⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 382 443**
A2

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EUROPEAN PATENT APPLICATION

㉑ Application number: **90301164.1**

㉒ Date of filing: **05.02.90**

(51) Int. Cl.⁵: **G03C 7/38, G03C 7/396, G03C 7/34**

㉚ Priority: **15.02.89 JP 36572/89**
06.02.89 JP 26953/89
03.03.89 JP 52494/89

㊸ Date of publication of application:
16.08.90 Bulletin 90/33

(84) Designated Contracting States:
DE FR GB NL

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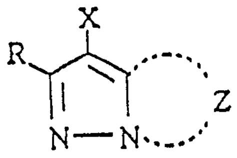
(54) A silver halide light-sensitive photographic material.

(57) There is disclosed the silver halide light-sensitive photographic material having an excellent color reproduction and capable of providing an image having an superior light fastness, wherein the photographic component layers comprise one of the following Constitutions (1) and (2):

Constitution (1): a silver halide emelsion layer containing emulsified lipophilic particles comprising a magenta coupler represented by the following Formula M-1 and having a molecular weight of not more than 600, and a polymer insoluble in water and soluble in an organic solvent, and

Constitution (2): a silver halide emulsion layer containing the same magenta coupler as the above, and a silver halide emulsion layer containing emulsified lipophilic particles comprising a phenol-type cyan coupler and the same polymer as the above;

Formula M-1



A SILVER HALIDE LIGHT-SENSITIVE PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a silver halide light-sensitive photographic material with improved color reproducibility and image preservability.

BACKGROUND OF THE INVENTION

In a color photoprint for visual appreciation, a yellow coupler, a magenta coupler and a cyan coupler have conventionally been employed in combination.

5-pyrazolone ring compounds have been widely employed as a magenta coupler. 5-pyrazolone magenta couplers have poor reproducibility for brilliant blue, since a dye formed therefrom has a yellow component generated by an unnecessary absorption around 430 nm.

A recently developed pyrazoloazole magenta coupler, unlike conventional 5-pyrazolone magenta couplers, has an advantage of improved color reproducibility, since a dye formed therefrom has no secondary absorption in around 430 nm.

However, this coupler is inferior to 5-pyrazolone magenta couplers in image preservability, especially in a light fastness as is known well, and the improvement thereof is expected.

As for a cyan coupler, an improved stability to heat and humidity (dark fading property) has been required in recent years.

Conventional cyan couplers, such as those disclosed in Japanese Patent Publication Open to Public Inspection (hereinafter abbreviated as "Japanese Patent O.P.I. Publication") Nos. 37425/1972, 10135/1975, 25228/1975, 112038/1975, 117422/1975, and 130441/1975, U.S. Patent Nos. 2,369,929, 2,423,730, 2,434,272, 2,474,293, and 2,698,794, have a poor dark fading property.

As a result of many attempts to develop a cyan coupler with improved dark fading property, there have been found as the cyan coupler satisfying such demand, a 2,5-diacylamino cyan coupler disclosed in U.S. Patent No. 2,895,826, Japanese Patent O.P.I. Publication Nos. 112038/1975, 109630/1978 and 163537/1980, and a phenol cyan coupler having at a 5-position an alkyl group with 2 or more carbon atoms disclosed in U.S. Patent Nos. 3,772,002 and 4,443,536.

As compared with a conventional phenol cyan coupler having no acylamino group at the 5-position, the 2,5-diacylamino cyan coupler has an insufficient reproducibility for brilliant green, since a dye formed therefrom has a maximum absorption shifted to a shorter wavelength range and has a significant secondary absorption in around 550 nm, and in order to achieve the sufficient reproducibility of a green color, the other cyan couplers have to be used in combination, which in turn results in badly affecting the improvement of the dark fading property.

The phenol cyan coupler having an alkyl group with 2 or more carbon atoms at the 5-position has more improved dark fading property, though still unsatisfactory, than the conventional phenol cyan couplers having a methyl group at the 5-position.

The methods for improving the light fastness of a coupler are disclosed in Japanese Patent O.P.I. Publication Nos. 44658/1988, 250648/1988, 537/1989 and WO-88100723 where a water-insoluble, organic solvent-soluble polymer is emulsified together with a coupler. Light fastness can be improved by applying this method to the pyrazoloazole magenta coupler, but to an unsatisfactory extent under the condition of a high temperature and humidity. In addition, the above polymer impairs a color developability. To avoid this problem, there are used the techniques in which a high boiling organic solvent is used together with a coupler and a polymer, or hydrophilic bonds such as sulfonamido and ether are introduced into a non-diffusible group of the coupler. It has been found, however, that the light-sensitive materials prepared by these methods cause a "sweating phenomenon" (hereinafter referred to as "sweating"), whereby a part of the components constituting lipophilic particles migrate to the surface of photographic component layers during storage and cause significant deterioration of image quality.

As is apparent from the above, any of the conventional techniques is unsatisfactory, and there is a strong demand in the art for technique which can improve a color reproducibility and a light fastness with the pyrazoloazole magenta coupler and phenol cyan coupler, and effectively prevent sweating to thereby provide an excellent image preservability.

SUMMARY OF THE INVENTION

The first object of the present invention is to provide a silver halide light-sensitive photographic material having an improved color reproducibility.

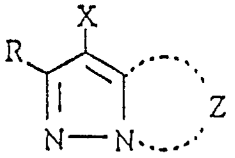
The second object is to provide a silver halide light-sensitive photographic material having an improved light fastness, free from sweating and thereby having an excellent image preservability.

The third object is to provide a silver halide light-sensitive photographic material with an excellent color developability.

DETAILED DESCRIPTION OF THE INVENTION

The above objects of the invention can be attained by a silver halide light-sensitive photographic material having a support and provided thereon the silver halide emulsion layers, wherein at least one of the silver halide emulsion layers contains emulsified lipophilic particles comprising a magenta coupler with a molecular weight of not more than 600 represented by Formula M-I, and a polymer insoluble in water but soluble in an organic solvent, or by a silver halide light-sensitive photographic material having a support and provided thereon the silver halide emulsion layers, wherein at least one of the emulsion layers contains emulsified lipophilic particles comprising a phenol cyan coupler and a polymer insoluble in water but soluble in an organic solvent, and another layer contains a magenta coupler with a molecular weight of not more than 600 represented by Formula M-I:

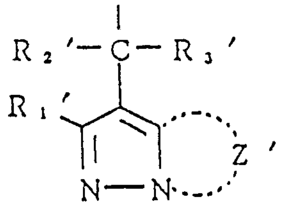
M-I



wherein Z represents a group of non-metal atoms necessary to form a nitrogen-containing heterocycle which may have a substituent; X represents a hydrogen atom or a group which can be released by a reaction with an oxidation product of a color developing agent; and R represents a hydrogen atom or a substituent.

The examples of the substituent represented by R are an alkyl group, an aryl group, an anilino group, an acylamino group, a sulfonamide group, an alkylthio group, an arylthio group, an alkenyl group, a cycloalkyl group, a halogen atom, a cycloalkenyl group, an alkynyl group, a heterocyclic group, a sulfonyl group, a sulfinyl group, a phosphonyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclic oxy group, a siloxy group, an acyloxy group, a carbamoyloxy group, an amino group, an alkylamino group, an imido group, an ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic thio group, a spiro compound residue, a bridged hydrocarbon compound residue. The respective groups represented by R are as follows: the alkyl group has preferably 1 to 32 carbon atoms; the aryl group is preferably a phenyl group; the acylamino group includes an alkylcarbonylamino group and an arylcarbonylamino group; the sulfonamide group includes an alkylsulfonylamino group and an arylsulfonylamino group; the alkyl and aryl components in the alkylthio and arylthio groups may be the above alkyl and aryl groups; the alkenyl group has preferably 2 to 32 carbon atoms the cycloalkyl and cycloalkenyl groups each have 3 to 12, preferably 5 to 7 carbon atoms; the sulfonyl group includes an alkylsulfonyl group and an arylsulfonyl group; the sulfinyl group includes an alkylsulfinyl group and an arylsulfinyl group; the phosphonyl group includes an alkylphosphonyl group, an alkoxyphosphonyl group, an aryloxyphosphonyl group and an arylphosphonyl group; the acyl group includes an alkylcarbonyl group and an arylcarbonyl group; the carbamoyl group includes an alkylcarbamoyl group and an arylcarbamoyl group; the sulfamoyl group includes an alkylsulfamoyl group and an arylsulfamoyl group; the acyloxy group includes an alkylcarbonyloxy group and an arylcarbonyloxy group; the carbamoyloxy group includes an alkylcarbamoyloxy group and an arylcarbamoyloxy group; the ureido group includes an alkylureido group and an arylureido group; the sulfamoylamino group includes an alkylsulfamoyl group and an arylsulfamoylamino group; the heterocyclic group is preferably a 5 to 7-membered ring such as 2-furyl, 2-thienyl, 2-pyrimidyl and 2-benzothiazolyl; the heterocyclic oxy group is preferably a 5 to 7-membered heterocyclic ring such as 3,4,5,6-tetrahydropyranyl-2-oxy and 1-phenyltetrazole-5-oxy; the heterocyclic thio group is preferably a 5 to 7-membered ring such as 2-pyridylthio, 2-benzothiazolylthio and 2,4-diphenoxy-1,3,5-triazole-6-thio; the siloxy group includes a trimethylsiloxy group, a triethylsiloxy group and a dimethylbutylsiloxy group; the imido group includes a succinic imido group, a 3-heptadecyl succinic imido group, a phthalimido group and a glutarimido group; the spiro compound residue includes spiro [3.3] heptane-1-yl; the bridged hydrocarbon compound residue includes bicyclo [2.2.1] heptane-1-yl, tricyclo [3.3.1.1$^{3\ 7}$] decane-1-yl and 7,7-dimethyl-bicylco [2.2.1] heptane-1-yl.

The group represented by X includes a halogen atom, an alkoxy group, an aryloxy group, a heterocyclic oxy group, an acyloxy group, a sulfonyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an alkyloxalyloxy group, an alkoxyoxalyloxy group, an alkylthio group, an arylthio group, a heterocyclic thio group, an alkyloxythiocarbonylthio group, an acylamino group, a sulfonamide group, a nitrogen-containing heterocycle having a bonding site at a nitrogen atom, an alkyloxycarbonylamino group, an aryloxycarbonylamino group, a carboxyl group,

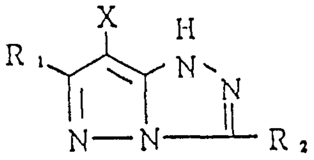


wherein R·′ and Z′ are the same as defined for R and Z in Formula M-I, respectively, and R_2' and R_3' each represent a hydrogen atom, an aryl group and a heterocyclic group. Of them, a halogen atom, in particular chlorine, is preferable.

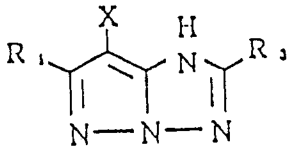
The nitrogen-containing heterocycle formed by Z or Z′ includes a pyrazole ring, an imidazole ring, a triazole ring and a tetrazole ring, and may have the same substituents as those defined for R.

The magenta couplers represented by Formula M-I are represented by the following Formulas M-II to M-VII.

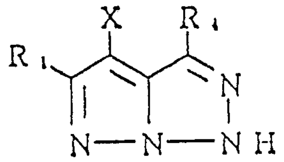
Formula M-II



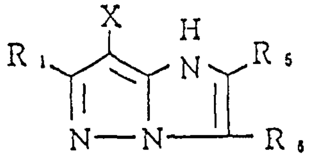
Formula M-III



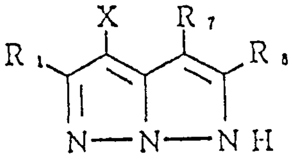
Formula M-IV



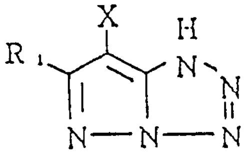
Formula M-V



Formula M-VI

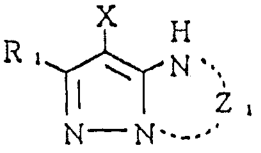


Formula M-VII



wherein R_1 through R_8 and X represent the same groups as defined for R and X in Formula M-I.

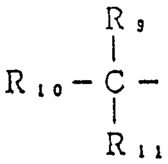
The magenta coupler represented by Formula M-I is preferably represented by the following Formula M-VIII:



wherein R_1, X and Z_1 represent the same groups as defined for R, X and Z in Formula M-I.

Of the magenta couplers represented by Formulae M-II to M-VII, preferable are those represented by Formula M-II.

R and R_1 each are represented most preferably by the following Formula M-IX:



$$R_{10}-\overset{\displaystyle R_9}{\underset{\displaystyle R_{11}}{C}}-$$

wherein R_9, R_{10} and R_{11} each represent the same groups as defined for R, provided that two of R_9, R_{10} and R_{11} may combine to form a saturated or unsaturated ring such as cycloalkane, cycloalkene, heterocycle, and that another may combine with this ring to form a bridged hydrocarbon residue.

In M-IX, preferable is (i) the case in which at least two of R_9 through R_{11} are alkyl groups, or (ii) the case in which at least one of R_9 through R_{11} is a hydrogen atom and the other two combine to form cycloalkyl together with a root carbon atom.

In the case (i), further preferable is the case in which two of R_9 through R_{11} are an alkyl groups, and the remaining one is either a hydrogen atom or an alkyl group. Especially preferable is the case in which all of R_9 through R_{11} are alkyl groups.

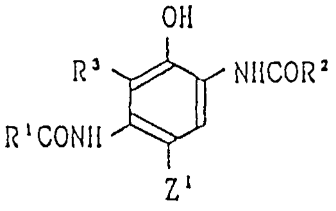
The substituents for the ring formed by Z in Formula M-I or Z_1 in Formula M-VIII, and the groups represented by R_2 to R_8 in Formulae M-II to M-VI are represented preferably by the following Formula M-X:
$-R^1-SO_2-R^2$
wherein R^1 represents an alkylene group, and R^2 represents an alkyl group, a cycloalkyl group or an aryl group.

The alkylene group represented by R^1 is a linear or branched alkylene group which preferably has 2 or more, more preferably 3 to 6 carbon atoms in its linear structure. The alkyl group represented by R^2 is an alkyl group which has preferably 6 to 20 carbon atoms. The cycloalkyl group represented by R^2 is preferably 5 to 6-membered. The aryl group represented by R^2 is preferably a phenyl group which may have a substituent.

The magenta coupler represented by Formula M-I has a molecular weight of not more than 600, preferably 400 to 550.

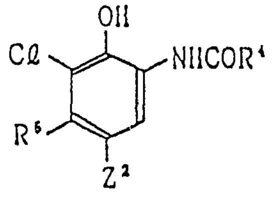
The phenol cyan coupler used in the present invention is represented preferably by Formula I or II:

Formula I



wherein R^1 represents an alkyl group or an aryl group; R^2 represents an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; R^3 represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group, and may combine with R^1 to form a ring; and Z^1 represents a group which can be released by a reaction with an oxidation product of a color developing agent;

Formula II

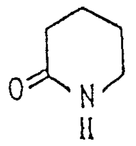


wherein R^4 represents a ballast group; R^5 represents an alkyl group having 1 to 6 carbon atoms; and Z^2 represents a hydrogen atom or a group which can be released by a reaction with an oxidation product of a color developing agent.

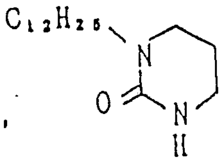
The alkyl group represented by R^1 is an alkyl group having preferably 1 to 32 carbon atoms. The aryl group represented by R^1 is preferably a phenyl group. The alkyl group represented by R^2 is an alkyl group having preferably 1 to 32 carbon atoms. The cycloalkyl group represented by R^2 preferably has 3 to 12 carbon atoms. The aryl group represented by R^2 is preferably a phenyl group. The heterocyclic ring represented by R^2 is preferably 5- to 7-membered.

R^3 represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group, preferably a hydrogen atom.

The ring formed by R^1 and R^3 is preferably 5 to 6-membered, the examples of which are:



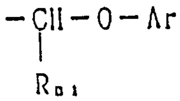
,



In Formula II, the alkyl group represented by R^5 have preferably 2 to 6 carbon atoms.

The ballast group represented by R^4 is an organic group having a size and shape enabling coupler molecules to be bulky enough to substantially prevent the diffusion of the coupler from a coupler-containing layer to the other layers.

The preferable ballast group is represented by the following Formula II-B.

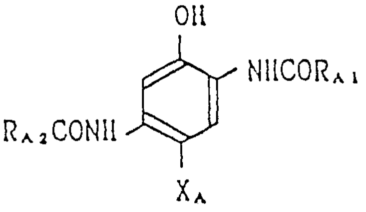


$$-\underset{R_{B1}}{\underset{|}{CH}}-O-Ar$$

wherein R_{B1} represents an alkyl group having 1 to 12 carbon atoms; Ar represents an aryl group such as a phenyl group.

The groups represented by Z^1 and Z^2 in Formulae I and II are a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, a sulfonyloxy group, an acylamino group, a sulfonylamino group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, and an imido group. Of them, preferable are a halogen atom, an aryloxy group and an alkoxy group.

The above cyan coupler is represented preferably by the following Formula I-A:



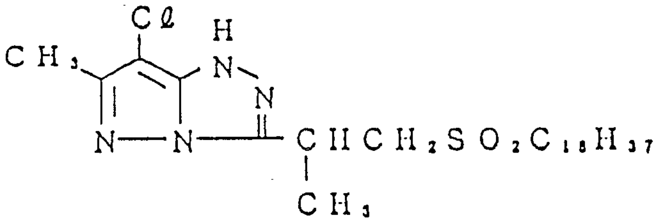
wherein R_{A1} represents a phenyl group substituted by at least one halogen atom, which may further contain a substituent other than a halogen atom; R_{A2} represents the same groups as defined for R^1; and X_A represents a halogen atom, an aryloxy group or an alkoxy group.

The examples of the magenta coupler represented by Formula M-I are shown below:

M - 1

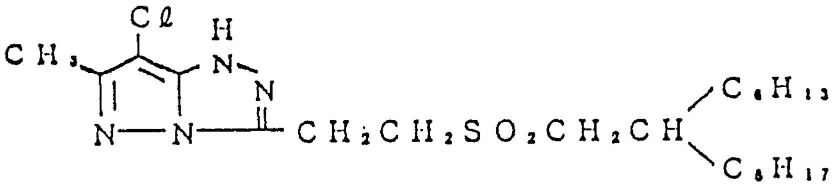
Molecular weight

515.2



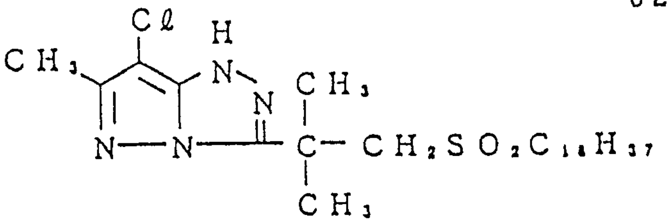
M - 2

473.1



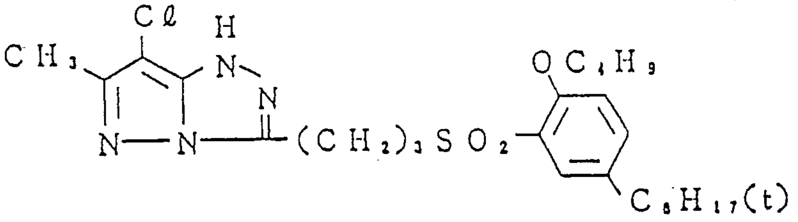
M - 3

529.2



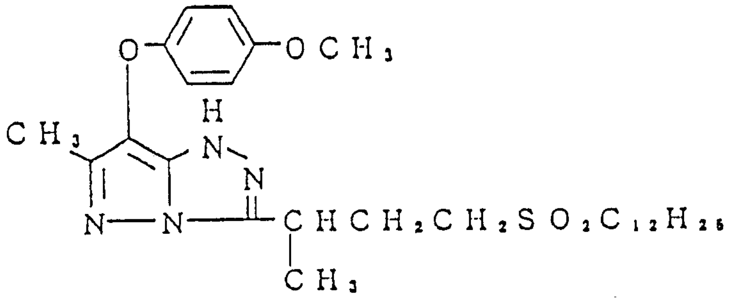
M - 4

523.1



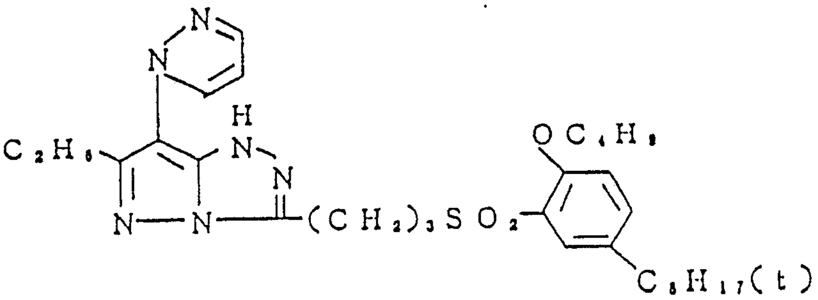
M - 5

532.7



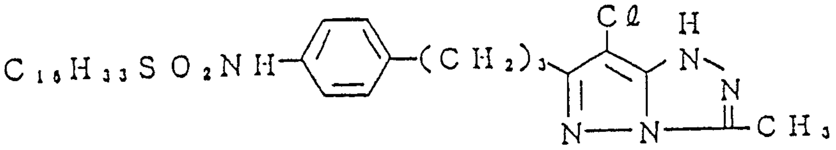
M - 6

568.8



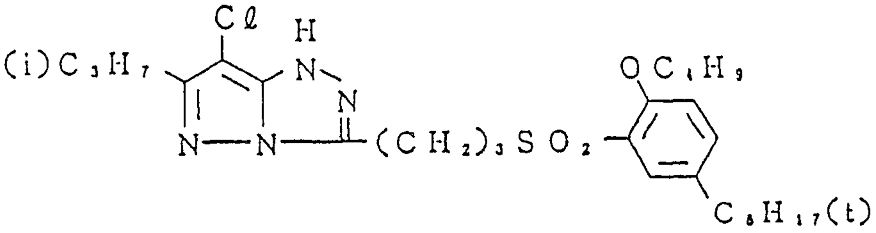
M - 7

578.3



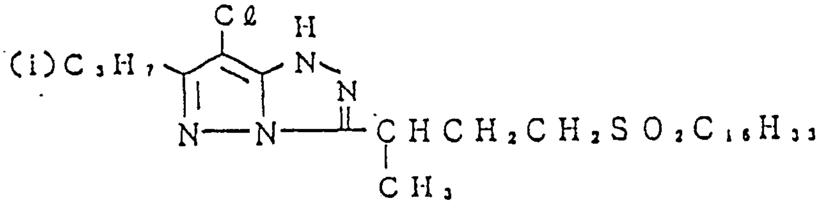
M－8

551.2



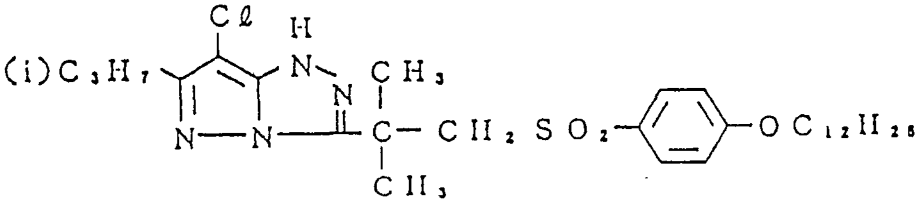
M－9

529.2



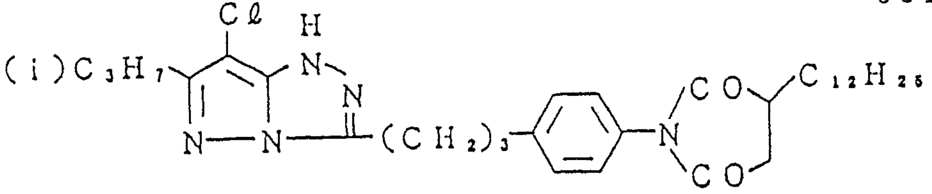
M－10

565.2



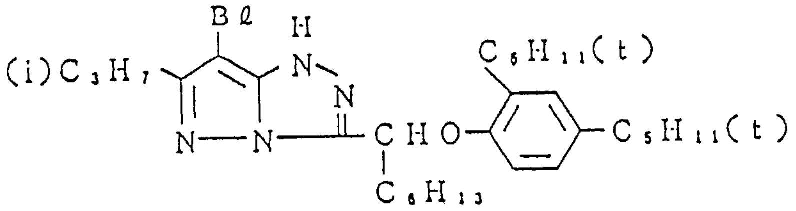
M－11

531.7



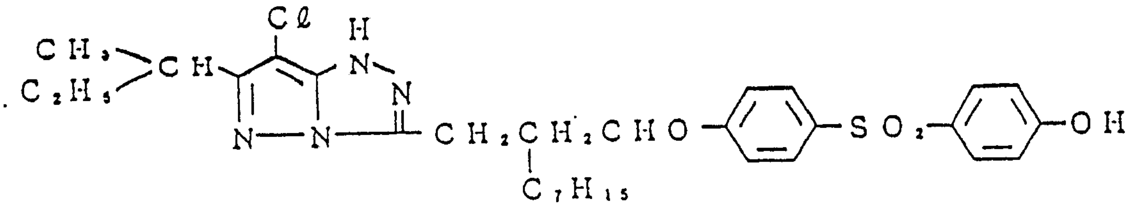
M - 12.

559.6



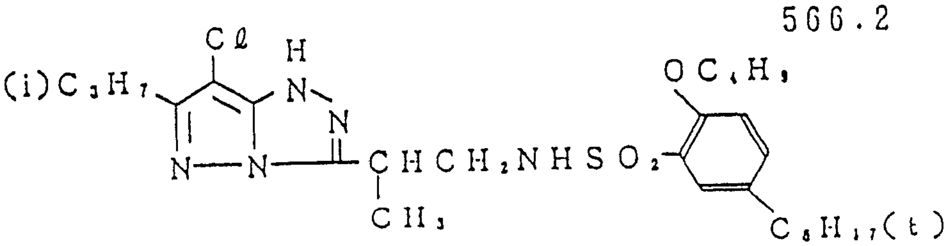
M - 13

587.2



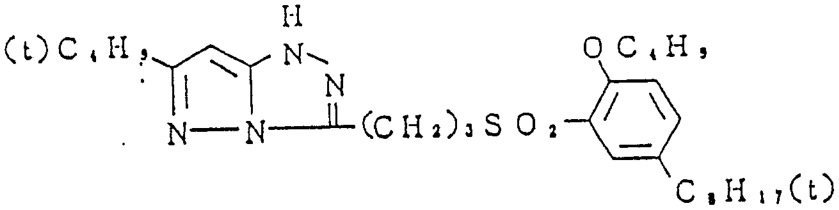
M - 14

566.2



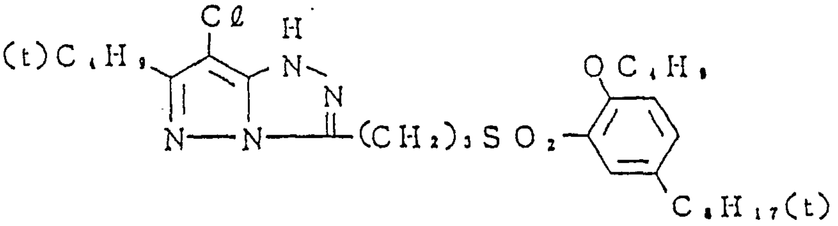
M - 15

530.8



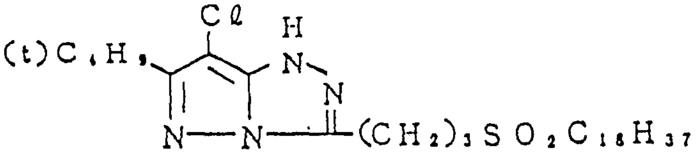
M - 16

565.2



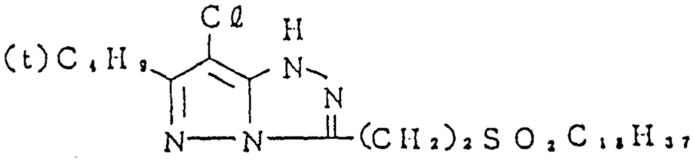
M - 17

557.3



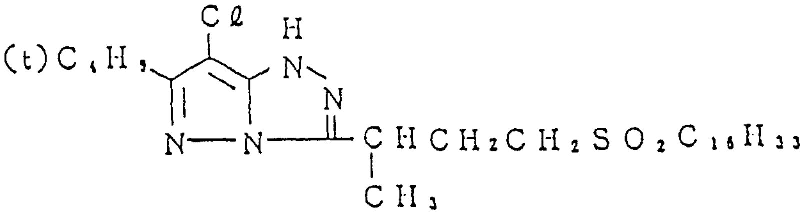
M - 18

543.2



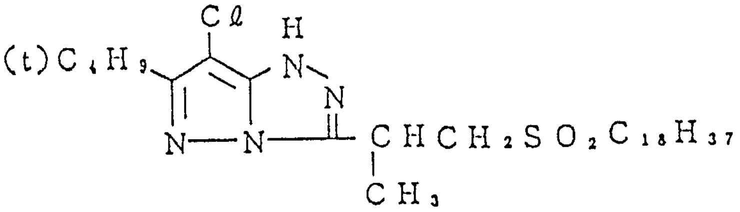
M - 19

543.2



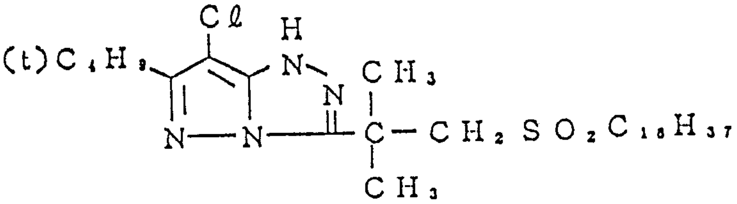
M － 20

557.3



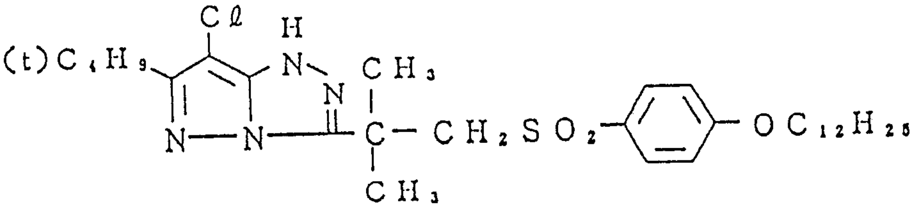
M － 21

571.3



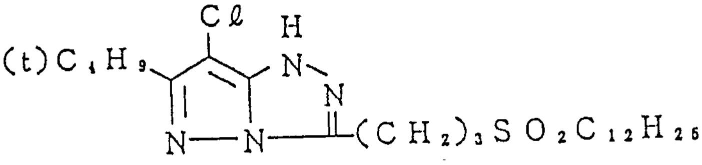
M － 22

579.2



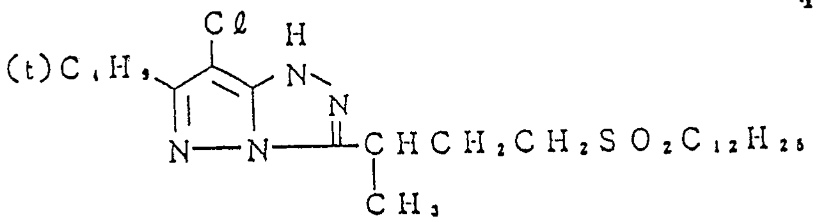
M － 23

473.1



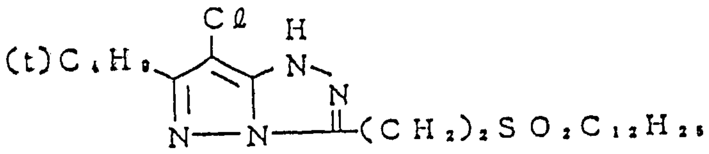
M - 24

487.1



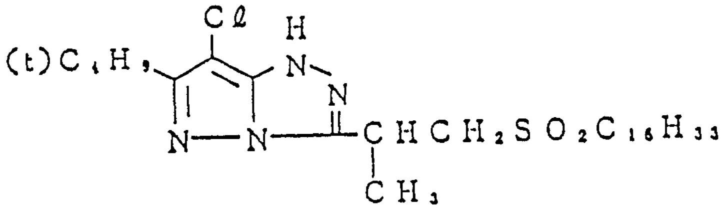
M - 25

459.1



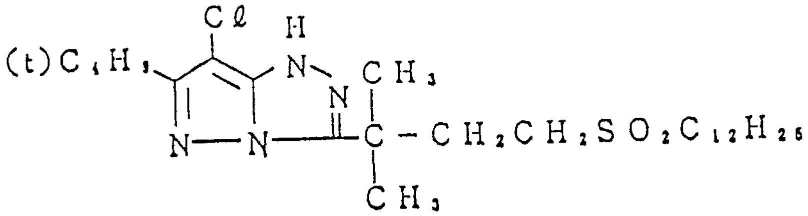
M - 26

529.2



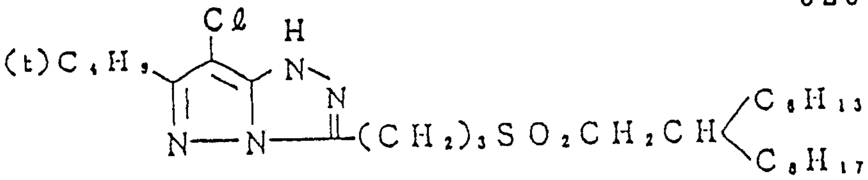
M - 27

501.2



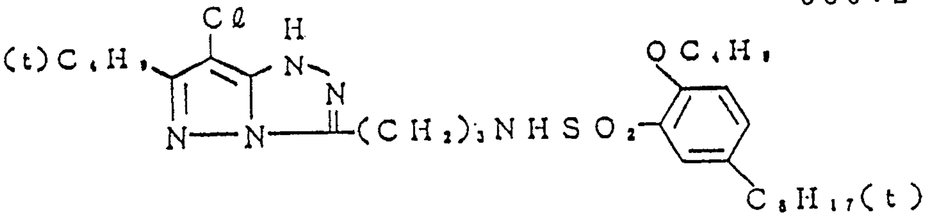
M - 28

529.2



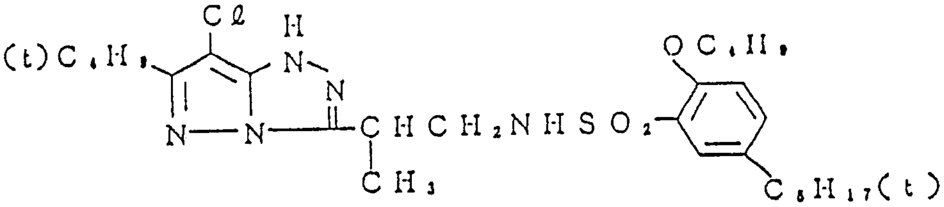
M - 29

580.2



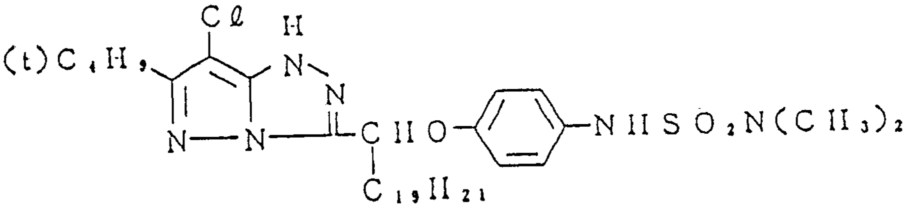
M - 30

580.2



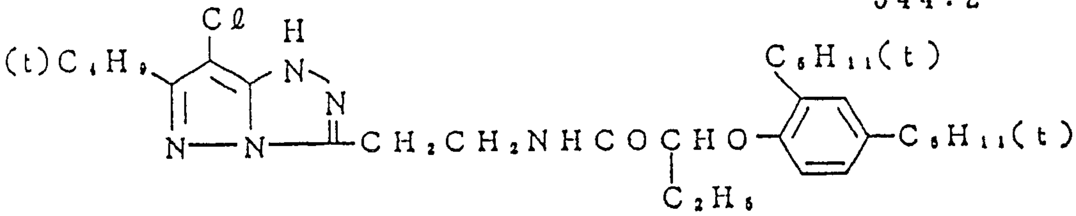
M - 31

568.2



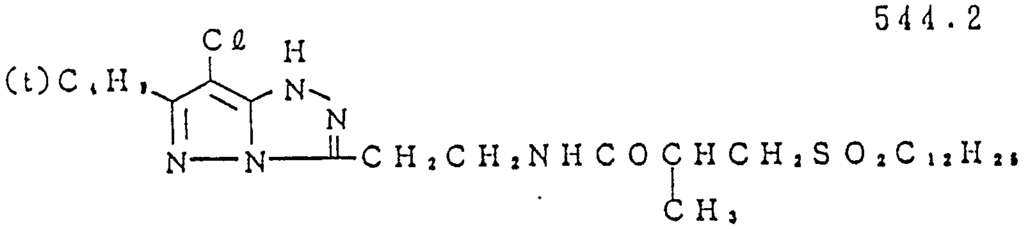
M - 32

544.2



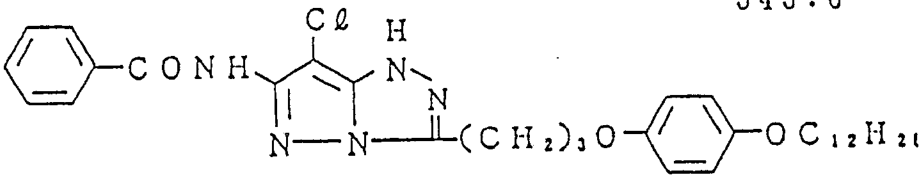
M - 33

544.2



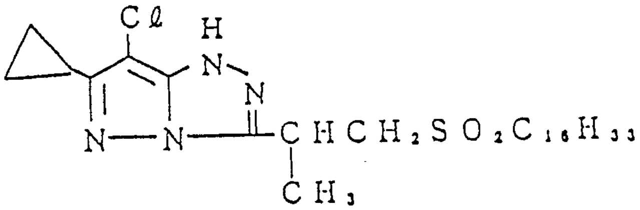
M - 34

545.6



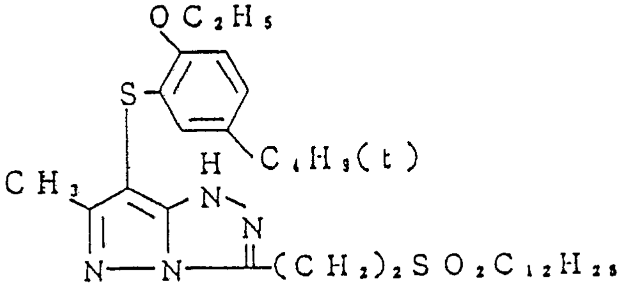
M - 35

512.2



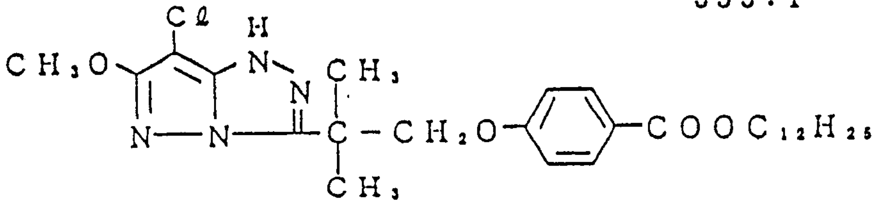
M - 36

590.9



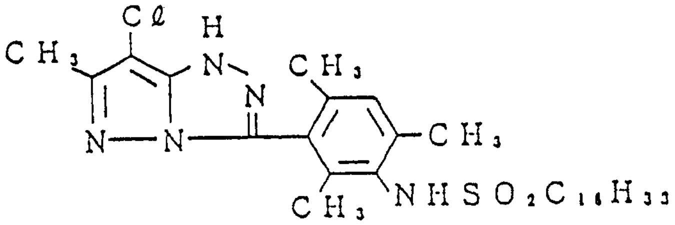
M - 37

533.1



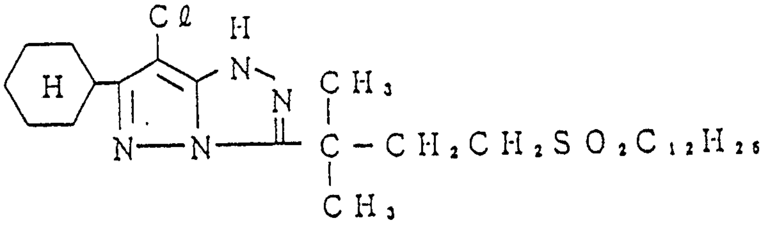
M - 38

578.3



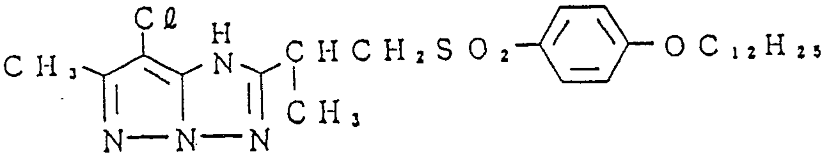
M - 39

527.2



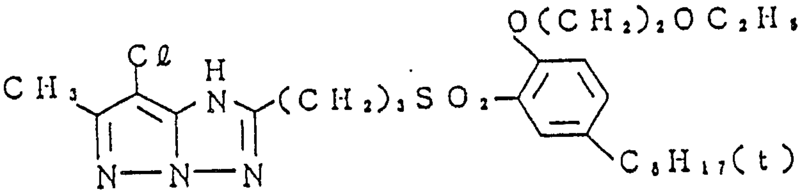
M - 40.

523.1



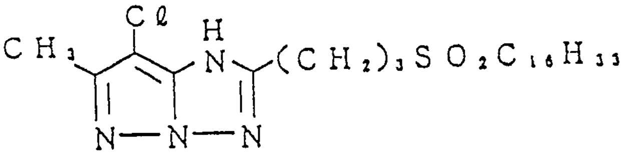
M - 41

539.1



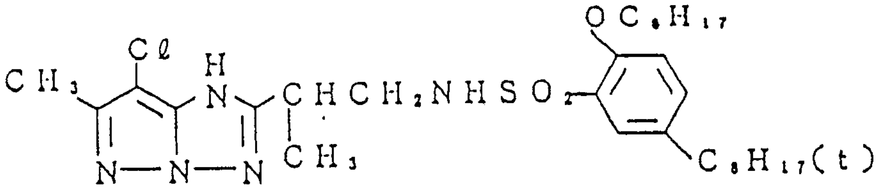
M - 42

487.1



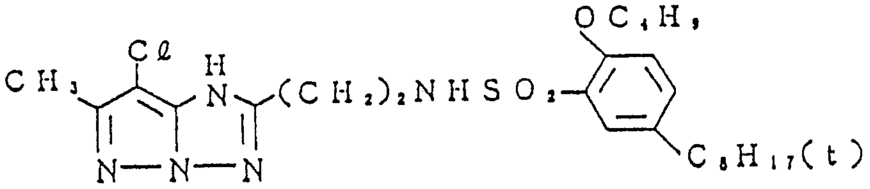
M - 43

594.3



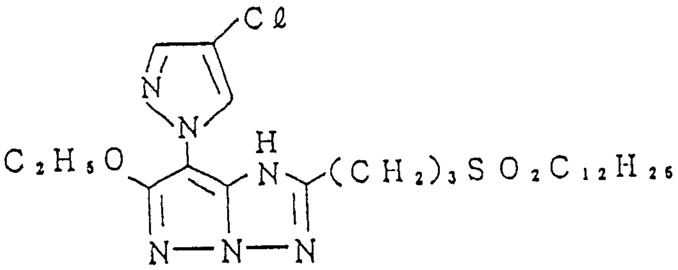
M - 44

524.1



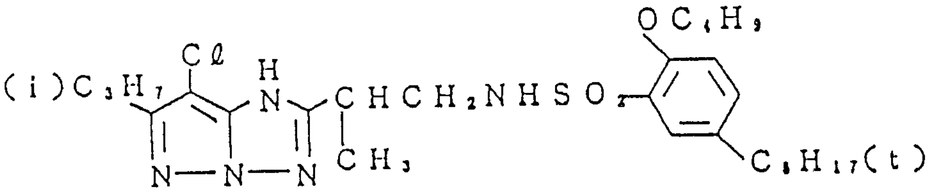
M - 45

527.1



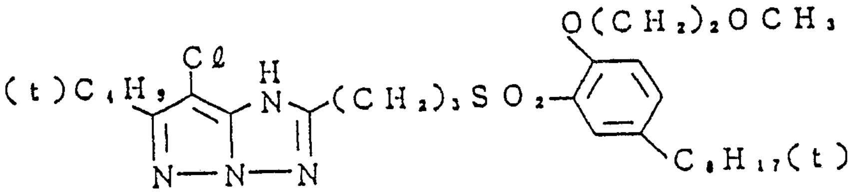
M - 46

566.2



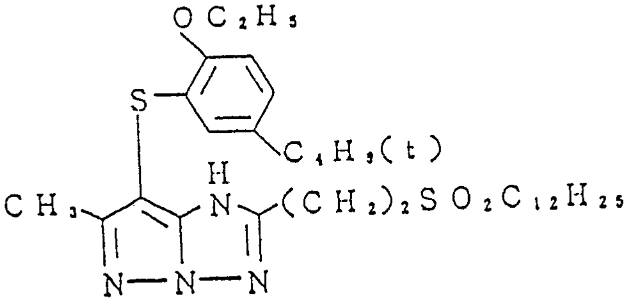
M - 47

567.2



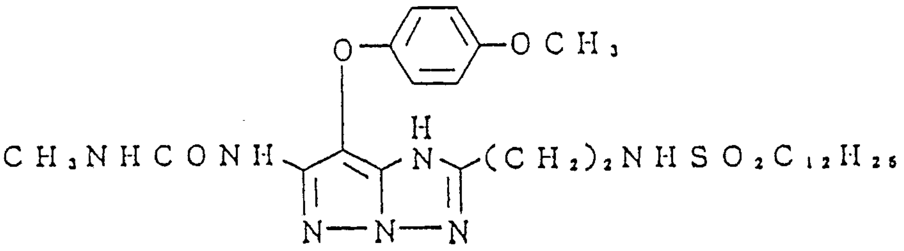
M - 48

590.9



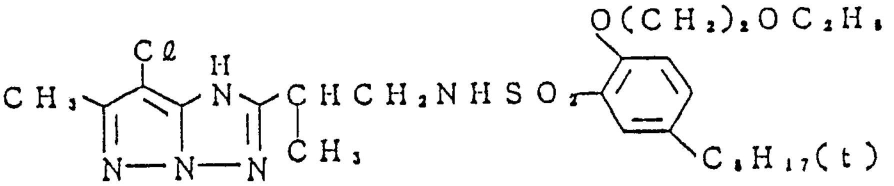
M - 49

577.7



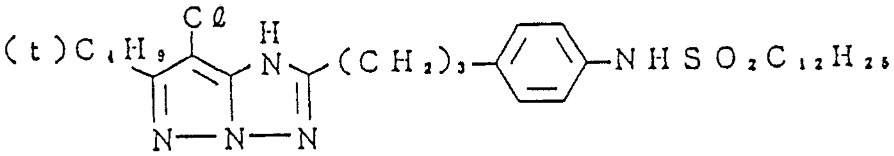
M - 50

554.1



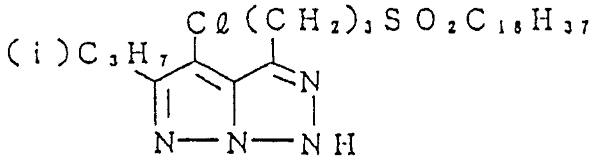
M - 51

563.2



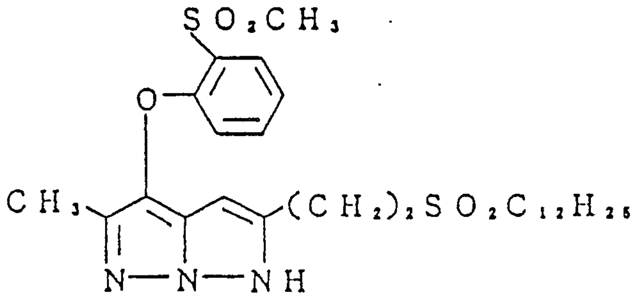
M - 52

543.2



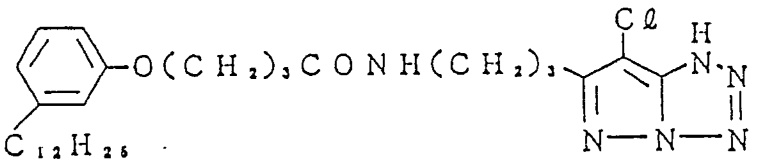
M - 53

551.8

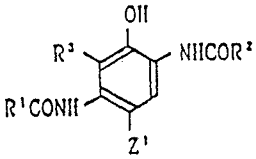


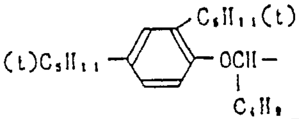
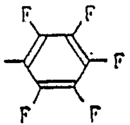
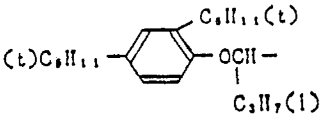
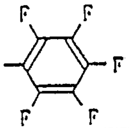
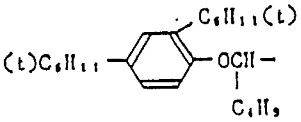
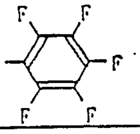
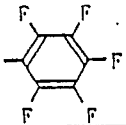
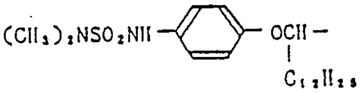
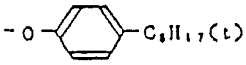
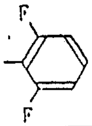
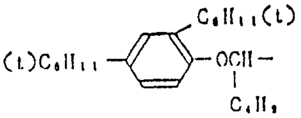
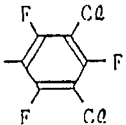
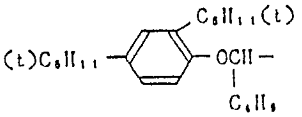
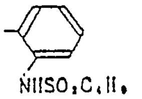
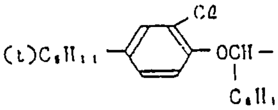
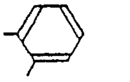
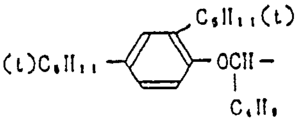
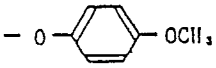
M - 54

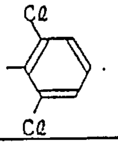
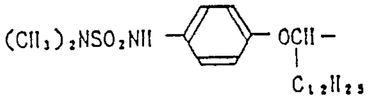
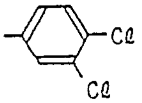
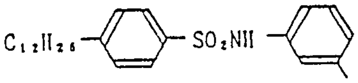
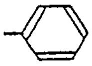
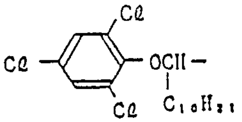
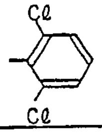
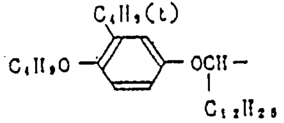
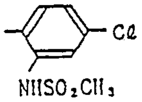
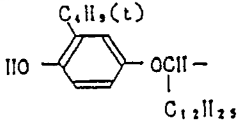
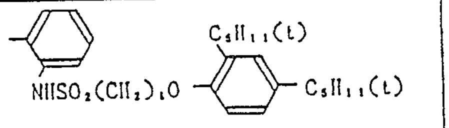
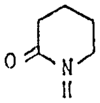
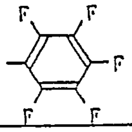
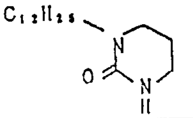
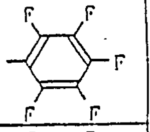
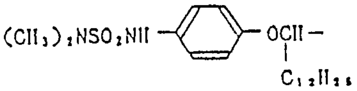
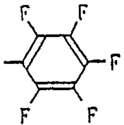
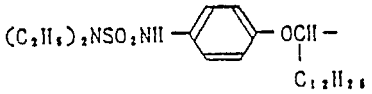
531.1

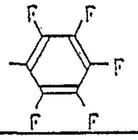
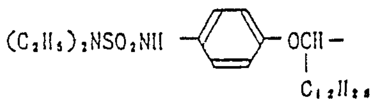
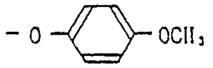
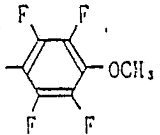
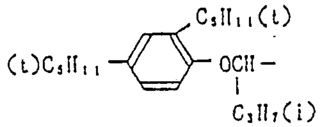
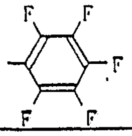
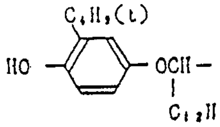
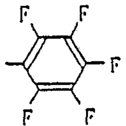
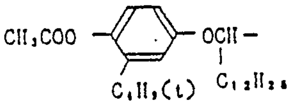
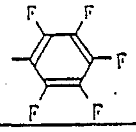
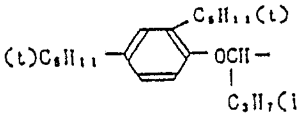
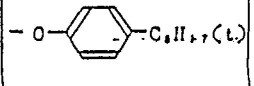
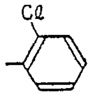
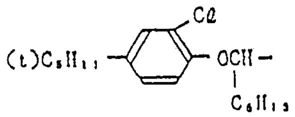
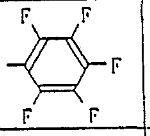
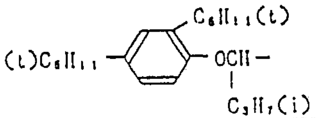
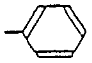
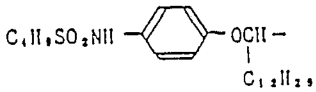
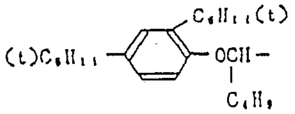
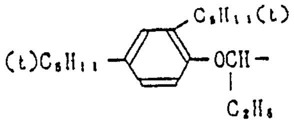


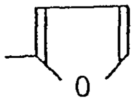
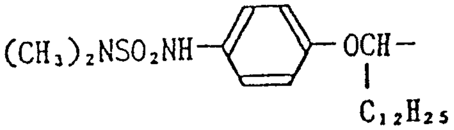
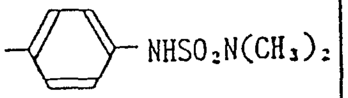
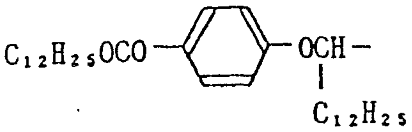
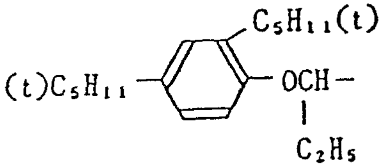
The examples of the cyan coupler represented by Formula I are shown below:



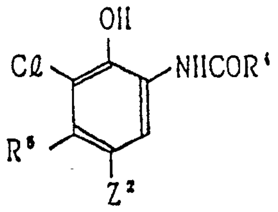
Example compound	R²	R¹	R³	Z¹
I - 1	$-(CF_2)_4H$		H	$-Cl$
I - 2			H	$-Cl$
I - 3			H	$-Cl$
I - 4		$C_{16}H_{33}-$	$-Cl$	$-Cl$
I - 5			H	
I - 6			H	H
I - 7			H	$-Cl$
I - 8			H	$-Cl$
I - 9			H	

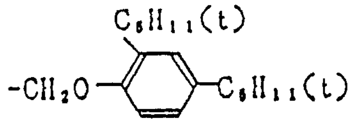
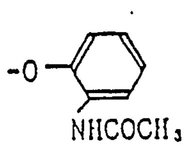
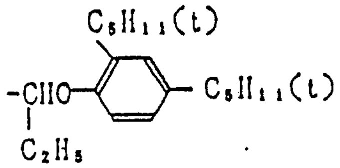
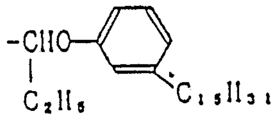
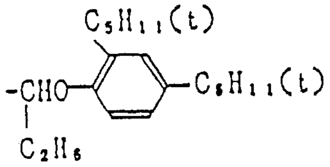
Example compound	R^2	R^1	R^3	Z^1
I - 10			H	$-Cl$
I - 11			H	$-Cl$
I - 12			H	$-OCH_2CONHC_3H_7$
I - 13			H	$-Cl$
I - 14			H	$-Cl$
I - 15				$-Cl$
I - 16				$-Cl$
I - 17			H	$-Cl$
I - 18			H	$-Cl$

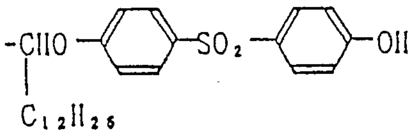
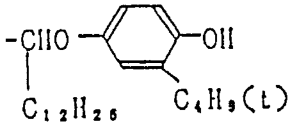
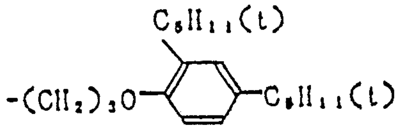
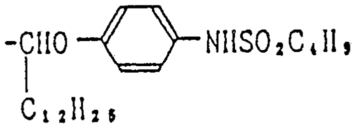
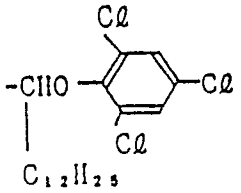
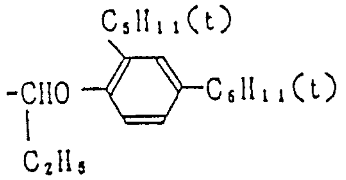
Example compound	R^2	R^1	R^3	Z^1
I - 19			H	
I - 20			H	−Cl
I - 21			H	−Cl
I - 22			H	−Cl
I - 23			H	
I - 24			H	−Cl
I - 25			H	$-OCH_2CONH(CH_2)_2OCH_3$
I - 26			H	−Cl
I - 27	$-C_3F_7$		H	H
I - 28	$-C_3F_7$		H	H

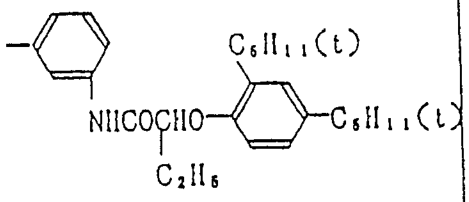
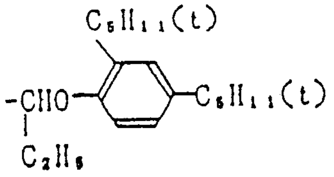
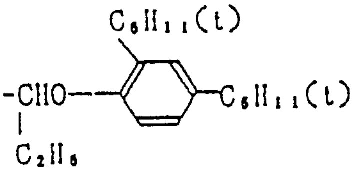
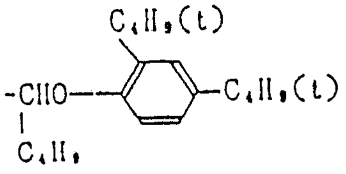
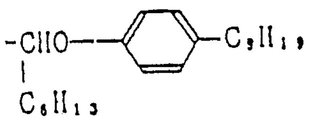
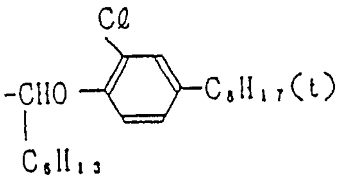
Example compound	R^2	R^1	R^3	Z^1
I - 29			H	Cl
I - 30			CH_3O	Cl
I - 31			H	Cl

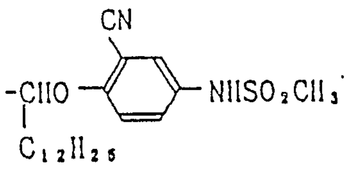
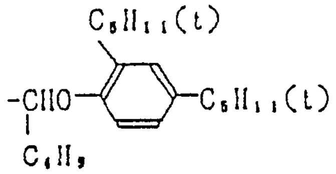
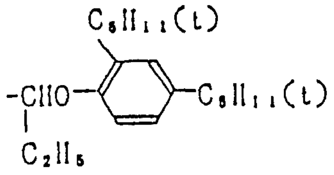
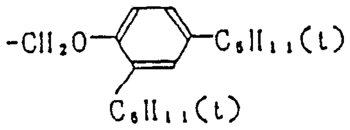
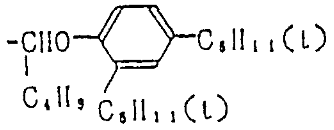
The examples of the cyan coupler represented by Formula II are shown below:



Coupler No.	R^5	Z^2	R^4
II - 1	$-C_2H_5$	$-C\ell$	
II - 2	$-C_2H_5$		
II - 3	$-C_3H_7(i)$	$-C\ell$	
II - 4	$-C_2H_5$	$-C\ell$	

Coupler No.	R^6	Z^2	R^4
II - 5	$-C_4H_9$	-F	
II - 6	$-C_2H_5$	-F	
II - 7	$-C_2H_5$	$-Cl$	
II - 8	$-C_2H_5$	$-Cl$	
II - 9	$-C_2H_5$	$-Cl$	
II -10	$-C_3H_7(i)$	$-Cl$	$-C_{18}H_{37}$
II -11	$-C_6H_{13}$	$-Cl$	

Coupler No.	R^5	Z^2	R^4
II-12	$-C_3H_7$	-Cl	
II-13	$-(CH_2)_2NHCOCH_3$	-Cl	
II-14	$-(CH_2)_2OCH_3$	-Cl	
II-15	$-C_2H_5$	-Cl	
II-16	$-C_4H_9(t)$	$-O(CH_2)_2-$* *$-SO_2CH_3$	
II-17	$-C_2H_5$	-Cl	

Coupler No.	R^5	Z^2	R^4
II -18	$-C_2H_5$	$-Cl$	
II -19	$-C_2H_5$	$-Cl$	
II -20	$-CH_3$	$-Cl$	
II -21	$-CH_3$	$-Cl$	
II -22	$-CH_3$	$-Cl$	
II -23	$-C_2H_5$	$-Cl$	$-C_{15}H_{31}$

The above magenta couplers can be synthesized by the methods described in Journal of the Chemical Society, Perkin I (1977), pp. 2047 to 2052, U.S. Patent No. 3,725,067, Japanese Patent O.P.I. Publication Nos. 99437/1984, 42045/1983, 162548/1984, 171956/1984, 33552/1985, 43659/1985, 172982/1985, and 190779/1985.

The preceding magenta coupler is added normally in an amount of 1 x 10^{-3} to 1 mol, preferably 1 x 10^{-2} to 8 x 10^{-1} mol per mol of silver halide, and may be employed in combination with other couplers.

The cyan coupler used in the present invention is added preferably in an amount of 2 x 10^{-3} to 8 x 10^{-1} mol, more preferably 1 x 10^{-2} to 5 x 10^{-2} mol per mol of silver halide.

An explanation will be made on the polymer according to the present invention.

(1) Vinyl polymer and copolymer

The examples of the monomers forming a vinyl polymer and a vinyl copolymer are acrylates such as methyl acrylate, ethyl acrylate, isopropyl acrylate, butyl acrylate, t-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, t-octyl acrylate, 2-chloroethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, methoxybenzyl acrylate, cyclohexyl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-iso-propoxyacrylate, 2-(2-methoxyethoxy)-ethyl acrylate, ω-methoxypolyethylene glycol acrylate (the number of moles added n = 9) and 1-bromo-2-methoxyethyl acrylate; methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, amyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, octyl methacrylate, sulfopropyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, dimethylaminophenoxyethyl methacrylate, furfuryl methacrylate, phenyl methacrylate, cresyl methacrylate, naphthyl methacrylate, 2-hydroxyethyl methacrylate, triethylene glycol methacrylate, 2-methoxyethyl methacrylate, 2-acetoxyethyl methacrylate, 2-ethoxyethyl methacrylate, 2-(2-methoxyethoxy)-ethyl methacrylate, and ω-methoxypolyethylene glycol methacrylate (the number of moles added n = 9); vinyl esters such as vinyl acetate, vinyl propionate, vinyl butylate, vinyl isobutylate, vinyl caproate, vinyl chloroacetate, vinyl methoxyacetate, vinyl phenylacetate, vinyl benzoate and vinyl salicylate; acrylamides such as acrylamide, ethyl acrylamide, propyl acrylamide, butyl acrylamide, t-butyl acrylamide, cyclohexyl acrylamide, benzyl acrylamide, hydroxymethyl acrylamide, methoxyethyl acrylamide, dimethylaminoethyl acrylamide, phenyl acrylamide, dimethyl acrylamide, β-cyanoethyl acrylamide, N-(2-acetoacetoxyethyl) acrylamide, and diacetone acrylamide; methacrylamides such as methacrylamide, methyl methacrylamide, ethyl methacrylamide, propyl methacrylamide, butyl methacrylamide, t-butyl methacrylamide, cyclohexyl methacrylamide, benzyl methacrylamide, hydroxymethyl methacrylamide, methoxyethyl methacrylamide, dimethylaminoethyl methacrylamide, phenyl methacrylamide, dimethyl methacrylamide, β-cyanoethyl methacrylamide, and N-(2-acetoacetoxyethyl) methacrylamide; olefins such as dicyclopentadiene, ethylene, propylene, 1-butene, 1-pentene, vinyl chloride, vinylidene chloride, isoprene, chloroprene, butadiene and 2,3-dimethyl butadiene; styrenes such as styrene, methylstyrene, trimethylstyrene, ethylstyrene, chloromethylstyrene, methoxystyrene, chlorostyrene, dichlorostyrene and methyl vinylbenzoate; crotonates such as butyl crotonate and hexyl crotonate; itaconates such as dimethyl itaconate and dibutyl itaconate; and maleates such as diethyl maleate, dimethyl maleate and dibutyl maleate; fumaric diesters such as diethyl fumarate, dimethyl fumarate and dibutyl fumarate. The examples of the other monomers are allyl compounds such as allyl acetate, allyl caproate, allyl laurate and allyl benzoate; vinyl ethers such as methyl vinyl ether, butyl vinyl ether, methoxyethyl vinyl ether, and dimethylaminoethyl vinyl ether; vinyl ketones such as methyl vinyl ketone, phenyl vinyl ketone and methoxyethyl vinyl ketone; vinyl heterocyclic compounds such as vinyl pyridine, N-vinyl imidazole, N-vinyl oxazolidone, N-vinyl triazole and N-vinyl pyrrolidone; glycidyl esters such as glycidyl acrylate and glycidyl methacrylate; and unsaturated nitriles such as acrylonitrile and methacrylonitrile.

The polymer used in the present invention may be either a homopolymer of the above monomers or a copolymer of two or more monomers, and may contain a monomer having the following acid group in such an amount as will not make the polymer water-soluble, preferably in an amount of not more than 20% of the total amount. It is especially preferred that the polymer contains no such monomer.

The examples of the monomer having the acid group are acrylic acid, methacrylic acid, itaconic acid, maleic acid, monoalkyl, itaconic acid, monoalkyl maleic acid, citraconic acid, styrene sulfonic acid, vinylbenzyl sulfonic acid, acryloyloxy alkylsulfonic acid, methacryloyloxy alkylsulfonic acid, acrylamide alkylsulfonic acid, methacrylamide alkylsulfonic acid, acryloyloxy alkylphosphate and methacryloyloxy alkylphosphate.

These acids may be a salt of an alkali metal such as Na and K or of an ammonium ion.

Acrylates, acrylamides and methacrylates are preferable as the monomer forming the polymer used in the present invention.

The polymer can be prepared by a solution polymerization, a bulk polymerization, a suspension polymerization and a latex polymerization, using water-soluble initiators and lipophilic polymerization initiators. The examples of the water-soluble polymerization initiators are persulfate salts such as potassium persulfate, ammonium persulfate, and sodium persulfate; water-soluble azo compounds such as sodium 4,4′-azobis-4-cyanovalerate, and 2,2′-azobis(2-aminopropane) chlorate; and hydrogen peroxide. The examples of the lipophilic polymerization initiators are lipophilic azo compounds such as azobisisobutylonitrile, 2,2′-azobis-2,4-dimethylvaleronitrile, 1,1′-azobis (cyclohxanone-1-carbonitrile), 2,2′-azobis-dimethyl isobutyrate and 2,2′-azobis-diethyl isobutyrate; benzoyl peroxide, lauryl peroxide, diisopropyl peroxydicarbonate and di-t-butyl-peroxide.

(2) Polyester resins prepared by a condensation polymerization of a polyhydric alcohol and a polybasic acid:

Polyhydric alcohols used in the invention are glycols of a HO-R_1-OH structure (R_1 represents a hydrocarbon chain having 2 to 12 carbon atoms; in particular, an aliphatic hydrocarbon chain) or a polyalkylene glycol. Polybasic acids used in the invention have preferably a HOOC-R_2-COOH structure (R_2 represents a linkage or a hydrocarbon chain having 1 to 12 carbon atoms).

The examples of the polyhydric alcohols are ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, trimethylol propane, 1,4-butane diol, isobutylene diol, 1,5-pentane diol, neopentyl glycol, 1,6-hexane diol, 1,8-octane diol, 1,9-nonane diol, 1,10-decane diol, glycerine, diglycerine, triglycerine, 1-methylglycerine, erythritol, mannite and sorbite.

The examples of the polybasic acids are oxalic acid, succinic acid, glutaric acid, adipic acid, pimeric acid, suberic acid, azelaic acid, sebacic acid, decane dicarboxylic acid, dodecane dicarboxylic acid, fumaric acid, maleic acid, itaconic acid, citraconic acid, phthalic acid, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, methaconic acid, isopimelic acid, an adduct of cyclopentadiene and maleic anhydride and an adduct of rosine and maleic anhydride.

(3) Polyester prepared by a ring-opening polymerization:

These polyesters are prepared from β-propiolactone, α-caprolactone and dimethyl propiolactone.

(4) Other polymers:

A polycarbonate resin prepared by a condensation polymerization of glycol or bisphenol with a carbonic ester or phosgene, a polyurethane resin prepared by an addition polymerization of a polyhydric alcohol with polyisocyanate and a polyamide resin prepared by a condensation polymerization of a polyvalent amine and a polybasic acid.

The number average molecular weight of the polymer used in the present invention is preferably not more than 200000, more preferably 5000 to 100000.

The weight ratio of the polymer to the coupler is preferably 1:20 to 20:1, more preferably 1:10 to 10:1.

The following are the examples of the polymer used in the present invention (composition of a copolymer: weight ratio).

A-1 poly-N-sec-butylacrylamide
A-2 poly-N-t-butylacrylamide
A-3 diacetone acrylamido-methyl methacrylate copolymer (25:75)
A-4 polycyclohexyl methacrylate
A-5 N-t-butyl acrylamide-methylmethacrylate copolymer (60:40)
A-6 poly-N,N-dimethyl acrylamide
A-7 poly-t-butyl methacrylate
A-8 polyvinyl acetate
A-9 polyvinyl propionate
A-10 polymethyl methacrylate
A-11 polyethyl methacrylate
A-12 polyethyl acrylate
A-13 vinyl acetate-vinyl alcohol copolymer (90:10)
A-14 polybutyl acrylate
A-15 polybutyl methacrylate
A-16 polyisobutyl methacrylate
A-17 polyisopropyl methacrylate
A-18 polyoctyl acrylate
A-19 butyl acrylate-acrylamide copolymer (95:5)
A-20 stearyl methacrylate-acrylic acid copolymer (90:10)
A-21 methyl methacrylate-vinyl chloride copolymer (70:30)
A-22 methyl methacrylate-styrene copolymer (90:10)
A-23 methyl methacrylate-ethyl acrylate copolymer (50:50)
A-24 butyl methacrylate-methyl methacrylate-styrene copolymer (50:20:30)

A-25 vinyl acetate-acrylamide copolymer (85:15)

A-26 vinyl chloride-vinyl acetate copolymer (65:35)

A-27 methyl methacrylate-acrylonitrile copolymer (65:35)

A-28 butyl methacrylate-pentyl methacrylate-N-vinyl-2-pyrrolidone copolymer (38:38:24)

A-29 methyl methacrylate-butyl methacrylate-isobutyl methacrylate-acrylic acid copolymer (37:29:25:9)

A-30 butyl methacrylate-acrylic acid copolymer (95:5)

A-31 methyl methacrylate-acrylic acid copolymer (95:5)

A-32 benzyl methacrylate-acrylic acid copolymer (93:7)

A-33 butyl methacrylate-methyl methacrylate-benzyl methacrylate-acrylic acid copolymer (35:35:25:5)

A-34 butyl methacrylate-methyl methacrylate-benzyl methacrylate copolymer (40:30:30)

A-35 diacetone acrylamide-methyl methacrylate copolymer (50:50)

A-36 methyl vinyl ketone-isobutyl methacrylate copolymer (55:45)

A-37 ethyl methacrylate-butyl acrylate copolymer (70:30)

A-38 diacetone acrylamide-butyl acrylate copolymer (60:40)

A-39 methyl methacrylate-styrene methacrylate-diacetoneacrylamide copolymer (40:40:20)

A-40 butyl acrylate-styrene methacrylate-diacetone acrylamide copolymer (70:20:10)

A-41 stearyl methacrylate-methyl methacrylate-acrylic acid copolymer (50:40:10)

A-42 methyl methacrylate-styrene-vinyl sulfonamide copolymer (70:20:10)

A-43 methyl methacrylate-phenyl vinyl ketone copolymer (70:30)

A-44 butyl acrylate-methyl methacrylate-butyl methacrylate copolymer (35:35:30)

A-45 butyl methacrylate-N-vinyl-2-pyrrolidone copolymer (90:10)

A-46 polypentyl acrylate

A-47 cyclohexyl methacrylate-methyl methacrylate-propyl methacrylate (37:29:34)

A-48 polypentyl methacrylate

A-49 methyl methacrylate-butyl methacrylate copolymer (65:35)

A-50 vinyl acetate-vinyl propionate copolymer (75:25)

A-51 butyl methacrylate-3-acryloxybutane-1-sodium sulfonate copolymer (97:3)

A-52 butyl methacrylate-methyl methacrylate-acrylamide copolymer (35:35:30)

A-53 butyl methacrylate-methyl methacrylate-vinyl chloride copolymer (37:36:27)

A-54 butyl methacrylate-styrene copolymer (82:18)

A-55 t-butyl methacrylate-methyl methacrylate copolymer (70:30)

A-56 poly-N-t-butyl methacrylamide

A-57 N-t-butyl acrylamide-methylphenyl methacrylate copolymer (60:40)

A-58 methyl methacrylate-acrylonitrile copolymer (70:30)

A-59 methyl methacrylate-methyl vinyl ketone copolymer (38:72)

A-60 methyl methacrylate-styrene copolymer (75:25)

A-61 methyl methacrylate-hexyl methacrylate copolymer (70:30)

A-62 butyl methacrylate-acrylic acid copolymer (85:15)

A-63 methyl methacrylate-acrylic acid copolymer (80:20)

A-64 methyl methacrylate-acrylic acid copolymer (90:10)

A-65 methyl methacrylate-acrylic acid copolymer (98:2)

A-66 methyl methacrylate-N-vinyl-2-pyrrolidone (90:10)

A-67 butyl methacrylate vinyl chloride copolymer (90:10)

A-68 butyl methacrylate-styrene copolymer (70:30)

A-69 1,4-butanediol-adipic acid polyester

A-70 ethylene glycol-sebacic acid polyester

A-71 polycaprolactam

A-72 polypropiolactam

A-73 polydimethyl propiolactam

A-74 N-t-butyl acrylamide-dimethylaminoethyl acrylamide copolymer (85:15)

A-75 N-t-butyl methacrylamide-vinyl pyridine copolymer (95:5)

A-76 diethyl maleate-butyl acrylate copolymer (65:35)

A-77 N-t-butyl acrylamide-2-methoxyethyl acrylate copolymer (55:45)

A-78 ω-methoxy polyethylene glycol methacrylate (the number of moles added : n=6)-methyl methacrylate (40:60)

A-79 ω-methoxy polyethylene glycol acrylate (the number of moles added : n=9)-N-t-butyl acrylamide (25:75)

A-80 poly-2-methoxyethyl acrylate
A-81 poly-2-methoxyethyl methacrylate
A-82 poly-2-(2-methoxyethoxy)ethyl acrylate
A-83 2-(2-butoxyethoxy)ethyl acrylate-methyl methacrylate (58:42)
A-84 poly-oxycarbonyloxy-1,4-phenyleneisobutylidene-1,4-phenylene
A-85 poly-oxyethyleneoxycarbonyl

The dispersion used in the present invention can be prepared by dispersing in the presence of a surface active agent, a coupler and a polymer insoluble in water but soluble in an organic solvent in a hydrophilic binder such as an aqueous gelatin solution by means of a stirrer, a homogenizer, a colloid mill, a flow jet mixer, and an ultrasonic apparatus. The dispersion is then added to a hydrophilic colloidal layer. If necessary, the coupler and the polymer may be dissolved in a low-boiling and/or water-soluble organic solvent before dispersion. The low-boiling and/or water-soluble organic solvent may be removed from the dispersion by distillation, noodle washing or ultrafiltration. The examples of the low-boiling organic solvents are ethyl acetate, butyl acetate, ethyl propionate, sec-butyl alcohol, methyl ethyl ketone, methyl isobutyl ketone, β-ethoxyethyl acetate, methylcellosolve acetate, and cyclohexanone. The examples of the water-soluble organic solvents are methyl alcohol, ethyl alcohol, acetone and tetrahydrofuran. These organic solvents may be used in combination.

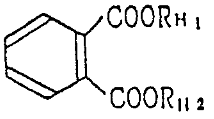
Alternatively, the dispersion used in the present invention can be prepared by the method described in Japanese Patent O.P.I. Publication No. 107642/1985, in which the polymers are prepared by polymerizing the monomers in the presence of the coupler according to a suspension polymerization, a solution polymerization or a bulk polymerization, and then dispersed in a hydrophilic binder as well.

The dispersion may contain a high-boiling organic solvent such as a phenol derivative, phthalate, phosphate, citrate, benzoate, alkylamide, aliphatic ester and trimesate, each of which has a boiling point of not lower than 150 °C and does not react with an oxidation product of a color developing agent.

The high-boiling organic solvent has preferably a dielectric constant of lower than 6.0 and not lower than 1.9.

The high boiling organic solvent has preferably a vapor pressure of not higher than 0.5 mmHg at 100 °C. Especially preferable are phthalates and phosphates of the above high boiling solvents. These organic solvents may be used in combination of two or more kinds, in which the mixture has a dielectric constant of lower than 6.0. In the present invention, the dielectric constant is measured at 30 °C.

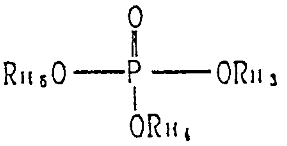
Phthalates used in the invention are represented by the following Formula HA:



wherein R_{H1} and R_{H2} each represent an alkyl group, an alkenyl group and an aryl group, provided that the total number of carbon atoms in R_{H1} and R_{H2} is 9 to 32, preferably 16 to 24.

The alkyl groups represented by R_{H1} and R_{H2} are butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl. The aryl groups are phenyl and naphthyl, and the alkenyl groups are hexenyl, heptenyl and octadecenyl. These alkyl, alkenyl and aryl groups each may have one or more substituents. The substituents for the alkyl and alkenyl groups are a halogen atom, an alkoxy group, an aryl group, an aryloxy group, an alkenyl group and an alkoxycarbonyl group, and the substituents for the aryl group are a halogen atom, an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an alkenyl group and an alkoxycarbonyl group.

Phosphates used in the invention are represented by the following Formula HB:



$$R_{H5}O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR_{H4}}{|}}{P}}-OR_{H3}$$

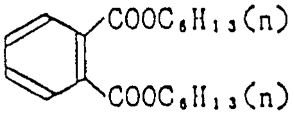
wherein R_{H3}, R_{H4} and R_H5 each represent an alkyl group, an alkenyl group and an aryl group, provided that the total number of carbon atoms contained in R_{H3}, R_{H4} and R_{H5} is 24 to 54.

The alkyl groups represented by R_{H3}, R_{H4} and R_{H5} are the same groups as defined for R_{H1} and R_{H2} in Formula HA.

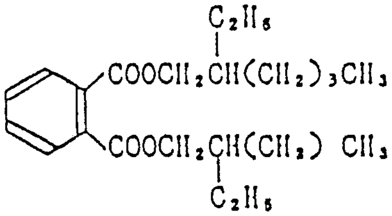
These alkyl, alkenyl and aryl groups may have one or more substituents. It is preferred that R_{H3}, R_{H4} and R_{H5} be an alkyl group such as 2-ethylhexyl, n-octyl, 3,5,5-trimethylhexyl, n-nonyl, n-decyl, sec-decyl, sec-dodecyl and t-octyl.

The following are the examples of the high-boiling organic solvent:

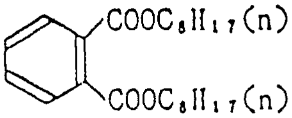
H・1



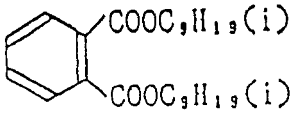
H・2



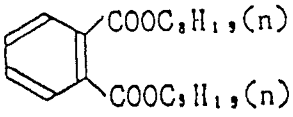
H・3



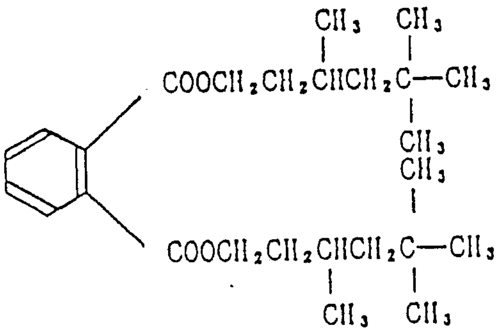
H - 4


COOC9H19(i)
COOC9H19(i)

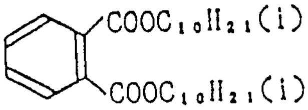
H - 5


COOC9H19(n)
COOC9H19(n)

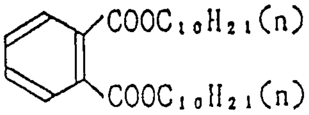
H - 6


COOCH2CH2CHCH2C—CH3
CH3
CH3
CH3
COOCH2CH2CHCH2C—CH3
CH3
CH3
CH3

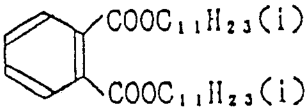
H - 7


COOC10H21(i)
COOC10H21(i)

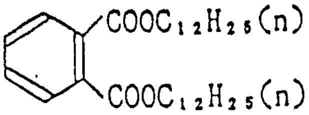
H - 8



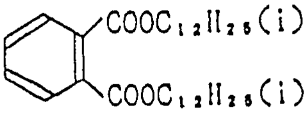
H - 9



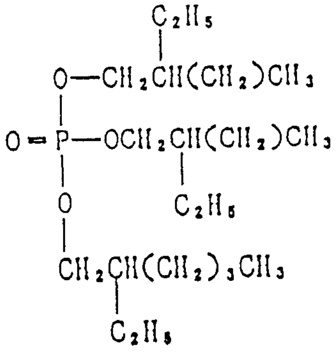
H - 10



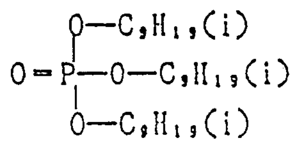
H - 11



H - 12

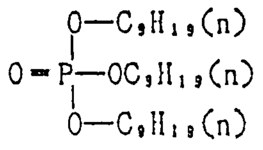


H-13



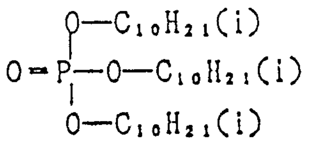
$$\begin{array}{l} \quad\; O\text{—}C_9H_{19}(i) \\ O=P\text{—}O\text{—}C_9H_{19}(i) \\ \quad\; O\text{—}C_9H_{19}(i) \end{array}$$

H-14



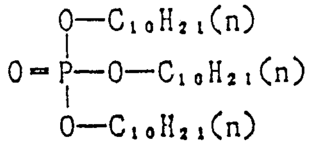
$$\begin{array}{l} \quad\; O\text{—}C_9H_{19}(n) \\ O=P\text{—}OC_9H_{19}(n) \\ \quad\; O\text{—}C_9H_{19}(n) \end{array}$$

H-15



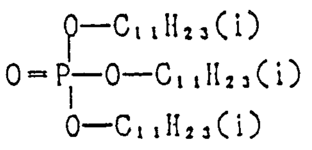
$$\begin{array}{l} \quad\; O\text{—}C_{10}H_{21}(i) \\ O=P\text{—}O\text{—}C_{10}H_{21}(i) \\ \quad\; O\text{—}C_{10}H_{21}(i) \end{array}$$

H-16



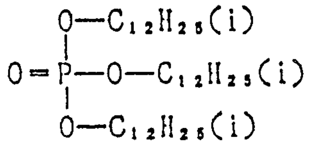
$$\begin{array}{l} \quad\; O\text{—}C_{10}H_{21}(n) \\ O=P\text{—}O\text{—}C_{10}H_{21}(n) \\ \quad\; O\text{—}C_{10}H_{21}(n) \end{array}$$

H-17



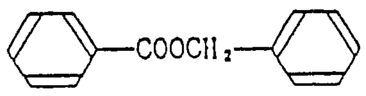
$$\begin{array}{l} \quad\; O\text{—}C_{11}H_{23}(i) \\ O=P\text{—}O\text{—}C_{11}H_{23}(i) \\ \quad\; O\text{—}C_{11}H_{23}(i) \end{array}$$

H-18

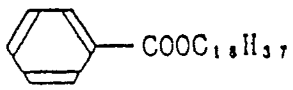


$$\begin{array}{l} \quad\; O\text{—}C_{12}H_{25}(i) \\ O=P\text{—}O\text{—}C_{12}H_{25}(i) \\ \quad\; O\text{—}C_{12}H_{25}(i) \end{array}$$

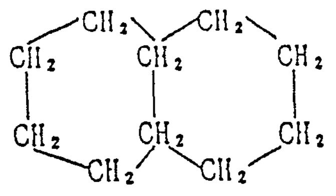
H-19



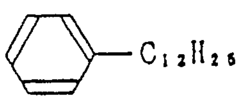
H-20



H-21



H-22



The high boiling organic solvent is added in an amount of 0.01 to 10 mol, preferably 0.05 to 5 mol per mol of silver halide.

The silver halides used in the present invention may be conventional ones such as silver chloride, silver bromide, silver iodide, silver bromochloride, silver bromoiodide and silver iodochloride.

The silver halide grains have preferably a silver chloride content of not less than 90 mol%, a silver bromide content of not more than 10% and a silver iodide content of not more than 0.5%. Especially preferable are silver halide grains of silver bromochloride containing 0.1 to 2 mol% silver bromide.

The silver halide grains may be used singly or in combination with other silver halide grains of different compositions, or with silver halide grains having a silver chloride content of not more than 90 mol%.

In a silver halide emulsion layer containing silver halide grains with a silver chloride content of not less than 90 mol%, said silver halide grains account for not less than 60 wt%, preferably not less than 80 wt% of the total silver halide grains.

The silver halide grain may or may not have a uniform composition from an inner portion to an outer portion. When the inner and outer portions have different compositions, the composition may change either continuously or discontinuously.

The size of the silver halide grains is preferably 0.2 to 1.6 µm, more preferably 0.25 to 1.2 µm, from a viewpoint of rapid processing, sensitivity and other photographic properties.

The grain size distribution may be either monodispersed or polydispersed. In the invention, monodispersed silver halide grains is preferable, in which the grain size distribution has a variation coefficient of not more than 0.22, preferably not more than 0.15. The variation coefficient represents the width of distribution, and is defined by the following equation:

$$\text{Variation coefficient } (S/r) = \frac{\text{standard deviation of grain size distribution}}{\text{average grain size}}$$

$$\text{Standard deviation of grain size distribution } (S) = \sqrt{\frac{\Sigma(\bar{r}-ri)^2 ni}{\Sigma ni}}$$

$$\text{Average grain size } (\bar{r}) = \frac{\Sigma\, ni\, ri}{\Sigma\, ni}$$

wherein ri is the size of the individual grain, and ni is the number of the grain. The grain size is represented by the grain diameter when the grain is spherical. When the grain is cube or of other shapes than sphere, the grain size is represented by the diameter of the circle having the same area as that of the projected image of the grain.

The silver halide grains can be prepared by the neutral method, the acid method or the ammonia method. The silver halide grains may be grown with or without seed grains.

Silver salts and halides may be reacted by the single-jet method, the reverse-jet method, the double-jet method, or the combination thereof. Of them, the double-jet method is preferable. The pAg-controlled double-jet method described in Japanese Patent O.P.I. Publication No. 48521/1979 is also usable as one form of the double-jet method.

If necessary, a solvent for a silver halide such as a thioether may be used. A mercapto compound, a nitrogen-containing heterocyclic compound or a sensitizer may also be added during or after the formation of silver halide grains.

The shape of the silver halide grains is not critical. Preferred is cube having (100) face as a crystal face. Octahedral, tetradecahedral and dodecahedral silver halide grains may also be used. Also usable are the silver halide grains with a twinned crystal face.

The silver halide grains may have the same shape or different shapes.

In the invention, the silver halide grains may be doped in an inside and/or on the surface of the grain with metal ions of cadmium, zinc, lead, thallium, iridium, rhodium and iron during forming and/or growing a silver halide grain. A reduction sensitization nucleus can be formed in the inside and/or on the surface of the grain in a reductive atmosphere.

Unnecessary soluble salts may or may not be removed after the growth of a silver halide grain. The removal of such salts can be performed by the method described in Research Disclosure No. 17643.

The silver halide grains may be such that a latent image is formed mainly in the inside of a grain, or on the surface of a grain. Preferable is the latter.

The silver halide emulsion is chemically sensitized by known methods including the sulfur sensitization method, the selenium sensitization method, the reduction sensitization method, and the noble metal sensitization method. These sensitization methods may be applied alone or in combination.

The silver halide emulsion can be spectrally sensitized to a prescribed wavelength region with a sensitizing dye such as a cyanine dye, a merocyanine dye, a composite cyanine dye, a composite merocyanine dye, a holopolar cyanine dye, a hemicyanine dye, a styryl dye and a hemioxazole dye.

Usually, a dye-forming coupler is selectively added to an emulsion layer so that there can be formed a dye capable of absorbing spectral light to which the emulsion layer is sensitive.

Gelatin is used as a binder or a protective colloid. Also usable as the binder are hydrophilic colloids such as gelatin derivative, a graft polymer of gelatin and the other polymers, protein, a sugar derivative, a cellulose derivative, a synthetic hydrophilic polymer including homo-and copolymers.

The light-sensitive material may further contain various additives including a hardening agent, an antistain agent, an image stabilizer, a UV absorber, a plasticizer, latex, a surfactant, a matting agent, a lubricant and an antistatic agent.

The light-sensitive material is subjected to color development to form an image by conventional methods.

The developer contains a conventional developing agent such as an aminophenol and p-phenylenediamine derivatives. The color developer generally has pH of not less than 7, more generally 10 to 13. The color development is conducted at 15° C or higher, normally 20 to 50° C. For rapid development, the processing temperature is preferably 30° C or higher.

The photographic material of the invention is developed preferably by a color developer containing no benzyl alcohol.

After the color development, the light-sensitive material is subjected to bleaching and fixing, which may be performed simultaneously.

After fixing, it is usually subjected to washing, which may be replaced with or carried out together with stabilizing.

EXAMPLES

The present invention will be described in more detail with reference to the following Examples.

Example 1

Preparation of silver halide emulsion

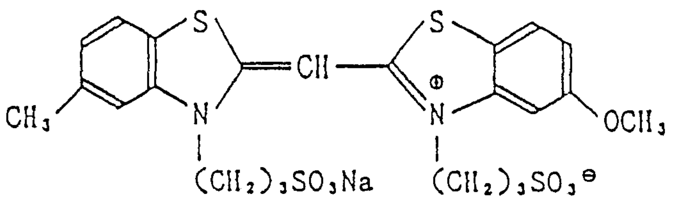
Six kinds of silver halide emulsion as shown in Table 1 were prepared by the neutral method and the double-jet method.

Table 1

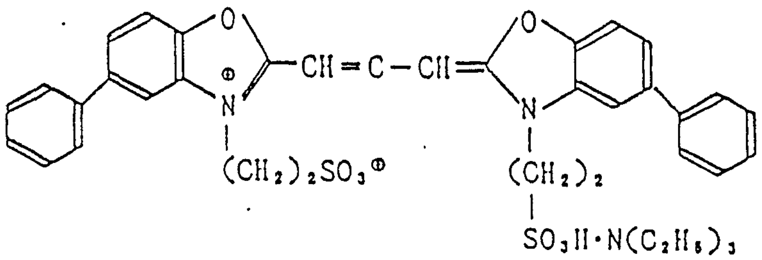
Emulsion No.	AgCℓ %	AgBr %	Average grain size μ	Chemical sensitizer	Sensitizing dye
Em-1	10	90	0.67	Sodium thiosulfate Sodium *1	SD-1 *3
Em-2	30	70	0.46		SD-2 *4
Em-3	30	70	0.43		SD-3 *5
Em-4	99.5	0.5	0.67	Sodium thiosulfate Sodium *1 Chloroauric acid *2	SD-1 *3
Em-5	99.5	0.5	0.46		SD-2 *4
Em-6	99.5	0.5	0.43		SD-3 *5

After chemical sensitization, STB-1 was added to each emulsion as an emulsion stabilizer in an amount of 2 x 10^{-4} mol per mol of silver halide.

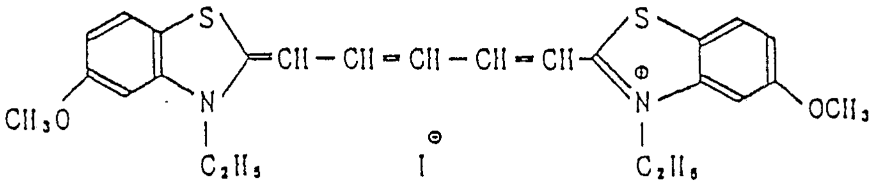
SD-1



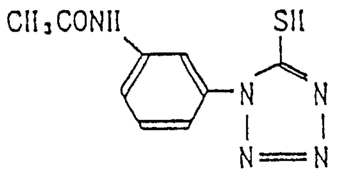
SD-2



SD-3



STB-1



Preparation of silver halide light-sensitive color photographic material

There were prepared the multilayered silver halide light-sensitive color photographic material Sample Nos. 101 to 123 in which a magenta coupler, a polymer and a high boiling organic solvent each added to the 3rd layer were changed as shown in Table 2, by providing the layers of the following constitutions on a paper support laminated on one side with polyethylene and on the other side with polyethylene containing titanium oxide. The coating solutions were prepared as follows:

Coating solution for the 1st layer

There were dissolved 26.7 g of a yellow coupler Y-1, 0.67 g of an antistain agent HQ-1 and 13.3 g of a high boiling organic solvent DNP in 60 mℓ of ethyl acetate. The solution was dispersed in 200 mℓ of an aqueous 10% gelatin solution containing 10 mℓ of 10% sodium alkylnaphthalene sulfonate by means of a homogenizer to thereby prepare a yellow coupler dispersion.

A coating solution for the 1st layer was prepared by mixing the above dispersion with a blue-sensitive silver bromochloride emulsion Em-1 (addition amount converted to silver: 10 g) and a gelatin solution.

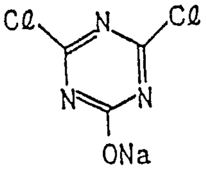
The coating solutions for the 2nd to 7th layers were prepared in the same manner as described above except for the preparation of a magenta coupler dispersion for the 3rd layer.

Magenta coupler dispersion

There were dissolved in 40 mℓ of ethyl acetate, 12.0 g of a magenta coupler, 6.0 g of a dye image stabilizer ST-1, 3.0 g of another dye image stabilizer ST-2, 0.3 g of an antistain agent HQ-1, 9.0 g of a high boiling organic solvent and 9.0 g of a polymer. The solution was dispersed in 200 mℓ of an aqueous 10% gelatin solution containing 10 mℓ of 10% sodium alkylnaphthalene sulfonate by means of a homogenizer. There was added 0.08 g/m^2 of a hardening agent H-1 for gelatin.

The respective coating solutions were prepared by replacing the magenta coupler, the organic high boiling solvent and the polymer as shown in Table 2.

H-1

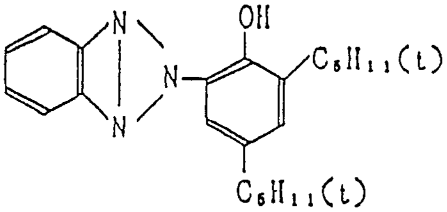


Layer	Composition	Amount added (g/m^2)
The 7th layer Protective layer	Gelatin	1.0
The 6th layer UV absorbing layer	Gelatin	0.6
	UV absorber (UV-1)	0.2
	UV absorber (UV-2)	0.2
	Antistain agent (HQ-1)	0.01
	DNP	0.2
The 5th layer Red-sensitive layer	Gelatin	1.40
	Red-sensitive silver bromochloride emulsion Em-3 in an amount converted to silver	0.24
	Cyan coupler II-4	0.35
	Polymer A-2	0.53
	DOP	0.30
The 4th layer UV absorbing layer	Gelatin	1.30
	UV absorber (UV-1)	0.40
	UV absorber (UV-2)	0.40
	Antistain agent (HQ-1)	0.03
	DNP	0.40

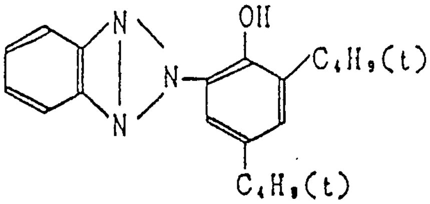
Layer	Composition	Amount added (g/m^2)
The 3rd layer Green-sensitive layer	Gelatin	1.40
	Green-sensitive silver bromochloride emulsion Em-2 in an amount converted to silver	0.21
	Magenta coupler shown in Table 2	0.7*
	Dye image stabilizer (ST-1)	0.20
	Dye image stabilizer (ST-2)	0.10
	Antistain agent (HQ-1)	0.01
	High boiling solvent shown in Table 2	0.30
	Polymer shown in Table 2	0.30
The 2nd layer Intermediate layer	Gelatin	1.20
	Antistain agent (HQ-1)	0.12
	DIDP	0.15
The 1st layer Blue-sensitive layer	Gelatin	1.30
	Blue-sensitive silver bromochloride emulsion Em-1 in an amount converted to silver	0.30
	Yellow coupler (Y-1)	0.80
	Antistain agent (HQ-1)	0.02
	DNP	0.40
Support	Polyethylene-laminated paper	

* $millimol/m^2$

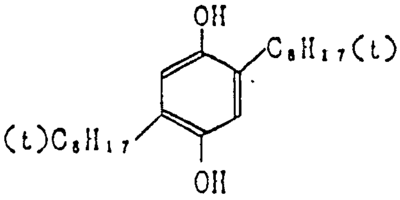
UV-1



UV-2



HQ-1



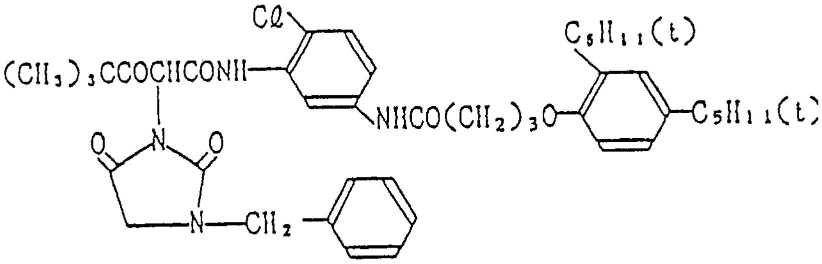
BDP (dibutyl phthalate)

DOP (dioctyl phthalate)

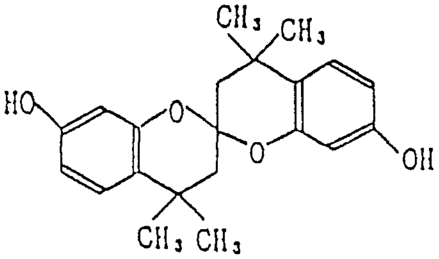
DNP (dinonyl phthalate)

DIDP (diisodecyl phthalate)

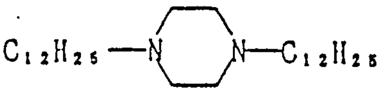
Y-1



ST-1



ST-2



Each of the samples was exposed to green light through an optical wedge by means of Sensitometer KS-7 manufactured by Konica Corporation, and then processed according to the following color developing procedures.

Processing procedures		
Color developing	3 min. 30 sec.	33 °C
Bleach-fixing	1 min. 30 sec.	33 °C
Rinsing	3 min.	33 °C

Color developer	
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.9 g
Hydroxylamine sulfate	2.0 g
Potassium carbonate	25.0 g
Sodium bromide	0.6 g
Sodium sulfite anhydride	2.0 g
Benzyl alcohol	13 mℓ
Polyethylene glycol (average polymerization degree 400)	3.0 mℓ
Water was added to make total quantity 1 liter, and pH was adjusted to 10.0 with sodium hydroxide.	

Bleach-fixer	
Ferric sodium ethylenediaminetetraacetate	6.0 g
Ammonium thiosulfate	100 g
Sodium bisulfite	10 g
Sodium metabisulfite	3 g
Water was added to make total quantity 1 liter, and pH was adjusted to 7.0 with aqueous ammonia.	

Each sample was evaluated for the following properties. The results are shown in Table 2.

1. Light fastness

Each sample was left exposed to sunlight at 60° C and 70%RH for one month. The light fastness was evaluated by measuring the rate of decrease (%) of a dye image density with the initial density of 1.0.

2. Sensitivity

Defined by the reciprocal of the exposure required to obtain a density of 0.8, and shown by the value relative to that of the standard sample set at 100.

3. Sweating

After 10 days storage at 85° C and 60%RH, the deterioration of surface gloss caused by sweating was visually checked.

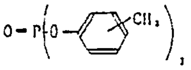
◎ No sweating
o Virtually no sweating
Δ Minor sweating with no practicable problem
x Considerable sweating without practicable value

Table 2

Sample No.	Magenta coupler in the 3rd layer	Polymer in the 3rd layer	High boiling organic solvent in the 3rd layer	Sensitivity*	Light fastness (%)	Sweating	
101	Comparative coupler-1	-	DOP	100	27	Δ	Comparison
102	Comparative coupler-1	A-2	-	77	21	Δ	Comparison
103	Comparative coupler-1	A-2	DOP	94	20	×	Comparison
104	Comparative coupler-2	-	DOP	104	67	Δ	Comparison
105	Comparative coupler-2	A-2	-	81	45	Δ	Comparison
106	Comparative coupler-2	A-2	DOP	100	48	×	Comparison
107	Comparative coupler-3	-	DOP	97	28	Δ	Comparison
108	Comparative coupler-3	A-2	-	73	20	○	Comparison
109	Comparative coupler-3	A-2	DOP	94	19	Δ	Comparison
110	M-21	-	DOP	102	29	○	Comparison
111	M-21	A-2	-	84	16	◎	Invention
112	M-21	A-2	DOP	100	16	○	Invention
113	M-32	-	DOP	91	30	◎	Comparison
114	M-32	A-2	DOP	88	14	◎	Invention
115	M-44	-	DOP	95	23	◎	Comparison
116	M-44	A-2	DOP	92	11	◎	Invention
117	M-23	-	DOP	102	26	◎	Comparison
118	M-23	A-2	DOP	97	11	◎	Invention
119	M-18	A-10	DOP	98	12	◎	Invention
120	M-42	A-10	DOP	95	10	◎	Invention
121	M-27	A-22	DOP	97	13	◎	Invention
122	M-23	A-22	DBP	101	17	◎	Invention
123	M-23	A-22	TCP	99	16	◎	Invention

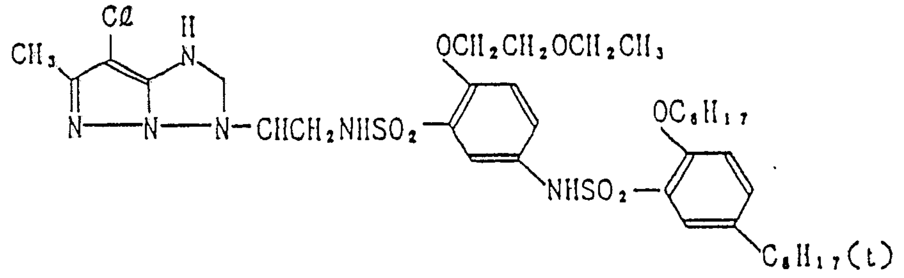
* Sensitivity relative to that of Sample No. 101 which is set at 100

TCP :



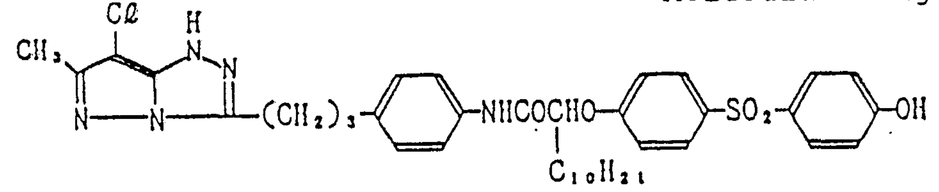
Comparative coupler 1

Molecular weight 837.5



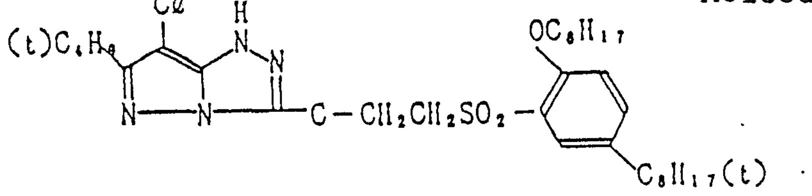
Comparative coupler 2

Molecular weight 720.3



Comparative coupler 3

Molecular weight 649.4



As is evident from the results in Table 2, among Sample Nos. 101 to 109 each containing a comparative coupler, Sample Nos. 102, 105 and 108 each containing the polymer and no high boiling organic solvent were slightly improved in light fastness though insufficiently, while the sensitivity was deteriorated. In Sample Nos. 103, 106 and 109 each containing a high boiling organic solvent in combination with the polymer, sweating was observed to such an extent that the image was deteriorated, while the sensitivity was hardly deteriorated. On the contrary, Samples No. 111, 112, 114, 116 and 118 to 123 of the invention each containing the magenta coupler related to the invention and the polymer did not cause sweating and had the improved light fastness with little deterioration of the sensitivity. Among the samples of the invention, Sample Nos. 112, 114, 116 and 118 to 121 each containing the polymer and the high boiling organic solvent with a dielectric constant of lower than 6.0 in combination had the higher sensitivity than Sample No. 111 containing no high boiling solvent, and had more improved light fastness than Sample Nos. 122 and 123 each containing the high boiling organic solvent with the dielectric constant of not less than 6.0 and the polymer. Sample Nos. 114, 116 and 118 to 123 each containing the preferable magenta coupler with a molecular weight of not more than 550 were found excellent without sweating. Sample Nos. 112 and 118 to 123 each containing the preferable magenta coupler having the substituent represented by Formula M-X were found to have the excellent sensitivity.

Example 2

Multilayered silver halide light-sensitive photographic materials were prepared in the same manner as in Example 1, except that the blue-sensitive emulsion Em-1 in the 1st layer, the green-sensitive emulsion Em-2 in the 3rd layer and the red-sensitive emulsion Em-3 in the 5th layer were replaced with Em-4, Em-5 and Em-6, respectively, and that the magenta coupler, the polymer and the high boiling organic solvent in the

3rd layer were replaced as shown in Table 3.

The samples were exposed to light through an optical wedge in the same manner as in Example 1, and then processed according to the following color developing procedures. The processed samples were subjected to the same evaluation as in Example 1. The results are shown in Table 3.

Processing procedures		
	Temperature	Time
Color developing	35.0 ± 0.3° C	45 sec.
Bleach-fixing	35.0 ± 0.5° C	45 sec.
Stabilizing	30 to 34° C	90 sec.
Drying	60 to 80° C	60 sec.

Color developer	
Pure water	800 mℓ
Triethanolamine	10 g
N,N-diethylhydroxyamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-hydroxyethylidene-1,1-diphosphonic acid	1.0 g
Ethylenediaminetetraacetic acid	1.0 g
Catechol-3,5-disodium disulfonate	1.0 g
N-ethyl-N-β-methanesulfonamido-ethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Fluorescent bleaching agent, a 4,4′-diaminostilbenedisulfonic acid derivative	1.0 g
Potassium carbonate	27 g
Water was added to make total quantity 1 liter, and pH was adjusted to 10.10.	

Bleach-fixer	
Ferric ammonium ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate, an aqueous 70% solution	100 mℓ
Ammonium sulfite, an aqueous 40% solution	27.5 mℓ
Water was added to make total quantity 1 liter and pH was adjusted to 6.2 with potassium carbonate or glacial acetic acid.	

Stabilizer	
5-chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediaminetetraacetic acid	1.0 g
Ammonium hydroxide, an aqueous 20% solution	3.0 g
Ammonium sulfite	3.0 g
Fluorescent bleaching agent, a 4,4′-diaminostilbenedisulfonic acid derivative	1.5 g
Water was added to make total quantity 1 liter and pH was adjusted to 7.0 with sulfuric acid or potassium hydroxide.	

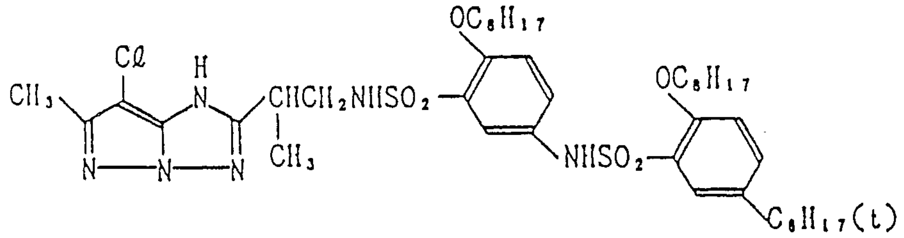
Table 3

Sample No.	Magenta coupler in the 3rd layer	Polymer in the 3rd layer	High boiling organic solvent in the 3rd layer	Sensitivity*	Light fastness (%)	Sweating	
201	Comparative coupler-4	-	DOP	100	26	Δ	Comparison
202	Comparative coupler-4	A-2	-	72	20	Δ	Comparison
203	Comparative coupler-4	A-2	DOP	92	19	×	Comparison
204	Comparative coupler-5	-	DOP	102	30	Δ	Comparison
205	Comparative coupler-5	A-2	-	75	22	○	Comparison
206	Comparative coupler-5	A-2	DOP	94	21	Δ	Comparison
207	M-16	-	DOP	104	28	○	Comparison
208	M-16	A-2	-	85	15	◎	Invention
209	M-16	A-2	DOP	98	15	○	Invention
210	M-24	-	DOP	109	27	◎	Comparison
211	M-24	A-2	-	89	12	◎	Invention
212	M-24	A-2	DOP	104	10	◎	Invention
213	M-23	-	DOP	112	26	◎	Comparison
214	M-23	A-2	DOP	109	11	◎	Invention
215	M-32	-	DOP	89	29	◎	Comparison
216	M-32	A-2	DOP	84	13	◎	Invention
217	M-41	-	DOP	101	24	◎	Comparison
218	M-41	A-80	DOP	95	10	◎	Invention

* Sensitivity relative to that of Sample No. 201, which is set at 100.

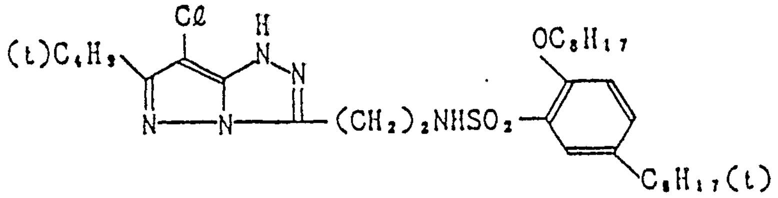
Comparative coupler 4

Molecular weight 877.6



Comparative coupler 5

Molecular weight 622.3

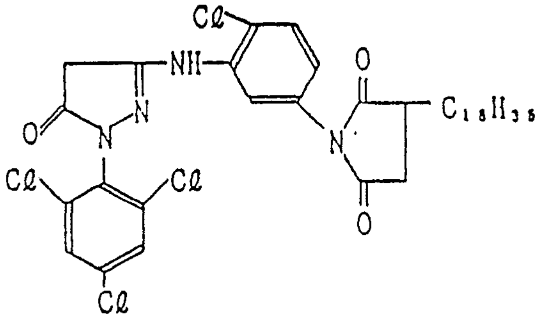


As is evident from the results in Table 3, among the samples each containing a comparative coupler, the samples each containing the polymer and no high boiling organic solvent were slightly improved in light fastness, though insufficiently, while the sensitivity was deteriorated. In the samples each containing the high boiling organic solvent in combination with the polymer, sweating was observed to such an extent that the image was deteriorated, while the sensitivity was hardly deteriorated. On the contrary, the samples of the invention each containing the magenta coupler related to the invention and the polymer in combination did not cause sweating and had the improved light fastness with little deterioration of the sensitivity. Among the samples of the invention, those each containing the polymer and the high boiling organic solvent with a dielectric constant of lower than 6.0 in combination had the higher sensitivity than those containing no high boiling solvent. The samples each containing the preferable magenta coupler with a molecular weight of not more than 550 were found excellent without causing sweating. The samples each containing the preferable magenta coupler having the substituent represented by Formula M-X were found to have the excellent sensitivity. The effects of the invention were confirmed also in the samples prepared by replacing the magenta coupler in Sample 218 with M-4, M-8, M-28, M-33, M-35, M-37 and M-53, and the polymer with A-5 and A-77.

Example 3

Sample No. 301 was prepared in the same manner as in Example 2, except that the magenta coupler in the 3rd layer of Sample No. 212 was replaced with the following comparative coupler 6, and that the amount of the green-sensitive silver bromochloride emulsion in the 3rd layer was varied to 0.31 g/m^2 in an amount converted to silver.

Comparative coupler 6



Color Checker manufactured by Macbeth was photographed by Konica Color GX 100 manufactured by Konica Corporation, followed by developing to thereby prepare a negative. The negative was printed on Sample Nos. 212 and 301, after adjusting the tone of gray color portion, and the color reproducibility was evaluated in the respective color phases. The results revealed Sample No. 212 had a better reproducibility in blue, red and magenta colors than Sample No. 301.

Example 4

A silver halide emulsion consisting of cubic silver bromide grains having an average grain size of 0.15 µm was prepared by adding equimole of an aqueous silver nitrate solution and an aqueous potassium bromide to an aqueous gelatin solution by the double-jet method at 50° C for 50 minutes. To this emulsion, an aqueous silver nitrate solution and a mixed aqueous solution of sodium chloride and potassium bromide (molar ratio: 1:1) were simultaneously added to thereby prepare an emulsion of cubic core/shell type silver halide emulsion EMP-1 consisting of a silver bromide core and a silver bromochloride shell and having an average grain size of 0.225 µm.

Further, the core/shell type emulsions were prepared by varying the time of adding the silver nitrate solution and the halide solution as shown in Table 4.

Table 4

Emulsion	Core size	Shell size
EMP-1	0.050 µm	0.225 µm
EMP-2	0.181 µm	0.272 µm
EMP-3	0.293 µm	0.44 µm
EMP-4	0.550 µm	0.75 µm

Using the above emulsions, the direct positive light-sensitive color photographic materials were prepared by providing on a 140 µm-thick polyethylene-coated paper support the emulsion layers, the non-emulsion layers and a back layer of the following constitutions.

The amounts added are shown in mg/dm^2, and the amounts of a silver halide emulsion and a yellow colloid silver in the amounts converted to silver.

Layer	Composition	Amount added (g/m^2)
The 8th layer UV absorbing layer	UV absorber (UV-1)	0.65
	UV absorber (UV-2)	1.95
	Solvent (SO-3)	1.0
	Colloidal silica	0.07
	Gelatin	7.8
The 7th layer Blue-sensitive layer	Emulsion (EMP-3)	4.4
	Emulsion (EMP-4)	1.2
	Blue-sensitizing dye (BD-1)	0.2*
	Yellow coupler (YC-1)	8.2
	Solvent (SO-1)	5.2
	ST-2	0.003
	ST-3	0.03
	Gelatin	14.3
The 6th layer Intermediate layer	Antistain agent (AS-1)	0.55
	Solvent (SO-2)	0.72
	Gelatin	5.4
The 5th layer Colloid silver layer	Yellow colloid silver	1.05
	Antistain agent (AS-1)	0.40
	Solvent (SO-2)	0.49
	Gelatin	9.2

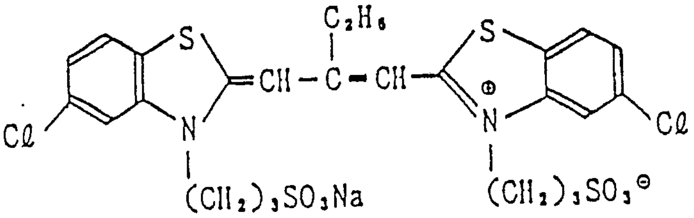
Layer	Composition	Amount added (g/m^2)
The 4th layer Intermediate layer	Antistain agent (AS-1)	0.55
	Solvent (SO-2)	0.72
	Gelatin	5.4
The 3rd layer Green-sensitive layer	Emulsion (EMP-2)	1.30
	Emulsion (EMP-3)	2.0
	Green-sensitizing dye (GD-1)	0.09*
	Magenta coupler shown in Table 5	$4x10^{-5}$
	Image stabilizer (AO-1)	2.2
	Image stabilizer (AO-2)	1.25
	Polymer	2.4
	SO-2	2.4
	Inhibitor (ST-2)	0.003
	Inhibitor (ST-3)	0.03
	Gelatin	13.0
The 2nd layer Intermediate layer	Antistain agent (AS-1)	0.55
	Solvent (SO-2)	0.72
	Gelatin	7.5

Layer	Composition	Amount added (g/m^2)
The 1st layer Red-sensitive layer	Emulsion (EMP-1)	0.5
	Emulsion (EMP-2)	0.7
	Emulsion (EMP-3)	4.0
	Red-sensitizing dye (RD-1)	0.06*
	Red-sensitizing dye (RD-2)	0.06*
	Cyan coupler (CC-1)	2.08
	Polymer (A-2)	4.0
	Solvent (SO-1)	3.3
	ST-1	0.003
	ST-2	0.003
	ST-3	0.03
	Gelatin	13.8
Support	Polyethylene-laminated paper	
Back layer	Colloidal silica	6.0
	Gelatin	5.3

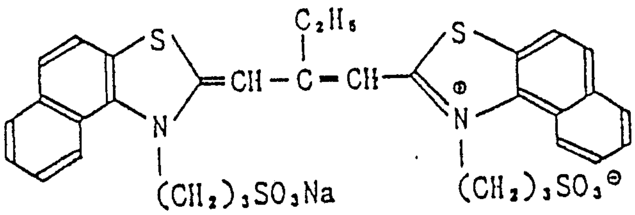
* mg/mol AgX

HA-1 and HA-2 were added to the emulsion layers and the back layer as a hardening agent.

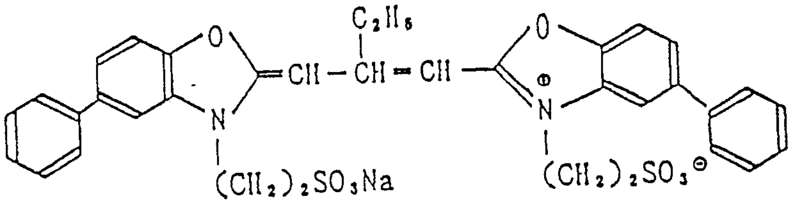
RD-1



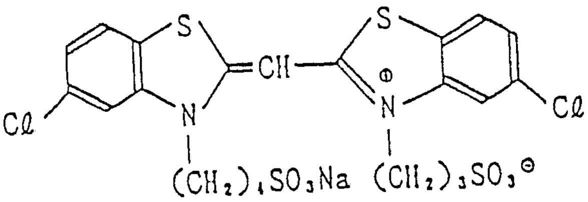
RD-2



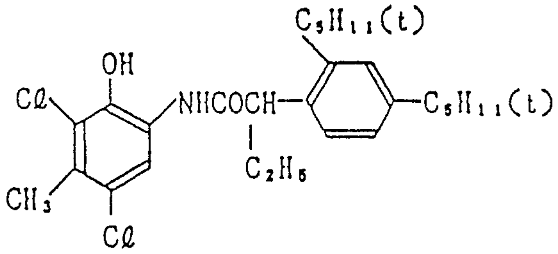
GD-1



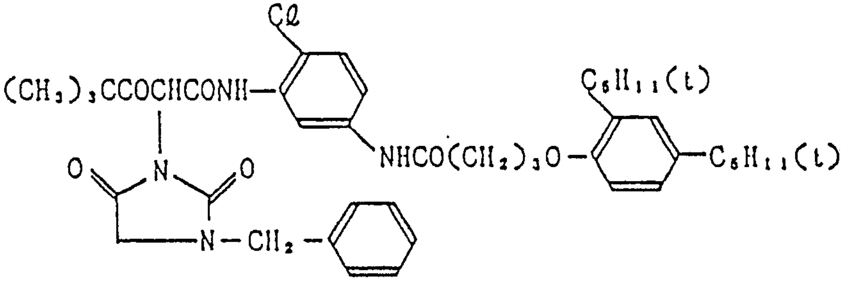
BD-1



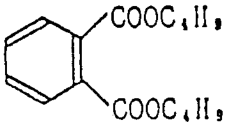
CC-1



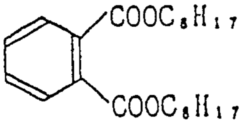
YC-1



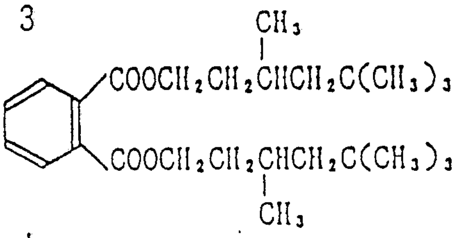
SO-1



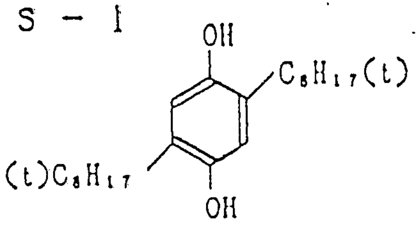
SO-2



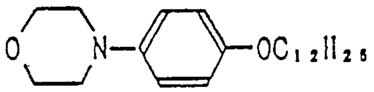
SO-3



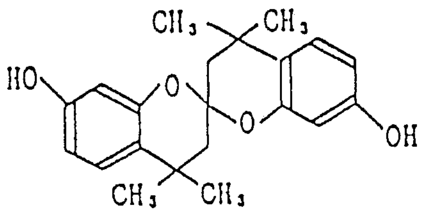
AS-1



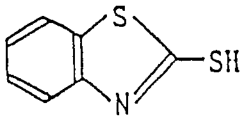
AO-1



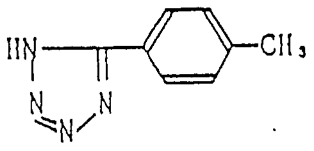
AO-2



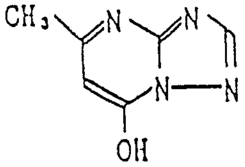
ST-1



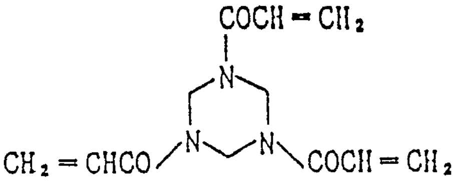
ST-2



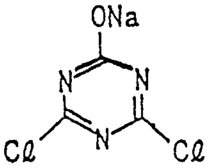
ST-3



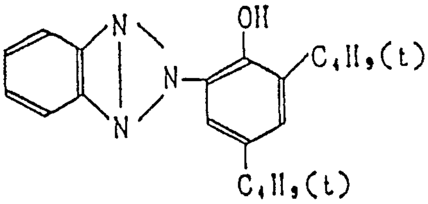
H A - 1



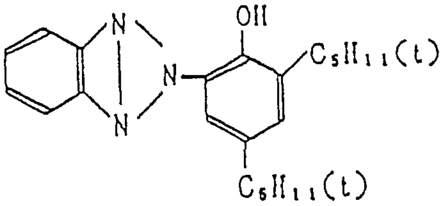
H A - 2



U V - 1



U V - 2



Each sample was exposed to green light through an optical wedge, and then processed according to the following processing procedures. The light fastness and sweating were evaluated in the same manner as in Example 1. The results are shown in Table 5.

Processing Procedures		
Immersion in color developer	38 ° C	8 sec.
Fogging exposure	-	10 sec. at 1 lux
Color developing	38 ° C	2 min.
Bleach-fixing	35 ° C	60 sec.
Stabilizing	25 to 30 ° C	1 min. 30 sec.
Drying	75 to 80 ° C	1 min.

Color developer	
Benzyl alcohol	10 mℓ
Ethylene glycol	15 mℓ
Potassium sulfite	2.0 g
Potassium bromide	1.5 g
Sodium chloride	0.2 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	3.0 g
Polyphosphoric acid (TPPS)	2.5 g
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	5.0 g
Fluorescent bleaching agent, a 4,4′-diaminostilbenedisulfonic acid derivative	1.0 g
Potassium hydroxide	2.0 g
Water was added to make total quantity 1 liter and pH was adjusted to 10.20.	

Bleach-fixer	
Ferric ammonium ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate, 70% solution	100 mℓ
Ammonium sulfite, 40% solution	27.5 mℓ
Water was added to make total quantity 1 liter and pH was adjusted to 7.1 with potassium carbonate or glacial acetic acid.	

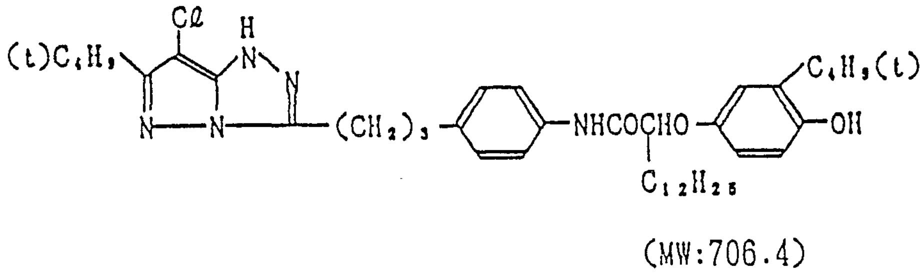
Stabilizer	
5-chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	10. g
1-hydroxyethylidene-1,1-diphosphonic acid	2.5 g
Bismuth chloride	0.2 g
Magnesium chloride	0.1 g
Ammonium hydroxide, an aqueous 28% solution	2.0 g
Sodium nitrilotriacetate	1.0 g
Water was added to make total quantity 1 liter and pH was adjusted to 7.0 with ammonium hydroxide.	

The stabilizing was conducted by the dual-bath counter-current system.

Table 5

Sample No.	Magenta coupler in the 3rd layer	Polymer in the 3rd layer	Solvent in the 3rd layer	Light fastness (%)	Sweating	
1	Comparative coupler-7	-	SO-2	27	Δ	Comparison
2	Comparative coupler-7	A-2	SO-2	18	x	Comparison
3	M-23	-	SO-2	25	o	Comparison
4	M-23	A-2	SO-2	10	o	Invention

Comparative coupler 7



As is evident from the results in Table 5, the samples each containing the comparative coupler and the polymer had the improved light fastness, while sweating was caused. On the contrary, the combined use of the magenta coupler related to the invention and the polymer led not only to the significant improvement in the light fastness but also to the effective prevention of sweating.

Example 5

Light-sensitive photographic material Sample Nos. 501 to 511 were prepared in the same manner as in Example 1, except that the high boiling organic solvent in each layer was replaced with DBP and the polymer in the 3rd layer was removed and that the magenta coupler in the 3rd layer, and the cyan coupler and the polymer in the 5th layer were varied as shown in Table 6.

Each sample was exposed, developed and evaluated in the same manner as in Example 1. The results are shown in Table 6.

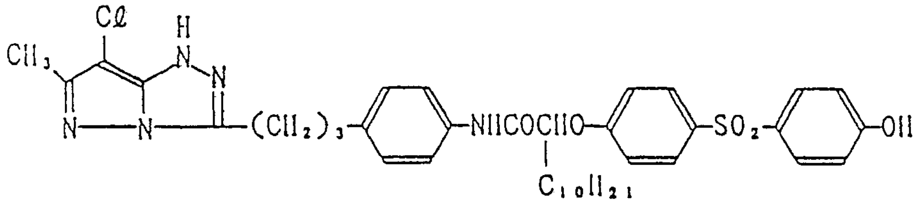
Table 6

Sample No.	Magenta coupler in the 3rd layer	Cyan coupler in the 5th layer	Polymer in the 5th layer	Light fastness (%)		Dark fading property (%)*		Sweating	
				Magenta	Cyan	Magenta	Cyan		
501	Comparative coupler-1	II-4	-	30	80	89	67	x	Comparison
502	Comparative coupler-1	II-4	A-2	32	84	90	85	x	Comparison
503	Comparative coupler-2	II-4	-	85	81	92	69	x	Comparison
504	Comparative coupler-2	II-4	A-2	88	83	92	84	x	Comparison
505	M-20	II-4	-	75	82	90	68	Δ	Comparison
506	M-20	II-4	A-2	77	86	88	83	Δ	Invention
507	M-20	II-20	-	74	85	92	38	Δ	Comparison
508	M-20	II-20	A-2	76	88	89	77	Δ	Invention
509	M-23	II-23	A-2	75	84	88	84	o	Invention
510	M-27	II-23	A-2	76	83	93	82	o	Invention
511	M-40	II-23	A-22	75	84	90	84	o	Invention

* Survival rate of the density 1.0 after 20 days storage at 85 ° C and 60%RH.

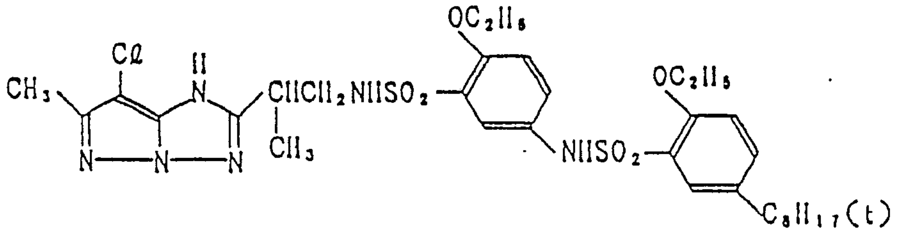
Comparative magenta coupler 1

Molecular weight 720.3



Comparative magenta coupler 2

Molecular weight 709.3



As is evident from the results in Table 6, Sample Nos. 501 and 502 each containing the comparative magenta coupler 1 caused so marked sweating and had so poor light fastness of a magenta dye image that they were of no practicability. Sample Nos. 503 and 504 each containing the comparative magenta coupler 2 had the improved dark fading property and light fastness of the magenta and cyan dye images, while sweating was not improved. Sample No. 503 containing no polymer in the 5th layer had a slightly poor balance of the dark fading property between a cyan dye image and a magenta dye image (hereinafter referred to as the dark facing balance). Sample Nos. 505 and 507 each containing the magenta and cyan couplers each related to the invention and no polymer had the poor dark fading property of the cyan dye image and the inferior dark fading balance.

Sample Nos. 506, 508 to 511 of the invention each containing the magenta coupler, the cyan coupler each related to the invention and the polymer were found to have the excellent light fastness, dark fading property and dark fading balance without causing sweating.

Among the samples of the invention, Sample Nos. 509 to 511 each containing the magenta coupler with a molecular weight of not more than 550 were found virtually free from sweating.

The effects of the invention were confirmed also in the samples prepared by replacing the magenta coupler in Sample 510 with M-16, M-28, M-35 and M-47, the cyan coupler with II-15 and II-19 and the polymer with A-5 and A-77.

Example 6

Light-sensitive photographic material Sample Nos. 601 to 610 were prepared in the same manner as in Example 5, except that the silver halide compositions of the blue-sensitive emulsion in the 1st layer, the green-sensitive emulsion in the 3rd layer and the red-sensitive emulsion in the 5th layer were varied to 99.5 mol% of silver chloride and 0.5 mol% of silver bromide, and that the magenta coupler in the 3rd layer, the cyan coupler and the polymer in the 5th layer were varied as shown in Table 7.

The samples were exposed to light through an optical wedge in the same manner as in Example 5 and processed in accordance with the following processing procedures. The processed samples were evaluated in the same manner as in Example 5.

The results are shown in Table 7.

Processing Procedures		
	Temperature	Time
Color developing	35.0°C ± 0.3°C	45 sec.
Bleach-fixing	35.0°C ± 0.5°C	45 sec.
Stabilizing	30 to 34°C	90 sec.
Drying	60 to 80°C	60 sec.

Color developer	
Pure water	800 mℓ
Triethanolamine	10 g
N,N-diethylhydroxyamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-hydroxyethylidene-1,1-diphosphonic acid	1.0 g
Ethylenediaminetetraacetic acid	1.0 g
Disodium catechol-3,5-disulfonate	1.0 g
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Fluorescent bleaching agent, a 4,4′-diaminostilbenedisulfonic acid derivative	1.0 g
Potassium carbonate	27 g
Water was added to make total quantity 1 liter and pH was adjusted to 10.10.	

Bleach-fixer	
Ferric ammonium ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate, an aqueous 70% solution	100 mℓ
Ammonium sulfite, an aqueous 40% solution	27.5 mℓ
Water was added to make total quantity 1 liter and pH was adjusted to 6.2 with potassium carbonate or glacial acetic acid.	

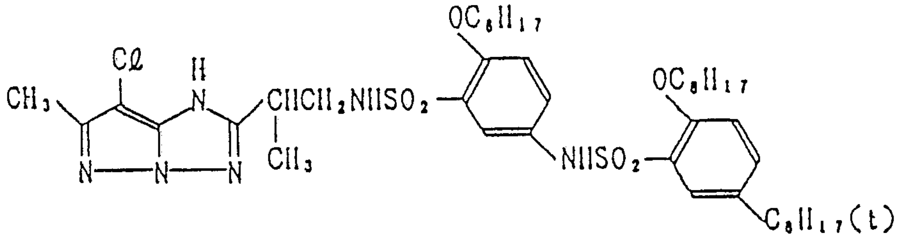
Stabilizer	
5-chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediamine tetraacetic acid	1.0 g
Ammonium hydroxide, an aqueous 20% solution	3.0 g
Ammonium sulfite	3.0 g
Fluorescent bleaching agent, a 4,4′-diaminostilbenedisulfonic acid derivative	1.5 g
Water was added to make total quantity 1 liter and pH was adjusted to 7.0 with sulfuric acid or potassium carbonate.	

Table 7

Sample No.	Magenta coupler in the 3rd layer	Cyan coupler in the 5th layer	Polymer in the 5th layer	Light fastness (%)		Dark fading property (%)*		Sweating	
				Magenta	Cyan	Magenta	Cyan		
601	Comparative coupler-3	II-22	-	86	84	92	44	x	Comparison
602	Comparative coupler-3	II-22	A-22	85	88	91	79	x	Comparison
603	Comparative coupler-4	II-22	-	72	84	90	43	x	Comparison
604	Comparative coupler-4	II-22	A-22	71	87	92	77	x	Comparison
605	M-50	II-22	A-22	84	86	90	79	△	Invention
606	M-50	II-22	A-22	86	88	89	76	△	Invention
607	M-44	II-4	A-2	82	82	92	82	o	Invention
608	M-44	II-4	A-2	83	84	91	84	o	Invention
609	M-23	II-4	A-2	75	81	90	84	◎	Invention
610	M-23	II-4	A-2	77	82	90	83	◎	Invention

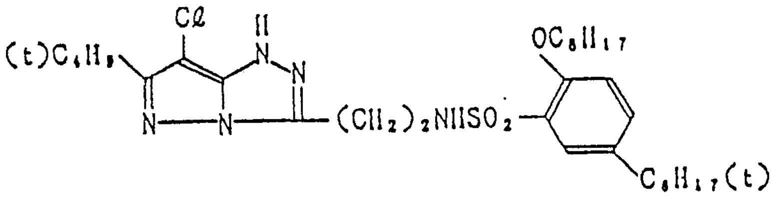
Comparative magenta coupler 3

Molecular weight 877.6



Comparative magenta coupler 4

Molecular weight 622.3



The above results demonstrate that Sample Nos. 601 to 604 each containing the comparative magenta couplers caused sweating and that Sample Nos. 601 and 603 each containing no polymer had the poor dark fading property of a cyan dye image and the poor dark fading balance.

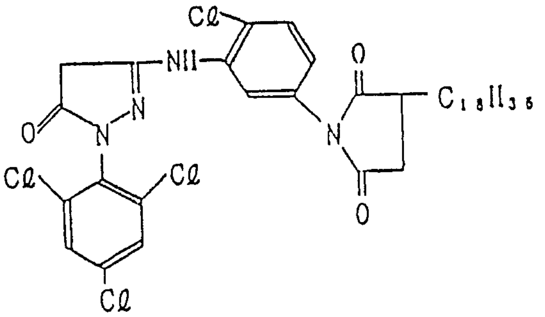
Sample Nos. 605 to 610 of the invention were found to have the excellent light fastness, dark fading property and dark fading balance without causing sweating. Among the samples of the invention, Sample Nos. 609 and 610 each containing the preferable magenta coupler represented by Formula M-II with a molecular weight of not more than 550 and the substituents represented by Formulae M-IX and M-X were found virtually free from sweating.

The effects of the present invention were confirmed also in the samples prepared by replacing the magenta coupler in Sample 607 with M-19, M-33 and M-41, the cyan coupler with II-17 and II-21 and the polymer with A-10 and A-80.

Example 7

The light-sensitive photographic material Sample No. 701 was prepared in the same manner as in Example 6, except that the magenta coupler in the 3rd layer was replaced with the following comparative magenta coupler 5 and the amount of the green-sensitive emulsion in the 3rd layer was varied to 0.31 g/m^2 in an amount converted to silver.

Comparative magenta coupler 5

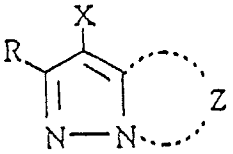


Color Checker manufactured by Macbeth was photographed by Konica Color GX100 manufactured by Konica Corporation, followed by developing to thereby prepare a negative. The negative was printed on each of Sample 610 and 701 after adjusting the tone of gray color portion, and the color reproducibility was evaluated in each color phase. The results revealed that Sample 610 had a higher color reproducibility in blue, red and magenta colors than Sample No. 701.

Claims

1. A silver halide light-sensitive photographic material comprising a support and provided thereon a photographic component layer comprising one of the following Constitutions (1) and (2):
Constitution (1): a silver halide emelsion layer containing emulsified lipophilic particles comprising a magenta coupler represented by the following Formula M-1 and having a molecular weight of not more than 600, and a polymer insoluble in water and soluble in an organic solvent, and
Constitution (2): a silver halide emulsion layer containing the magenta coupler represented by Formula M-1 and having a molecular weight of not more than 600, and a silver halide emulsion layer containing emulsified lipophilic particles comprising a phenol-type cyan coupler and a polymer insoluble in water and soluble in an organic solvent;

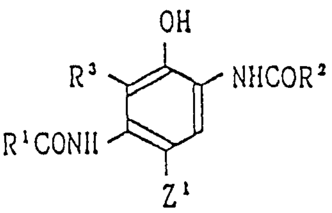
Formula M-1



wherein Z represents the group of non-metallic atoms necessary to form a nitrogen-containing heterocyclic ring which may have a substituent; X represents a hydrogen atom or a group capable of splitting off upon a reaction with an oxidation product of a developing agent; R represents a hydrogen atom or a substi tuent.

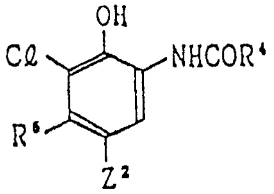
2. The photographic material of claim 1, wherein said cyan coupler is represented by Formula I or II:

Formula I



wherein R^1 represents an alkyl group or an aryl group; R^2 represents an alky group, a cycloalkyl group, an aryl group or a heterocyclic group; R^3 rrepresents a hydrogen atom, a halogen atom, an alky group or an alkoxy group, provided that R^3 may form a ring with R^1; and Z^1 represents a hydrogen atom or a group capable of splitting off upon a reaction with an oxidation product of a developing agent;

Formula II

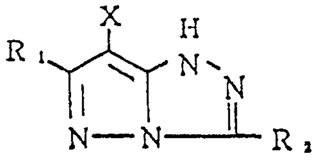


wherein R^4 represents a ballast group; R^5 represents an alkyl group having 1 to 6 carbon atoms; and Z^2 represents a hydrogen atom or a group capable of splitting off upon a reaction with an oxidation product of a developing agent.

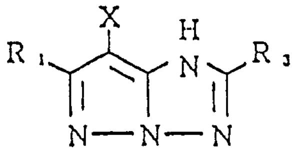
3. The photographic material of claim 1, wherein said molecular weight is 400 to 550.

4. The photographic material of claim 1, wherein said magenta coupler is one selected from the compounds represented by the following Formulas M-II to M-VII:

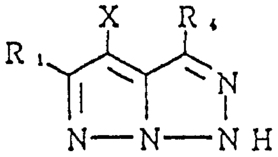
M-II



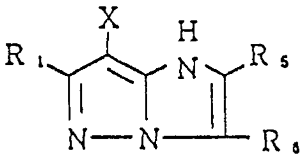
M-III



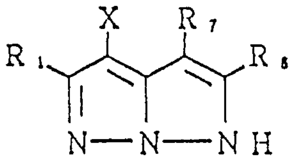
M-IV



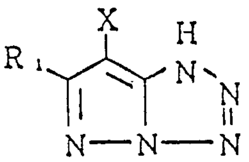
M-V



M-VI

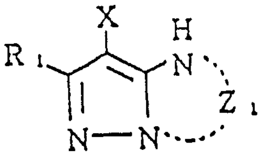


M-VII



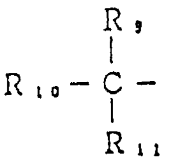
wherein R_1 to R_8 and X each represent the same groups as those defined for R, X and Z in Fromula M-1, respectively.

5. The photographic material of claim 1, wherein said magenta coupler is represented by the following Formula M-VIII:



wherein R_1, X and Z_1 each represent the same group as those defined for R, X and Z in Formula M-I, respectively.

6. The photographic material of any of claims 1, 4 or 5, wherein R and R_1 are represented by the following Formula M-IX:



$$R_{10}-\overset{R_9}{\underset{R_{11}}{C}}-$$

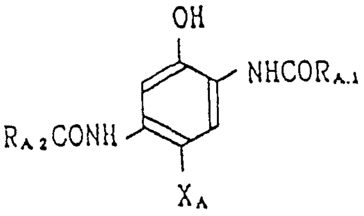
wherein R_9, R_{10} and R_{11} each represent the same groups as those defined for R in Formula M-1, provided that two of R_9 to R_{11} may be combined to form a ring and that the remaining one of R_9 to R_{11} may be combined with said ring to form a bridged hydrocarbon residue.

7. The photographic material of any of claims 1, 4 or 5, wherein a substituent for the ring formed by Z or Z_1 in Formula M-1 or M-VIII and R_2 to R_8 in Formulas M-II to M-VI each are represented by the following Formula M-X:

$-R^1-SO_2-R^2$

wherein R^1 represents an alkylene group and R^2 represents an alkyl group, a cycloalkyl group or an aryl group.

8. The photographic material of claim 2, wherein the cyan coupler is represented by the following Formula I-A:



wherein R_{A1} is phenyl having a substituent including at least one halogen atom; R_{A2} represents the same group as those defined for R^1 in Formula I; and X_A represents a halogen atom, an aryloxy group or an alkoxy group.

9. The photographic material of claim 1, wherein the polymer is selected from a vinyl polymer or copolymer, a polyester resin prepared by a condensation polymerization of polyhydric alcohol and polybasic acid, and a ployester resin prepared by a ring-opening polymerization.

10. The photographic material of claim 9, wherein a number-average molecular weight of the polymer is not more than 200 0000.

11. The photographic material of claim 10, wherein the number-average molecular weight is not more than 5 000 to 100 0000.

12. The photographic material of claim 10, wherein the ratio of the polymer to the coupler is 1 : 20 to 20 : 1.

13. The photographic material of claim 12, wherein the ratio is 1 : 10 to 10 : 1.

14. The photographic material of claim 1, wherein the silver halide comprises silver chloride of not less than 90 mol%, silver bromide of not more than 10 mol% and silver iodide of not more than 0.5 mol%.

15. The photographic material of claim 14, wherein the silver halide is silver bromochloride having a bromide content of 0.1 to 2 mol%.