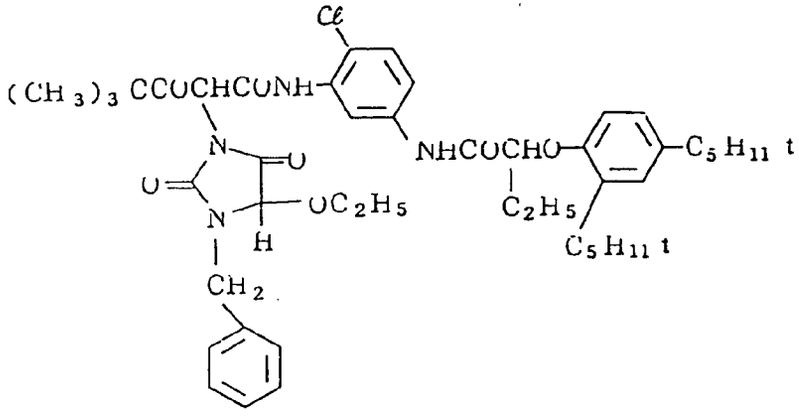
Ex S - 1



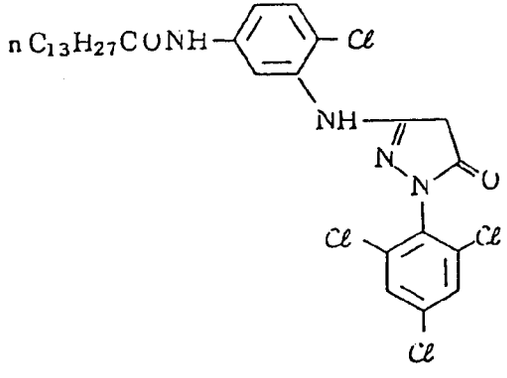
Ex S - 2



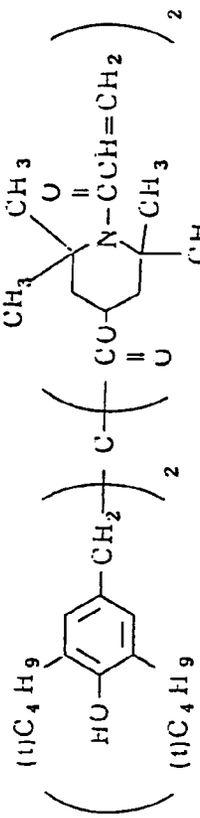
Ex Y - 1



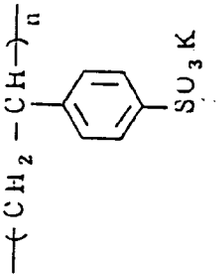
Ex M - 1



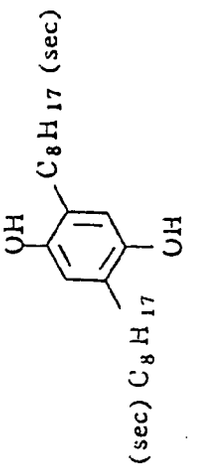
Cpd-1



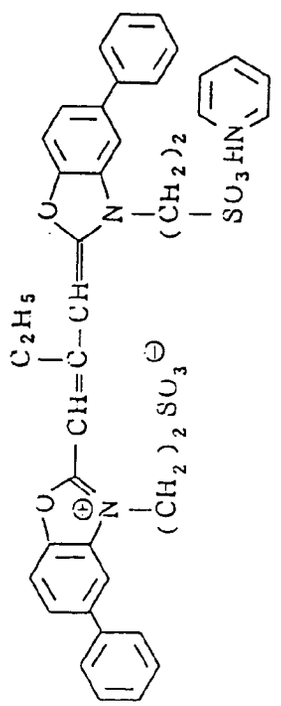
Cpd-2



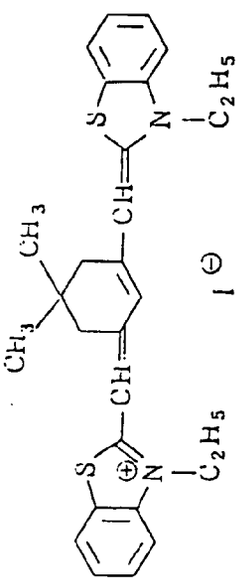
Cpd-3



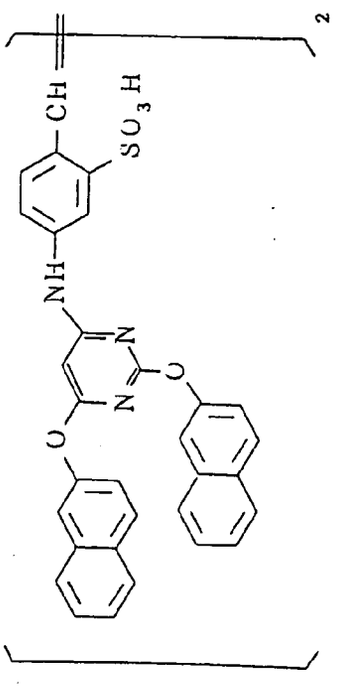
Ex S-3



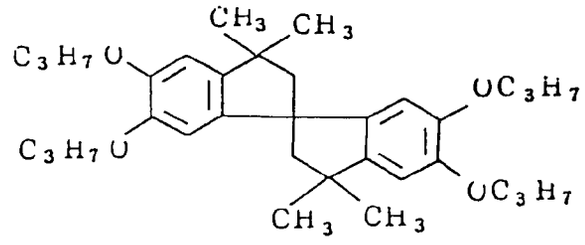
Ex S-4



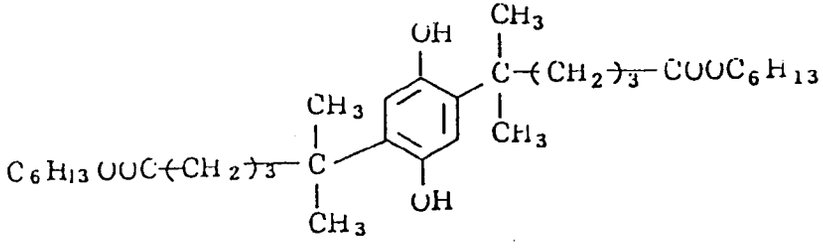
Ex S-5



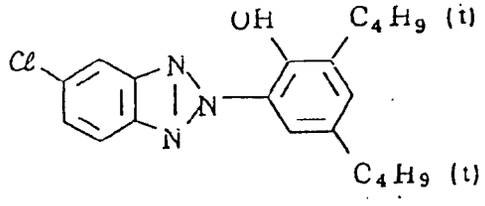
Cpd-4



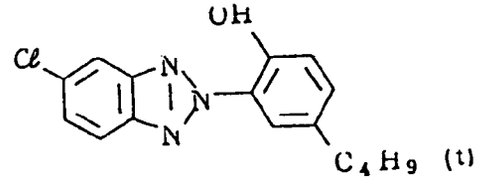
Cpd-5



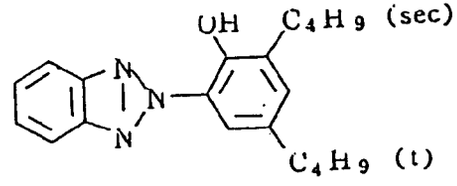
Cpd-6



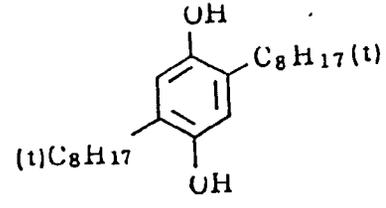
Cpd-7



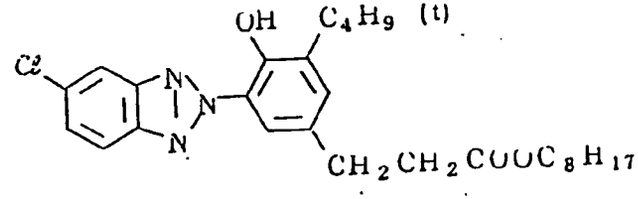
Cpd-8



Cpd-9

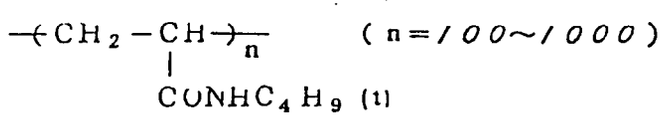


Cpd-10



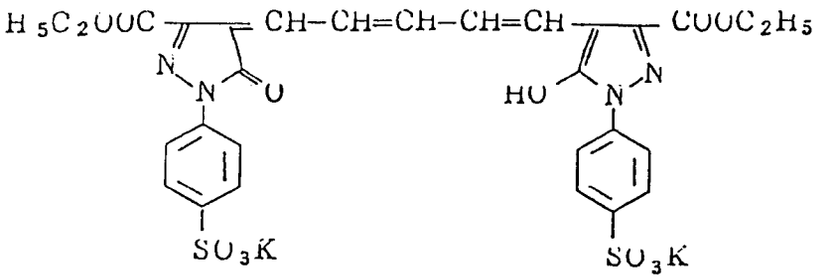
EP 0 368 340 B1

Cpd-11

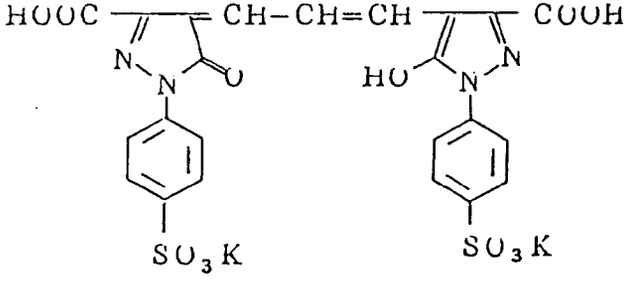


(n=100~1000)

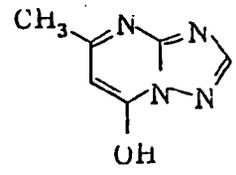
Cpd-12



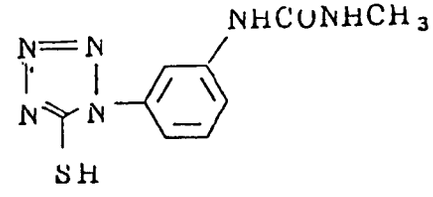
Cpd-13



Cpd-14



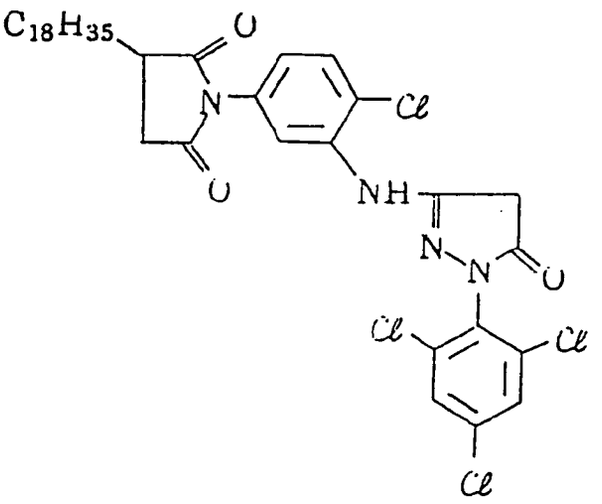
Cpd-15



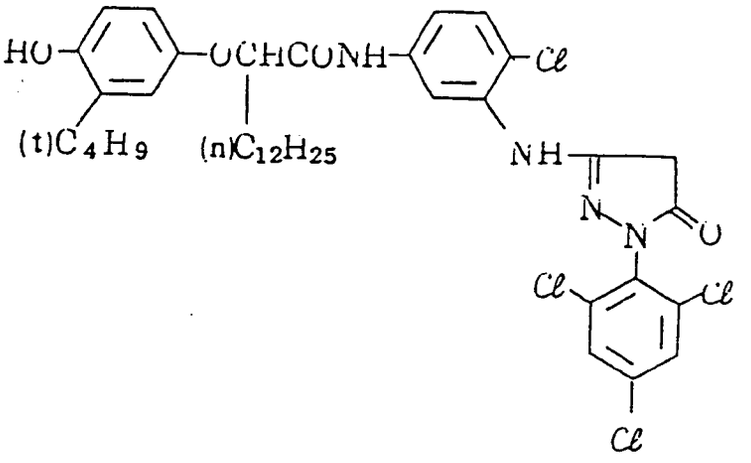
Solv-1 Dibutyl phthalate
Solv-2 Trioctyl phosphate
Solv-3 Trinonyl phosphate
Solv-4 Tricresyl phosphate

Samples 202 to 208 were prepared in the same manner as that described above except that magenta coupler EXM-1 of Sample 201 was replaced with the following coupler:

Sample 202



Sample 203



Sample 204: M-37
Sample 205: M-42
Sample 206: M-68
Sample 207: M-30
Sample 208: M-61

Samples 201 to 208 prepared as described above were processed in the same manner as that of Example 1 except that the conditions were changed as shown below. The results are shown in Table 2.

Process	Temperature	Time	Amount of replenisher*	Capacity of tank
Color development	35℃	45 sec	161 ml	17 ℓ
Bleach-fixing	30 to 36 ℃	45 sec	215 ml	17 ℓ
Stabilization (1)	30 to 37 ℃	20 sec	-	10 ℓ
Stabilization (2)	30 to 37 ℃	20 sec	-	10 ℓ
Stabilization (3)	30 to 37 ℃	20 sec	-	10 ℓ
Stabilization (4)	30 to 37 ℃	30 sec	248 ml	10 ℓ
Drying	70 to 85 ℃	60 sec		

* per m^2 of the photosensitive material

[4-tank counter current process in the stabilization steps (4) → (1)]
The compositions of the processing solutions used are as shown below:

Color developer	Tank	Replenisher
Water	800 ml	800 ml
Ethylenediaminetetraacetic acid	2.0 g	2.0 g
5,6-Dihydroxybenzene-1,2,4-trisulfonic acid	0.3 g	0.3 g
Triethanolamine	8.0 g	8.0 g
Sodium chloride	1.4 g (2.4×10^{-2} mol)	-
Potassium carbonate	25 g	25 g
N-ethyl-N-(β -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	5.0 g	7.0 g
Diethylhydroxylamine	4.2 g	6.0 g
Fluorescent brightener (UVITEX-CK; a product of Ciba Co.)	2.0 g	2.5 g
Water	ad 1000 ml	1000 ml
pH (25℃)	10.05	10.45

Bleach-fixing solution (the replenisher being the same as the tank solution)

Water	400 ml
Ammonium thiosulfate (700g/ℓ)	100 ml
Sodium sulfite	17 g
Ferric ammonium ethylenediaminetetra-acetate	55 g
Disodium ethylenediaminetetraacetate	5 g
Glacial acetic acid	9 g
Water	ad 1000 ml
pH (25℃)	5.40

Stabilizer (the replenisher being the same as the tank solution)

Formalin (37%)	0.1 g
Formalin-sulfurous acid adduct	0.7 g
5-Chloro-2-methyl-4-isothiazoline-3-on	0.02 g
2-Methyl-4-isothiazoline-3-on	0.01 g
Copper sulfate	0.005 g
Water	ad 1000 ml
pH (25℃)	4.0

The carryover of the bleach-fixing solution into the stabilization step in the processing in this example was 40mℓ per m^2 of the photosensitive material.

Method of regeneration of color developer:

The color developer was regenerated in the same manner as that of Example 1 except that only diethylhydroxylamine, N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate, potassium carbonate, fluorescent brightener and triethanolamine in the color developer were analyzed and, as for other components, 4.3 g of ethylenediaminetetraacetic acid and 0.6 g of 5,6-dihydroxybenzene-1,2,4-trisulfonic acid were added to 6 ℓ of the prepared replenisher. The pH was adjusted to be the same as that of the replenisher with potassium hydroxide and sulfuric acid.

Method for processing anion exchange resin:

The first step:

The same as that of Example 1

The second step and thereafter:

The same as that of Example 1 except that the processing with sodium chloride solution and subsequent washing step in Example 1 were omitted.

Table 2

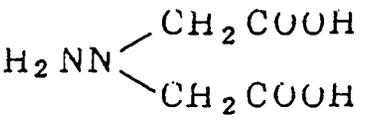
	Test No.	Sample No.	Change in sensitizing of magenta	Change in the minimum density of magenta (change of fog)	Change in the minimum yellow density after storage at 60°C at 70% relative humidity for 2 weeks	
					Start	After replenishment of 3-fold volume of replenisher
Comparative Example	7	201	0.06	0.04	0.06	0.12
〃	8	202	0.08	0.04	0.08	0.15
〃	9	203	0.07	0.03	0.07	0.13
Present Invention	10	204	0.01	0.00	0.03	0.03
〃	11	205	0.01	0.01	0.03	0.04
〃	12	206	0.02	0.01	0.04	0.05
〃	13	207	0.02	0.02	0.04	0.04
〃	14	208	0.02	0.02	0.04	0.04

It is thus apparent that according to the present invention, the changes are slight and excellent properties can be obtained.

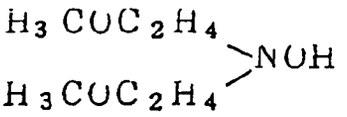
Example 3

The same procedure as that of Example 2 was repeated except that diethylhydroxylamine in the color developer was replaced with the same amount of the following compound to obtain the results which were substantially the same as those shown in Table 2.

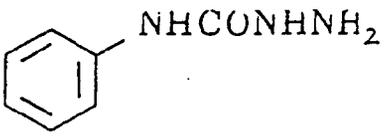
(1)



(2)



(3)



(4) H_3CCOCH_2OH

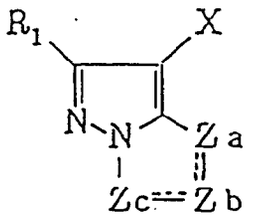
Example 4

The same procedure as that of Example 2 was repeated except that the stabilizer was replaced with deionized water having calcium content and magnesium content of not more than 3 mg/ℓ (conductivity: 2 μs/cm). The results were the same as those shown in Table 2.

Further the same procedure as that of Example 2 was repeated except that the processing with the stabilizer was replaced with washing with 3 ℓ/min of water at 30 °C to obtain the same results as those of Table 2.

Claims

1. A method for processing a silver halide color photosensitive material which contains at least one pyrazoloazole magenta coupler of the following general formula (I), comprising the steps of contacting a color developer used for color-developing the silver halide color photosensitive material with an anion exchanger, and then re-using the color-developer to develop further silver halide color photosensitive material:

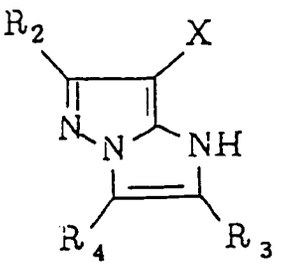


(I)

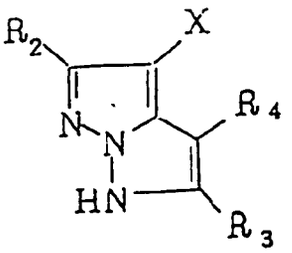
wherein R_1 represents a hydrogen atom or a substituent, X represents a hydrogen atom or a group capable of being eliminated by a coupling reaction with an oxidized product of an aromatic primary amine developing agent, and Za, Zb and Zc each represent methine, substituted methine, =N- or -NH- with the provisos that one of the Za ⎓ Zb bond and Zb-Zc bond is a double bond and the other is a single bond, that when the Zb ⎓ Zc bond is a carbon-to-carbon double bond, it may constitute a part of an aromatic ring, that R_1 or X may form a polymer (at least a dimer) by acting as a bridging group to one or more other groups of general formula (I) and that when Za, Zb or Zc is a substituted methine, the substituted methine may form a polymer (at least a dimer) by acting as a bridging group to one or more other groups of general formula (I).

2. A method according to claim 1, wherein the pyrazoloazole magenta coupler is a 1H-imidazo[1,2-b]pyrazole, a 1H-pyrazolo[1,5-b]pyrazole, a 1H-pyrazolo[5,1-c][1,2,4]triazole, a 1H-pyrazolo[1,5-b] [1,2,4]triazole, a 1H-pyrazolo[1,5-d)tetrazole or a 1H-pyrazolo[1,5-a]benzimidazole.

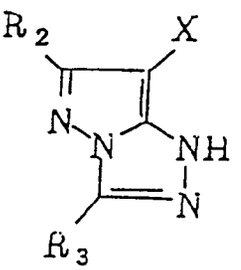
3. A method according to claim 1, wherein the pyrazoloazole magenta coupler is selected from the compounds represented by the general formulae (II) to (VII):



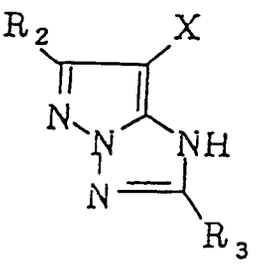
(II)



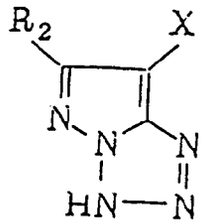
(III)



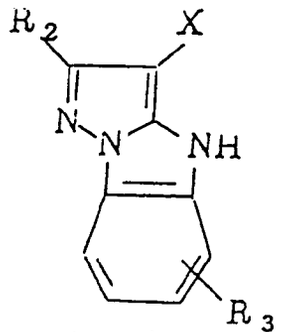
(IV)



(V)



(VI)



(VII)

wherein R_2, R_3 and R_4 each represent a hydrogen atom, a halogen atom, an alkyl group, an aryl group, a heterocyclic group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a carbamoyloxy group, a silyloxy group, a sulfonyloxy group, an acylamino group, an anilino a group, a ureido group, an imido group, a sulfamoylamino group, a carbamoylamino group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a sulfonamido group, a carbamoyl group, an acyl group, a sulfamoyl group, a sulfonyl group, a sulfinyl group, an alkoxycarbonyl group or an aryloxycarbonyl group, and X represents a hydrogen atom, a halogen atom, a carboxy group or a group bonded with the carbon atom at the coupling site through an oxygen atom, a nitrogen atom or a sulfur atom and capable of being coupled off.

4. A method according to claim 3, wherein the pyrazoloazole magenta coupler is a compound represented by the general formulae (II), (IV) or (V).

5. A method according to claim 1, wherein the pyrazoloazole magenta coupler is incorporated into an emulsion layer of the silver halide color photosensitive material in an amount of $2x10^{-3}$ to $5x10^{-1}$ mol per mol of silver in the emulsion layer.

6. A method according to claim 1, wherein the anion exchanger is a basic anion exchange resin having a quaternary ammonium salt-type exchange group.

7. A method according to claim 6, wherein the anion exchanger comprises a styrene/divinylbenzene copolymer.

8. A method according to claim 1, wherein the counter ion of the anion exchanger is an ion exchangeable with halogen ion in the color developer without exerting any influence on the color-developing capacity of the developer.

9. A method according to claim 8, wherein the counter ion of the anion exchanger is a carbonate ion, a bicarbonate ion, a hydroxyl ion, a sulfate ion, a nitrate ion, a phosphate ion, a hydrogenphosphate ion or a oxalate ion.

10. A method according to claim 1, wherein the color developer used for the photosensitive material is passed through a column containing the anion exchanger to continuously bring the color developer into contact with the anion exchanger.

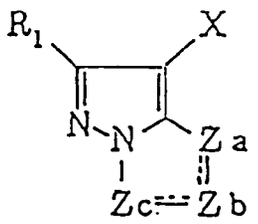
11. A method according to claim 1, wherein the color developer treated with the anion exchanger is re-used after compensation of necessary components due to their consumption during color-development or for their reduction due to adsorption on the anion exchanger.

12. A method according to claim 11, wherein the compensation is carried out in such a way that the ratio of concentrations of the components of the color developer to be used again to those of the color developer in the color developing tank is 1.0/1 to 2.0/1.

13. A method according to claim 1, wherein the color developer treated with the anion exchanger is replenished in the color developing tank in an amount of 50-300 ml per m^2 of a color paper or in an amount of 300-3000 ml per m^2 of a color negative film.

Patentansprüche

1. Verfahren zur photographischen Verarbeitung eines farblichtempfindlichen Silberhalogenid-Materials, das mindestens einen Pyrazoloazol-Magentakuppler der folgenden allgemeinen Formel (I) enthält, umfassend die Schritte des Inkontaktbringens eines Farbentwicklers, der zur Farbentwicklung des farblichtempfindlichen Silberhalogenid-Materials verwendet wird, mit einem Anionen-Austauscher und dann Wiederverwendung des Farbentwicklers zur Entwicklung von weiterem farblichtempfindlichen Silberhalogenid-Material:

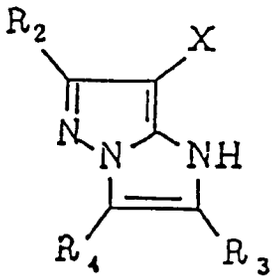


(I)

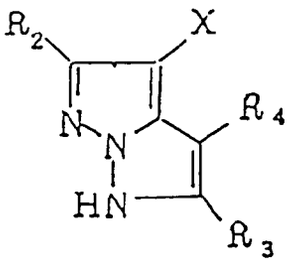
worin R_1 ein Wasserstoffatom oder einen Substituenten darstellt, X ein Wasserstoffatom oder eine Gruppe darstellt, die durch eine Kupplungsreaktion mit einem oxidierten Produkt eines aromatischen primären Amin-Entwicklungsmittels entfernt werden kann, und Za, Zb und Zc jeweils Methin, substituiertes Methin, =N- oder -NH- darstellen, mit den Maßgaben, daß eine der Bindungen Za ---- Zb und Zb ---- Zc eine Doppelbindung ist und die andere eine Einfachbindung ist, daß dann, wenn die Zb ---- Zc-Bindung eine Kohlenstoff-Kohlenstoff-Doppelbindung ist, sie einen Teil eines aromatischen Rings darstellen kann, daß R_1 oder X ein Polymer (mindestens ein Dimer) bilden können, indem sie als verbrückende Gruppe zu einer oder mehreren weiteren Gruppen der allgemeinen Formel (I) wirken und daß, wenn Za, Zb oder Zc substituiertes Methin ist, das substituierte Methin ein Polymer (mindestens ein Dimer) bilden kann, indem es als verbrückende Gruppe zu einer oder mehreren weiteren Gruppen der allgemeinen Formel (I) wirkt.

2. Verfahren gemäß Anspruch 1, worin der Pyrazoloazol-Magentakuppler ein 1H-Imidazo[1,2-b]pyrazol, ein 1H-Pyrazolo[1,5-b]pyrazol, ein 1H-Pyrazolo[5,1-c][1,2,4)triazol, ein 1H-Pyrazolo[1,5-b][1,2,4]triazol, ein 1H-Pyrazolo[1,5-d]tetrazol oder ein 1H-Pyrazolo[1,5-a]benzimidazol ist.

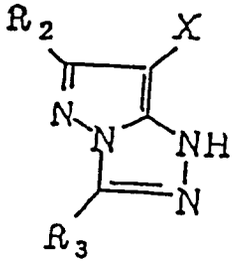
3. Verfahren gemäß Anspruch 1, worin der Pyrazoloazol-Magentakuppler aus Verbindungen ausgewählt ist, die durch die allgemeinen Formeln (II) bis (VII) dargestellt werden:



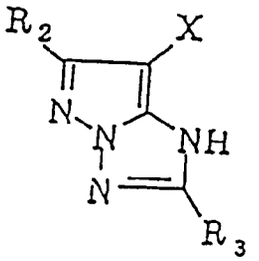
(II)



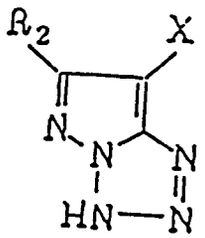
(III)



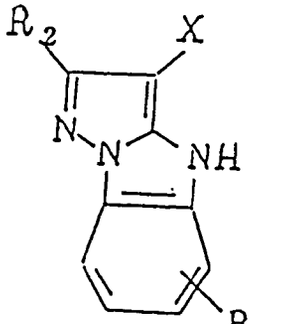
(IV)



(V)



(VI)



(VII)

worin R_2, R_3 und R_4 jeweils ein Wasserstoffatom, ein Halogenatom, eine Alkyl-Gruppe, eine Aryl-Gruppe, eine heterocyclische Gruppe, eine Cyano-Gruppe, eine Alkoxy-Gruppe, eine Aryloxy-Gruppe, eine heterocyclische Oxy-Gruppe, eine Acyloxy-Gruppe, eine Carbamoyloxy-Gruppe, eine Silyloxy-Gruppe, eine Sulfonyloxy-Gruppe, eine Acylamino-Gruppe, eine Anilino-Gruppe, eine Ureido-Gruppe, eine Imido-Gruppe, eine Sulfamoylamino-Gruppe, eine Carbamoylamino-Gruppe, eine Alkylthio-Gruppe, eine Arylthio-Gruppe, eine heterocyclische Thio-Gruppe, eine Alkoxycarbonylamino-Gruppe, eine Aryloxycarbonylamino-Gruppe, eine Sulfonamido-Gruppe, eine Carbamoyl-Gruppe, eine Acyl-Gruppe, eine Sulfamoyl-Gruppe, eine Sulfonyl-Gruppe, eine Sulfinyl-Gruppe, eine Alkoxycarbonyl-Gruppe oder eine Aryloxycarbonyl-Gruppe darstellen und X ein Wasserstoffatom, ein Halogenatom, eine Carboxy-Gruppe oder eine Gruppe, die mit dem Kohlenstoffatom an der Kupplungsstelle durch ein Sauerstoffatom, ein Stickstoffatom oder ein Schwefelatom gebunden ist und abgespalten werden kann, darstellt.

4. Verfahren gemäß Anspruch 3, worin der Pyrazoloazol-Magentakuppler eine Verbindung ist, die durch die allgemeinen Formeln (II), (IV) oder (V) dargestellt wird.

5. Verfahren gemäß Anspruch 1, worin der Pyrazoloazol-Magentakuppler in eine Emulsionsschicht des farblichtempfindlichen Silberhalogenid-Materials in einer Menge von 2×10^{-3} bis 5×10^{-1} Mol pro Mol Silber in der Emulsionsschicht inkorporiert wird.

6. Verfahren gemäß Anspruch 1, worin der Anionen-Austauscher ein basisches Anionen-Austauscherharz mit Austauschergruppen vom quaternären Ammoniumsalztyp ist.

7. Verfahren gemäß Anspruch 6, worin der Anionen-Austauscher ein Styrol/Divinylbenzol-Copolymer umfaßt.

8. Verfahren gemäß Anspruch 1, worin das Gegenion des Anionen-Austauschers ein mit einem Halogen-Ion im Farbentwickler austauschbares Ion ist, ohne daß es einen Einfluß auf die Farbentwicklungskapazität des Entwicklers ausübt.

9. Verfahren gemäß Anspruch 8, worin das Gegenion des Anionen-Austauschers ein Carbonat-Ion, ein Bicarbonat-Ion, ein Hydroxyl-Ion, ein Sulfat-Ion, ein Nitrat-Ion, ein Phosphat-Ion, ein Hydrogenphosphat-Ion oder ein Oxalat-Ion ist.

10. Verfahren gemäß Anspruch 1, worin der für das lichtempfindliche Material verwendete Farbentwickler durch eine Säule, die den Anionen-Austauscher enthält, geleitet wird, um den Farbentwickler mit dem Anionen-Austauscher kontinuierlich in Kontakt zu bringen.

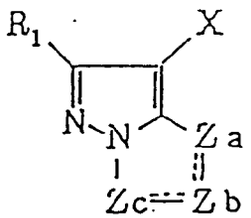
11. Verfahren gemäß Anspruch 1, worin der mit dem Anionen-Austauscher behandelte Farbentwickler nach Kompensation der notwendigen Komponenten aufgrund ihres Verbrauchs während der Farbentwicklung oder ihrer Abnahme aufgrund von Adsorption an den Anionen-Austauscher wiederverwendet wird.

12. Verfahren gemäß Anspruch 11, wobei die Kompensation so ausgeführt wird, daß das Konzentrations-Verhältnis der Komponenten des wiederzuverwendenden Farbentwicklers zu denen des Farbentwicklers im Farbentwicklungstank 1,0/1 bis 2,0/1 beträgt.

13. Verfahren gemäß Anspruch 1, worin der mit dem Anionen- Austauscher behandelte Farbentwickler im Farbentwicklungstank in einer Menge von 50 bis 300 ml pro m^2 Farbpapier oder in einer Menge von 300 bis 3000 ml pro m^2 Farbnegativfilm ergänzt wird.

Revendications

1. Procédé destiné au traitement d'un matériau photosensible couleur à base d'halogénure d'argent contenant au moins un coupleur magenta de pyrazoloazole de formule générale suivante (I), comprenant les étapes de mise en contact d'un développateur couleur utilisé pour développer en couleur le matériau photosensible couleur à base d'halogénure d'argent avec un échangeur d'anions et de réutilisation ensuite du développateur couleur pour développer ensuite le matériau photosensible couleur à base d'halogénure d'argent :



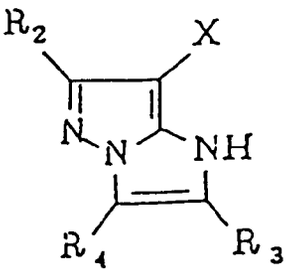
(I)

dans laquelle R_1 représente un atome d'hydrogène ou un substituant, X représente un atome d'hydrogène ou un groupe apte à être éliminé par une réaction de couplage avec un produit oxydé d'un agent de développement à base d'amine primaire aromatique et Za, Zb et Zc représentent chacun une méthine, une

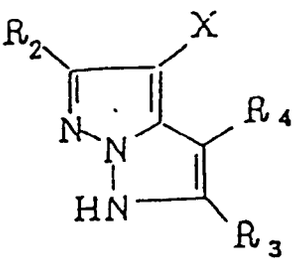
méthine substituée, =N- ou -NH- avec la condition qu'une de la liaison Za -:- Zb et la liaison Zb-Zc soit une double liaison et l'autre soit une simple liaison, que lorsque la liaison Zb -:- Zc est une double liaison carbonecarbone, elle puisse constituer une partie d'un cycle aromatique, que R_1 ou X puisse former un polymère (au moins un dimère) en agissant comme un groupe de pontage pour un ou plusieurs autres groupes de formule générale (I) et que lorsque Za, Zb ou Zc est une méthine substituée, la méthine substituée puisse former un polymère (au moins un dimère) en agissant comme un groupe de pontage pour un ou plusieurs autres groupes de formule générale (I).

2. Procédé selon la revendication 1, dans lequel le coupleur magenta de pyrazoloazole est 1H-imidazo[1,2-b]pyrazole, 1H-pyrazolo[1,5-b]pyrazole, 1H-pyrazolo[5,1-c][1,2,4]triazole, 1H-pyrazolo[1,5-b][1,2,4]triazole, 1H-pyrazolo[1,5-d]tétrazole ou 1H-pyrazolo[1,5-a]benzimidazole.

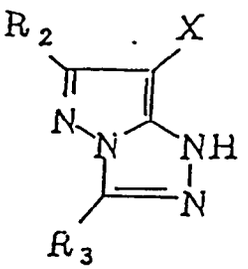
3. Procédé selon la revendication 1, dans lequel le coupleur magenta de pyrazoloazole est choisi à partir des composés représentés par les formules générales (II) à (VII) :



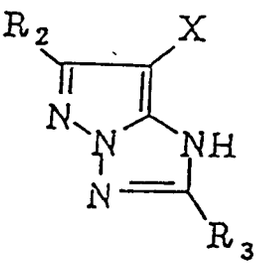
(II)



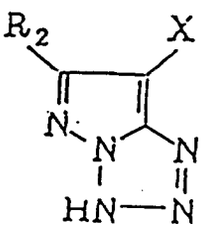
(III)



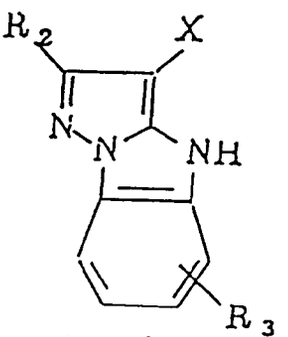
(IV)



(V)



(VI)



(VII)

dans lesquelles R_2, R_3 et R_4 représentent chacun un atome d'hydrogène, un atome d'halogène, un groupe alkyle, un groupe aryle, un groupe hétérocyclique, un groupe cyano, un groupe alcoxy, un groupe aryloxy, un groupe oxyhétérocyclique, un groupe acyloxy, un groupe carbamoyloxy, un groupe silyloxy, un groupe sulfonyloxy, un groupe acylamino, un groupe anilino, un groupe uréido, un groupe imido, un groupe sulfamoylamino, un groupe carbamoylamino, un groupe alkylthio, un groupe arylthio, un groupe thiohétérocyclique, un groupe alcoxycarbonylamino, un groupe aryloxycarbonylamino, un groupe sulfonamido, un groupe carbamoyle, un groupe acyle, un groupe sulfamoyle, un groupe sulfonyle, un groupe sulfinyle, un groupe alcoxycarbonyle ou un groupe aryloxycarbonyle et X représente un atome d'hydrogène, un atome d'halogène, un groupe carboxy ou un groupe lié avec l'atome de carbone au niveau du site de couplage à travers un atome d'oxygène, un atome d'azote ou un atome de soufre et apte à être éliminé.

4. Procédé selon la revendication 3, dans lequel le coupleur magenta de pyrazoloazole est un composé représenté par les formules générales (II), (IV) ou (V).

5. Procédé selon la revendication 1, dans lequel le coupleur magenta de pyrazoloazole est incorporé dans une couche d'émulsion du matériau photosensible couleur à base d'halogénure d'argent en une quantité comprise entre 2×10^{-3} et 5×10^{-1} mole par mole d'argent dans la couche d'émulsion.

6. Procédé selon la revendication 1, dans lequel l'échangeur d'anions est une résine échangeuse d'anions basique ayant un groupe d'échange de type de sel d'ammonium quaternaire.

7. Procédé selon la revendication 6, dans lequel l'échangeur d'anions comprend un copolymère de styrène et de divinylbenzène.

8. Procédé selon la revendication 1, dans lequel le contre-ion de l'échangeur d'anions est un ion échangeable par un ion halogène dans le développateur couleur sans exercer aucune influence sur l'aptitude de développement couleur du développateur.

9. Procédé selon la revendication 8, dans lequel le contre-ion de l'échangeur d'anions est un ion carbonate, un ion bicarbonate, un ion hydroxyle, un ion sulfate, un ion nitrate, un ion phosphate, un ion hydrogénophosphate ou un ion oxalate.

10. Procédé selon la revendication 1, dans lequel le développateur couleur utilisé pour le matériau photosensible est passé à travers une colonne contenant l'échangeur d'anions pour amener de manière continue le développateur couleur en contact avec l'échangeur d'anions.

11. Procédé selon la revendication 1, dans lequel le développateur couleur traité par l'échangeur d'anions est réutilisé après compensation des composants nécessaires du fait de leur consommation au cours du développement couleur ou pour leur réduction due à l'adsorption sur l'échangeur d'anions.

12. Procédé selon la revendication 11, dans lequel la compensation est effectuée de telle manière que le rapport de concentration des constituants du développateur couleur qui doit être utilisé de nouveau par rapport à ceux du développateur couleur dans le réservoir de développement couleur est situé entre 1,0/1 et 2,0/1.

13. Procédé selon la revendication 1, dans lequel le développateur couleur traité par l'échangeur d'anions est rechargé dans le réservoir de développement couleur en une quantité de 50 à 300 ml par m^2 d'un papier couleur ou en une quantité de 300 à 3 000 ml par m^2 d'un film négatif couleur.