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(54) Silver halide light-sensitive color photographic material excellent in the color reproducibility and method for processing the same.

(57) A silver halide light-sensitive color photographic material having improved color reproducibility, and a method of processing thereof is disclosed. The material has on a support a plurarity of light-sensitive silver halide emulsion layers including at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer, wherein at least one of the silver halide emulsion layers contains a silver halide consisting essentially of silver chloride, silver chlorobromide or silver chloroiodobromide, and at least one layer of the above silver halide emulsion layers contains a compound which is, during development, capable of releasing a compound selected from the group consisting of one which is capable of undergoing a coupling reaction with the oxidation product of a developing agent, one which is capable of reducing the oxidation product of a developing agent and one which is a precursor of either the compound which is capable of undergoing a coupling reaction with the oxidation product of a developing agent or the compound which is capable of reducing the oxidation product of a developing agent.

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SILVER HALIDE LIGHT-SENSITIVE COLOR PHOTOGRAPHIC MATERIAL EXCELLENT IN THE COLOR REPRODUCIBILITY AND METHOD FOR PROCESSING THE SAME

FIELD OF THE INVENTION

The present invention relates to a silver halide light-sensitive color photographic material, and more particularly to a silver halide light-sensitive color photographic material excellent in the color reproducibility and a method for processing the same. This invention is suitably applicable to various light-sensitive materials, and particularly, advantageously to, for example, light-sensitive materials for direct appreciation use, such as silver halide light-sensitive color photographic materials for making prints.

BACKGROUND OF THE INVENTION

In an ordinary silver halide color photographic process, as is well-known, a silver halide light-sensitive photographic material containing a dye-forming coupler is developed by using a paraphenylenediamine-type color developing agent to thereby effect coupling reaction of the oxidation product of the color developing agent with the dye-forming couplers to form dyes, whereby a color image is obtained.

Of color image forming processes, the existing process according to the subtractive color process includes one common method in which a light-sensitive material for photographing use, called 'color negative film' is imagewise exposed and then developed by using the above-mentioned color developing process to once obtain a color negative image, and after that, the negative is printed on a color photographic paper by means of a printer.

The color negative light-sensitive material has a multi-layer construction normally comprising, for example, three different silver halide emulsion layers spectrally sensitized to 400-500nm, 500-600nm and 600-700nm wavelength regions, containing a yellow coupler, a magenta coupler, and a cyan coupler, respectively. That is, a yellow dye is formed at the portion exposed to blue, a magenta dye at the portion exposed to green, and a cyan dye at the portion exposed to red, thus forming a color negative image. After that, generally, from the negative is printed a color positive image on a color photographic paper which also comprises a yellow coupler-containing blue-sensitive layer, magenta coupler- containing green-sensitive layer, and cyan coupler-containing red-sensi tive layer.

In a direct positive light-sensitive material which uses a direct positive emulsion, a direct positive image can be obtained without the use of any color negative.

However, unlike the block-type dye considered ideal for the subtractive color process, i.e., a dye considered sensitive to a specific wavelength region only, those dyes to be used in the color photography have considerable irregular absorptions in regions outside their regular spectral regions, and therefore they also absorb part of light desired not to be absorbed, so that no adequate color reproduction can be attained. Accordingly, for example, in the color negative film, masking by use of colored couplers to remove the irregular absorption for color correction is carried out to thereby realize a satisfactory color reproduction. Further, a negative spectral sensitivity compensation based on both the three primary colors principle in the subtractive color process and the human eye's nature takes place or the interimage effect is used in order to emphasize pure colors.

Thus, in the color negative light-sensitive material, various color correction means are used, but there still remains the problem that even in the case of the signals from an original that have been variously corrected to be recorded as mentioned above, when printing is made on a conventional color photographic paper, because the color paper in itself has no color correction function at all, the color reproduction of the whole system become eventually deteriorated in this stage.

Also, the direct positive light-sensitive material for use in color photo-copying apparatus or in other fields is not considered having an adequate color reproducibility and thus required to be improved on the ground that since it is a light-sensitive material which itself is to be directly observed by users, the masking technique utilizing colored couplers as used in color negative light-sensitive materials cannot be applied to it.

Further, the light-sensitive material for direct observation use, according to our knowledge, contains substantially silver chloride or silver chlorobromide as its silver halide component, so that where DIR

couplers as used for image quality improvement in conventional color negative films are tried to be used in such a material as, for example, a color photographic paper as described in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No.72240/1986, the DIR coupler retards the light-sensitive material developing speed, or if the developing is accelerated, the DIR coupler little displays its effect, so that we have found it difficult to apply such DIR couplers to the direct positive light-sensitive material. Thus, it has been the actual condition that no effective color correction means corresponding to the masking technique has been available to the above-mentioned light-sensitive material substantially containing silver chloride or silver chlorobromide.

In the case of a high-speed, high-silver-content light-sensitive material for photographing use (such as a color negative light-sensitive material or reversal light-sensitive material), it is known that if a common bleaching method using an aminopolycarboxylic acid ferric complex salt is applied, the bleaching bath, when its exhaustion makes progress, tends to cause silver retention. And particularly in the case of the rapid processing of color negative light-sensitive materials, which has been investigated in recent years, the rapid processing is one of factors rendering silver retention liable to occur.

In the processing of a high-speed color negative light-sensitive material for photographing use or a color reversal light-sensitive material for photographing use which each is comprised mainly of a silver iodobromide emulsion, usually the developed silver is first turned into silver halide by being subjected to oxidation/bleaching treatment in a bleaching bath comprising the foregoing aminopolycarboxylic acid ferric complex salt, and the silver halide is then fixed in a fixing solution. On the other hand, in the processing of a color photographic paper or a direct positive light-sensitive material which each is comprised mainly of silver chloride or silver chlorobromide, a bleach-fix bath in the form of a single bath containing both the above aminopolycarboxylic acid ferric complex salt and a thiosulfate is used.

The aminopolycarboxylic acid ferric complex salt is weaker in the bleaching power than red prussiate, bichromate, etc., and when used along with the thiosulfate having a reduction power in a monobath bleach-fix bath, which is used suitably for simplifying and speeding up the processing of color photographic paper, the bleaching power becomes more weakened to deteriorate the desilvering ability of the bath.

Therefore, in any case, increasing the desilvering speed and ability is highly demanded and essential for simplifying and speeding up the processing.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a color photographic light-sensitive material containing a silver halide comprised of silver chloride, silver chlorobromide or silver chloroiodobromide, which has a largely improved, excellent color reproducibility, and also to provide suitable method for processing the color photographic light-sensitive material.

The above object of this invention is accomplished by a silver halide light-sensitive color photographic material comprising a support and, provided thereon, a plurarity of light-sensitive silver halide emulsion layers including at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer, wherein at least one of the silver halide emulsion layers contains a silver halide consisting essentially of silver chloride, silver chlorobromide or silver chloroiodobromide, and at least one layer of the above silver halide emulsion layers contains a compound which is, during development, capable of releasing a compound selected from the group consisting of one which is capable of undergoing a coupling reaction with the oxidation product of a developing agent, one which is capable of reducing the oxidation product of a developing agent and one which is a precursor of either the compound which is capable of undergoing a coupling reaction with the oxidation product of a developing agent or the compound which is capable of reducing the oxidation product of a developing agent.

And the object is further accomplished by a method for processing silver halide light-sensitive photographic materials which is characterized by the processing of such the light-sensitive material as mentioned above in a bleach-fix bath.

An excellent color reproducibility can be realized by using the aforementioned light-sensitive material of this invention; for example, in the negative-positive system in the subtractive color process. Also, the light-sensitive material of this invention, when applied to a direct positive-type light-sensitive material for color-copying use, enables to obtain an excellent color reproducibility.

Thus, the light-sensitive material of this invention is effective and excellent in the color reproducibility.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 through 5 are drawings showing characteristic curves of the blue, green and red densities of the respective samples in the examples of this invention. Figures 6 and 7 are drawings showing relations between log E (E stands for Exposure) and photographic density D, which are provided for explaining the function of this invention, wherein B is blue density, G is green density and R is red density. Figures 8 and 9 are drawings showing relations between densities R, B and G and log E in the case where comparative samples and samples of this invention are exposed through an optical wedge to green light and then subjected to color development.

DETAILED DESCRIPTION OF THE INVENTION

The light-sensitive color photographic material containing a compounds capable of releasing a compound capable of effecting coupling reaction with an oxidized developing agent (oxidation product of a developing agent) or a compound capable of reducing the oxidized developing agent or precursors of these compound hardly causes silver retention even in the aforementioned bleach-fix treatment and enables to obtain images excellent in the color reproducibility as well as in the graininess and sharpness; this is what has been made on the basis of our knowledge, and the processing method according to this invention has been made on the basis of the knowledge. The processing method of this invention, since it is satisfactory in the desilvering ability, is considered suitable also for rapid processing.

In the present invention, the compound which, as a result of reacting with an oxidized developing agent, is capable of releasing a compound capable of effecting coupling reaction with the oxidized developing agent; or at least one compound capable of reducing the oxidized developing agent; or precursors of such compounds are considered assuming the following actions: Any of these compounds, by being contained in the interlayer effect-giving layer, release a compound which, at the time of development, effects coupling reaction with an imagewise oxidized developing agent or a compound which effects oxidation-reduction reaction with the oxidized developing agent, which compound reacts with the oxidized developing agent that has been produced as a result of the development in its own layer, whereby the compound functions to restrain the dye formation inside its own layer. By this, the gamma of its layer is lowered, and at the same time, the compound, which scavenges the oxidized developing agent, in addition to its effect inside the layer, diffuses into other layers and acts to restrain the color developing reaction in the layers.

By this action, where these compounds are incorporated into, e.g., a magenta layer, when the magenta color is developed, the color formation of the cyan dye in the cyan layer can be restrained in proportion to the density of the magenta dye in the magenta layer, whereby the absorption which the magenta dye has outside its intrinsic green region, for example, the absorption of red, is restrained to thus display a masking effect. Above all, the way of rendering the magenta layer an interlayer effect-giving layer and providing the interlayer effect from the magenta layer to other layers is suitable for the red-purple color reproduction and is particularly effective in highly pure red color formation.

Rendering the cyan layer an interlayer effect-giving layer is also preferable; for example, that the interimage effect from the cyan layer is provided to the magenta layer is also very effective in bluish color reproduction. In like manner, by increasing the diffusibility of the released compound which scavenges the oxidation product of a developing agent, it is also possible to provide the interimage effect from the cyan layer to the yellow layer or from the yellow layer to the magenta layer; thus the invention can be used in a variety of embodiments.

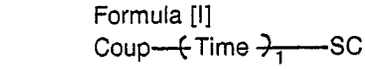
As the material for bringing about the interimage effect, iodide-containing silver halide emulsions, DIR couplers, or the like may also be used, but these have, as mentioned hereinbefore, disadvantage that they release a development inhibitor which retards the whole development or deteriorate the desilvering ability, and thus they run counter to the recent demand for speeding up the processing, and therefore they are hardly applicable to those light-sensitive materials which need to be rapidly processed. As for those multilayer light-sensitive materials which should be rapidly processed, since it is difficult to make a well-balanced stop of the development of each layer, a certain appropriate device must be made before applying the masking by development inhibitor release to such light-sensitive materials.

In the light-sensitive material having a silver halide comprised substantially of silver chloride, silver chlorobromide or silver chloroiodobromide, it is preferred to use a compound capable of releasing a compound capable of effecting coupling reaction with the oxidation product of a developing agent, a

compound capapble of reducing the oxidation product (hereinafter may sometimes be called a compound capable of scavenging the oxidation product of a developing agent), or precursors of these compounds, and as the processing therefor it is preferred to use a processing method which uses a bleach-fix bath.

The compound capable of releasing a compound or its precursor capable of reacting with the oxidation product of a developing agent to thereby scavenge the oxidation product (the compound is hereinafter called 'DSR compound'), which is suitably usable in this invention, will now be explained. The DSR compound is normally represented by Formula [I]:

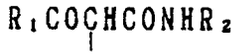
Formula [I]



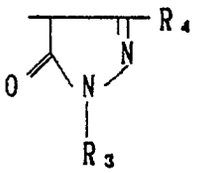
wherein Coup represents a coupler residue capable of releasing a  group upon reaction with the oxidation product of a color developing agent; Time is a timing group which, after being released from the Coup, is capable of releasing SC; and SC is a color developing agent's oxidation product scavenger which, after being released from the Coup, is capable of scavenging the oxidation product of a color developing agent by the oxidation-reduction reaction or coupling reaction therewith; and 1 is an integer of 0 or 1.

To explain further in detail the above compound, the coupler residue represented by the Coup of Formula [I] is in general a yellow coupler residue, magenta coupler residue, cyan coupler residue or a substantially colorless coupler residue, and preferably represents those coupler residues having the following Formulas [II] through [IX]:

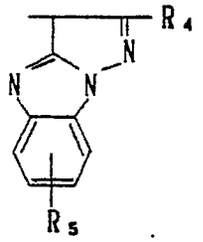
Formula [II]



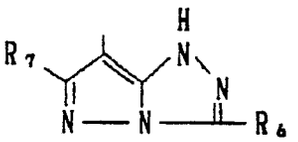
Formula [III]



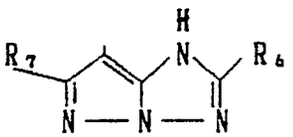
Formula [IV]



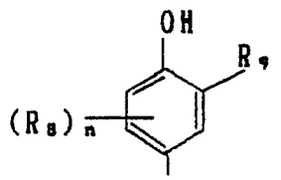
Formula [V]



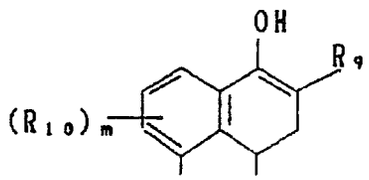
Formula [VI]



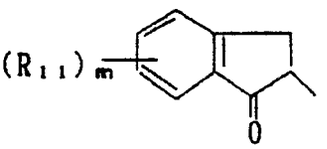
Formula [VII]



Formula [VIII]



Formula [IX]



In Formula [II], R_1 is an alkyl, aryl or arylamino group; and R_2 is an aryl or alkyl group.

In Formula [III], R_3 is an alkyl or aryl group; R_4 is an alkyl, acylamino, arylamino, phenylureido or alkylureido group.

In Formula [IV], R_4 is as defined in the R_4 of Formula [III]; and R_5 is an acylamino, sulfonamido, alkyl or alkoxy group or a halogen atom.

In Formulas [V] and [VI], R_7 is an alkyl, aryl, acylamino, arylamino, alkoxy, phenylureido or alkylureido group; and R_6 is an alkyl or aryl group.

In Formula [VII], R_9 is an acylamino, carbamoyl or phenyluredido group; and R_8 is a halogen atom, an alkyl, alkoxy, acylamino or sulfonamido group.

In Formula [VIII], R_9 is as defined in the R_9 of Formula [VII]; and R_{10} is an amino, substituted amino, carbamido, sulfonamido or hydroxyl group.

In Formula [IX], R_{11} is a nitro, acylamino, succinic acid imido, sulfonamido, alkoxy or alkyl group or a halogen atom or a cyano group.

In Formulas [VII] and [IX], n is an integer of up to 2, and in Formula [VIII], m is an integer of 0 or 1.

Further, the above groups include those with and without substituents, and in the case of having a substituent, the preferred substituent is one arbitrarily selected from the class consisting of halogen atoms, nitro, cyano, sulfonamido, hydroxyl, carboxyl, alkyl, alkoxy, carbonyloxy, acylamino and aryl groups.

In the above formulas, the oleophilicity assumed by the R_1 through R_{11} may be arbitrarily selected according to purposes, and in the case of ordinary image-forming couplers, the total number of the carbon atoms of the R_1 through R_{11} is preferably 10 to 60, and more preferably 15 to 30.

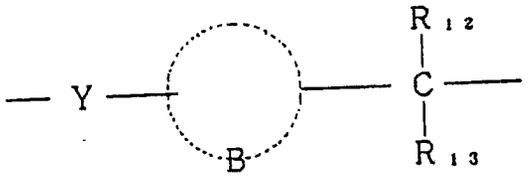
On the other hand, in the case of mobile dye-forming couplers from which the dye formed by color development moderately moves inside the light-sensitive material, the total number of the carbon atoms of the R_1 through R_{11} is preferably not more than 15.

In the case of substantially colorless couplers, the total number of the carbon atoms of the R_1 through R_{11} is preferably not more than 15, and the the R_1 through R_{11} each is desirable to have at least one carboxyl, arylsulfonamido or alkylsulfonamido group as its substituent.

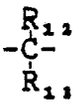
The foregoing 'substantial colorless coupler residue' herein represents those which, after dye forming reaction, have the dye dissolved out into the processing solution or have the dye bleached by reacting with the constituent of the solution, whereby no dye image remains after the processing, which are known as effluent dye-forming couplers and bleachable dye-forming couplers, respectively.

In the foregoing Formula [I], the timing group represented by the Time include those preferably having the following Formula [X], [XI] or [XII]:

Formula [X]

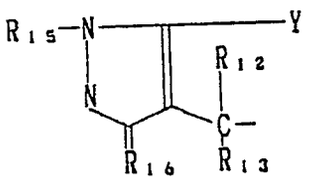


wherein B is a group of atoms necessary to complete a benzene ring or a naphthalene ring; Y represents a -O-, -S- or - $\overset{R}{N}^{14}$-group, which is linked to the coupling component Coup at its active site; R_{12}, R_{13} and R_{14} each represents a hydrogen atom, an alkyl or aryl group; and the



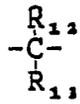
group is substituted to the ring in the ortho or para position with respect to the Y and is linked to the SC.

Formula [XI]



wherein Y, R_{12} and R_{13} are as defined in Formula [X]; R_{15} is a hydrogen atom, alkyl group, aryl group, acyl group, sulfo group, alkoxycarbonyl group or heterocyclic residue; and R_{16} is a hydrogen atom, alkyl group, aryl group, heterocyclic residue, alkoxy group, amino group, acid amido group, sulfonamido group, carboxy group, alkoxycarbonyl group, carbamoyl group or cyano group.

The timing group represented by Formula [XI], as in the foregoing Formula [X], is linked through the Y to the coupling component Coup at its active site and also linked through the



group to the SC.

As the Time group to release the SC by intramolecular nucleophilic substitution reaction, there are those having the following Formula [XII]:

-Nu-D-E-Z

wherein Nu is a nucleophilic group having an oxygen atom, sulfur atom or nitrogen atom each rich in electron, which is bonded to the coupling component Coup at its coupling position; E represents a carbonyl group, thiocarbonyl group, phosphinyl group or thiophosphinyl group which each is poor in electron, and the electrophilic group E is combined with the hetero atom of the SC; and D is a linkage group which serves to connect the Nu with the E in three dimensions and which, after the Nu is released from the coupling component, breaks the intramolecular nucleophilic substitution with 3- to 7-member ring formation and is thereby able to release the SC.

In Formula [I], the scavenger represented by the SC to scavenge the oxidation product of a color developing agent is classified into two types: oxidation-reduction type and coupling type.

In Formula [I], where the SC scavenges the oxidation product of a color developing agent by oxidation-reduction reaction, this scavenger is a group capable of reducing the oxidation product of a color developing agent and includes preferably those reducing agents as described in, e.g., Angew. Chemi. Int. Ed., 17 875-886 (1978), The Theory of the Photographic Process, 4th ed. Sec. 11 (Macmillan, 1977), Japanese Patent O.P.I. Publication No. 5247/1984, and the like, or may be any of those precursors capable of releasing these reducing agents at the time of developing. To be concrete, it is preferred to be an aryl or heterocyclic group which, when reacting with the oxidation product of a color developing agent, has at least two -OH groups, $-NH_2$ groups, -NHR groups or $-N\begin{matrix}R\\R'\end{matrix}$ groups (wherein R and R' each is an alkyl, cycloalkyl, alkenyl or aryl group), and above all the aryl group is preferred, and a phenyl group is more preferred. The oleophilicity of the SC may be arbitrarily selected as in the case of those couplers represented by the foregoing Formulas [II] through [IX], but in order to make the most of the effect of this invention, the total number of the carbon atoms of the SC should be from 6 to 50, more preferably from 6 to 30, and most preferably from 6 to 20.

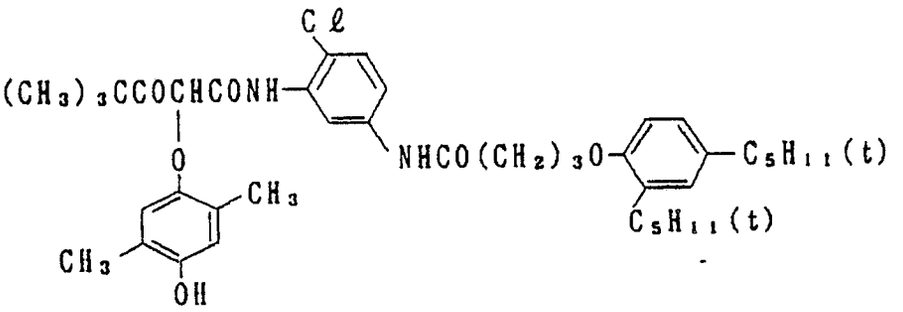
Where the SC, by coupling reaction, is to scavenge the oxidation product of a color developing agent, this SC is a substantially colorless coupler residue, and those may be utilized as the SC include the aforementioned effluent dye-forming couplers, bleachable dye-forming couplers and Weiss couplers, which has a nonsplittable substituent in their reaction active site to form no dyes.

Particular examples of the compounds represented by the Coup-(time)$_1$—SC of Formula [I] are found in, e.g., British Patent No. 1,546,837, Japanese Patent O.P.I. Publication Nos. 150631/1977, 111536/1982, 111537/1982, 138636/1982, 185950/1985, 203943/1985, 213944/1985, 214358/1985, 53643/1986, 84646/1986, 86751/1986, 102646/1986, 102647/1986, 107245/1986, 113060/1986, 231533/1986, 23374/1986, 236550/1986, 236551/1986, 238057/1986, 240240/1986 and 249052/1986.

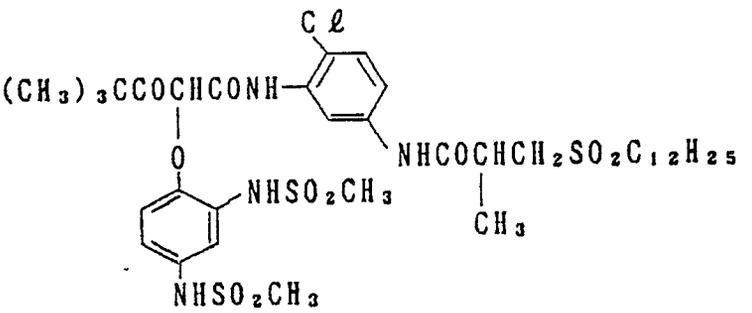
As the SC, an oxidation-reduction-type scavenger is suitably usable, and in this instance, by reducing the oxidation product of a color developing agent, the SC can be reused.

The following are examples of the DSR compounds represented by Formula [I], but the invention is not limited to and by the examples:

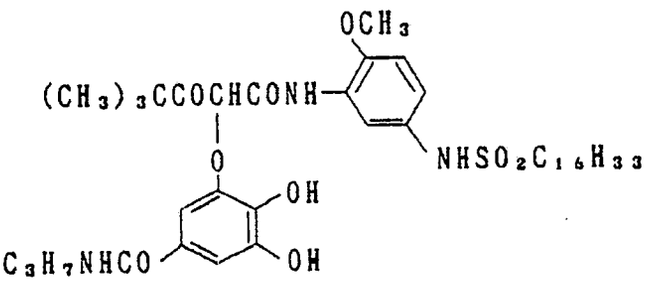
DSR－1



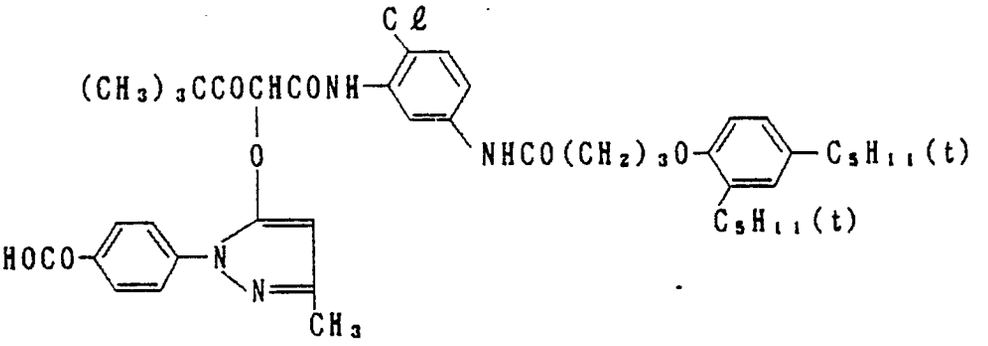
DSR－2



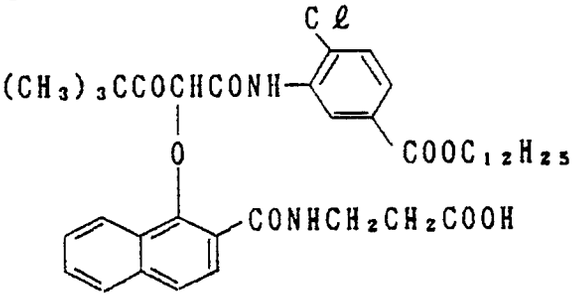
DSR－3



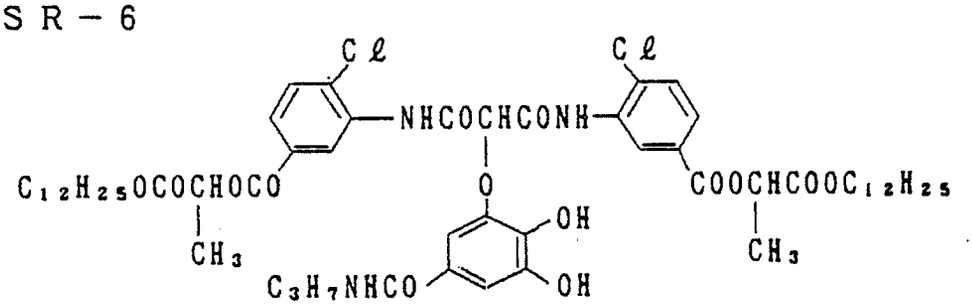
DSR－4



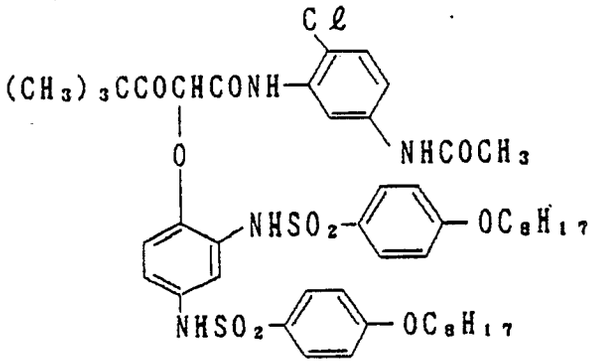
DSR－5



DSR－6



DSR－7



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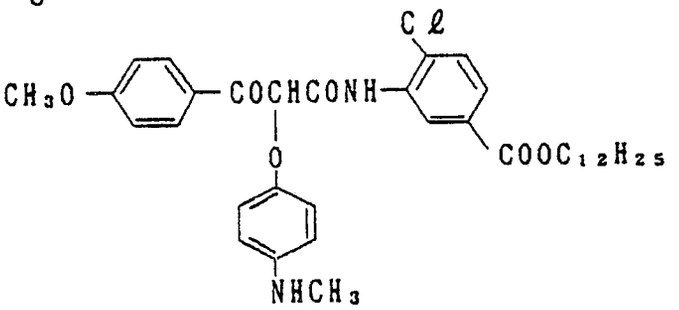
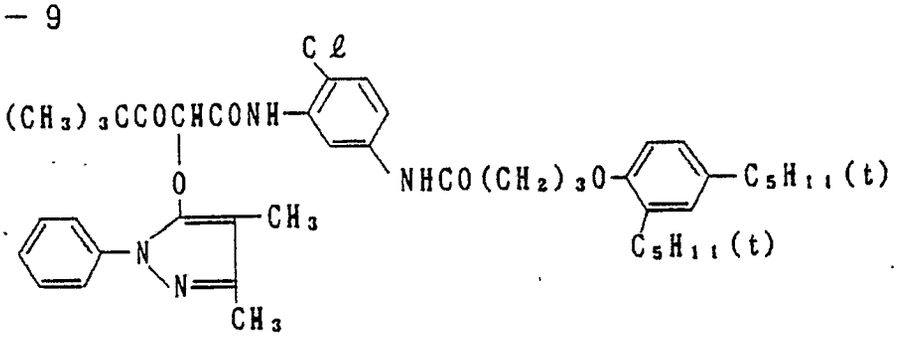


DSR－9



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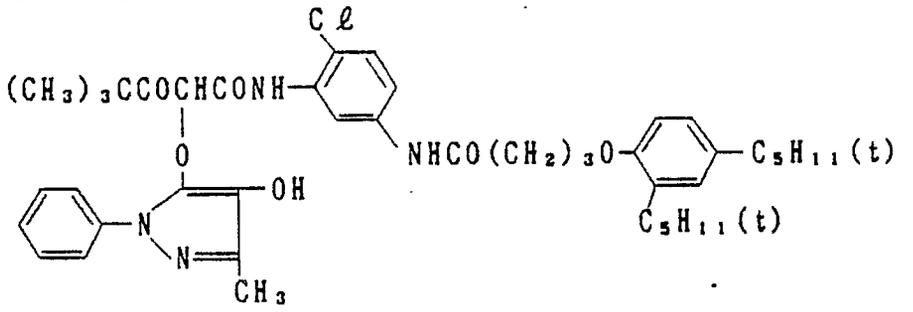

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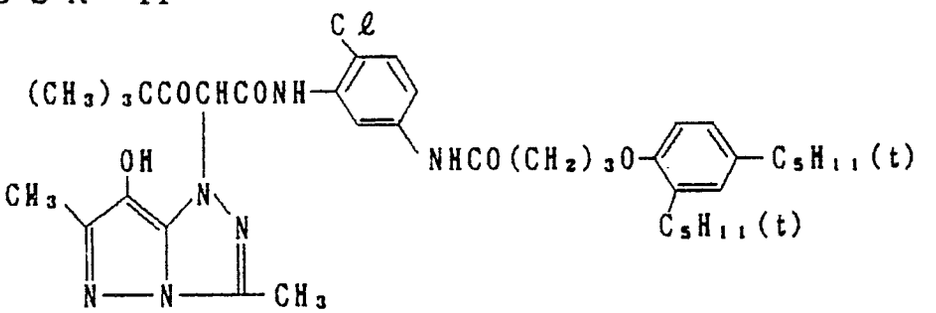

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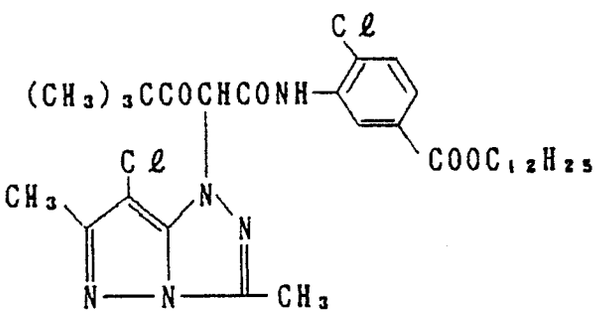

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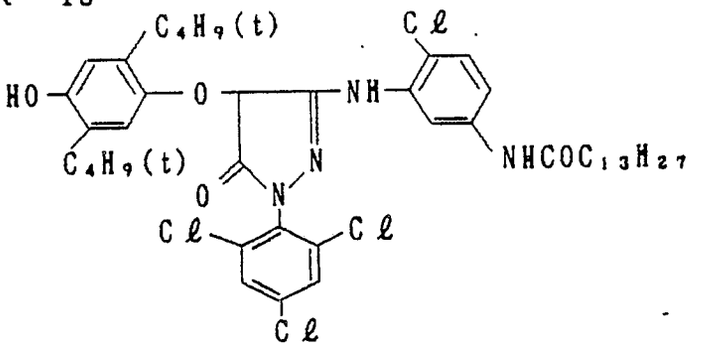

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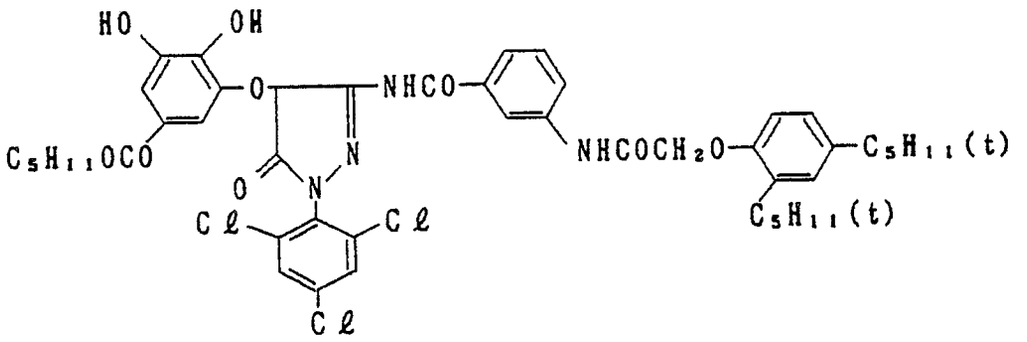

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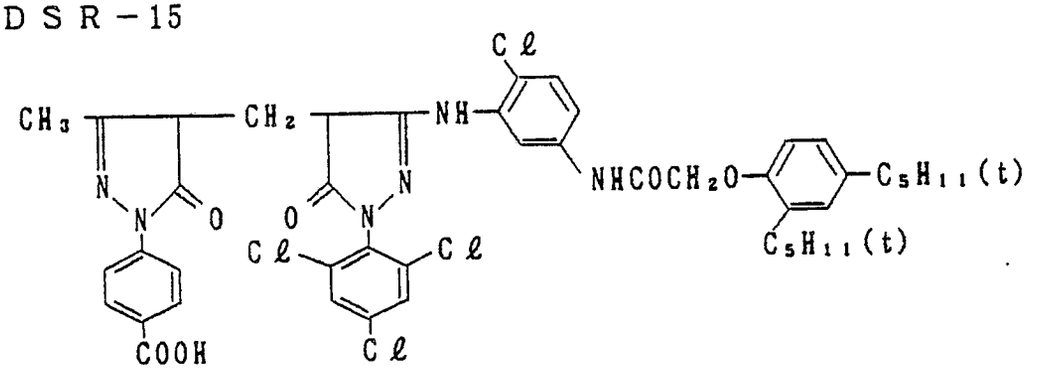

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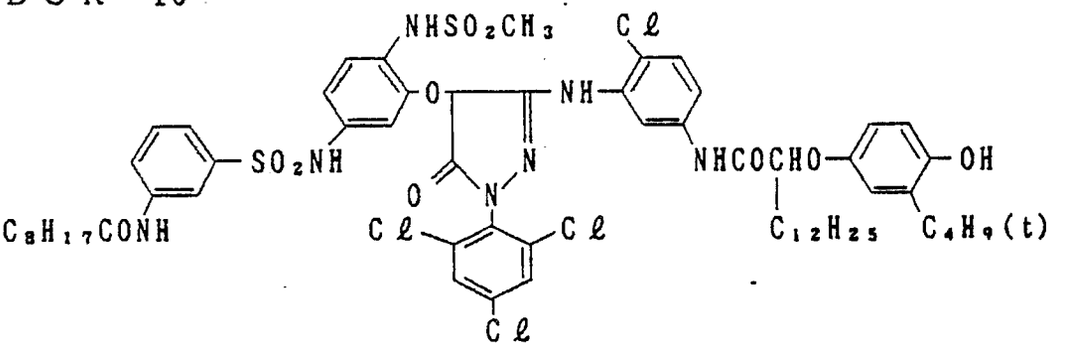

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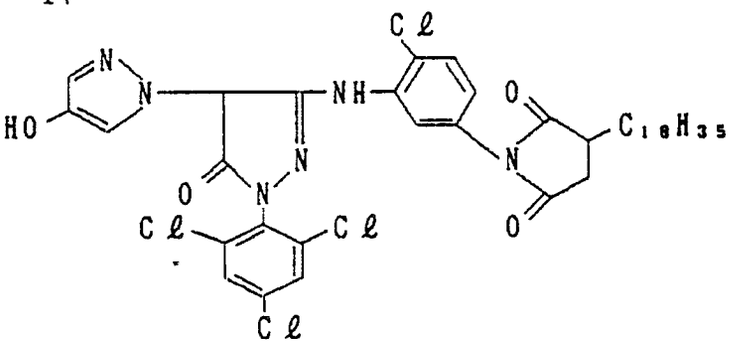

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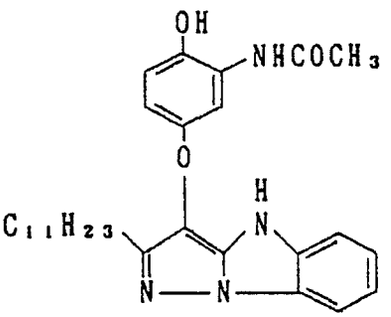

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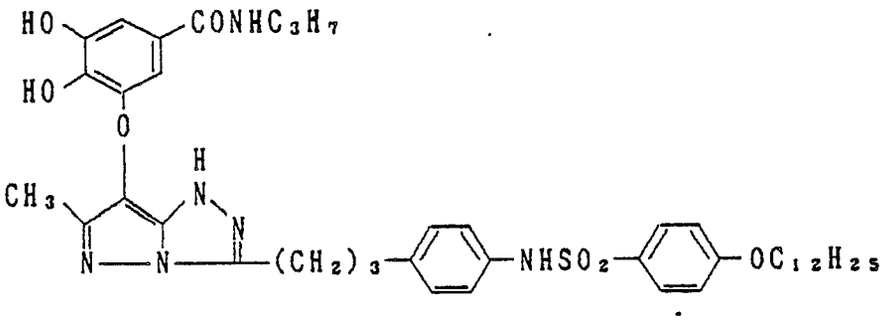

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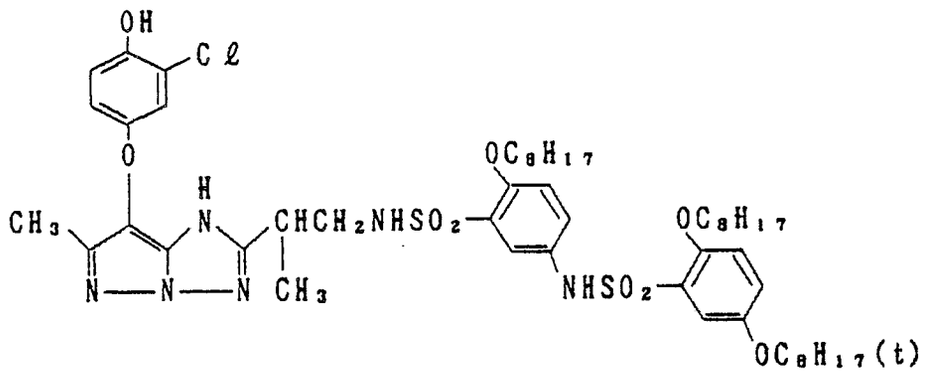

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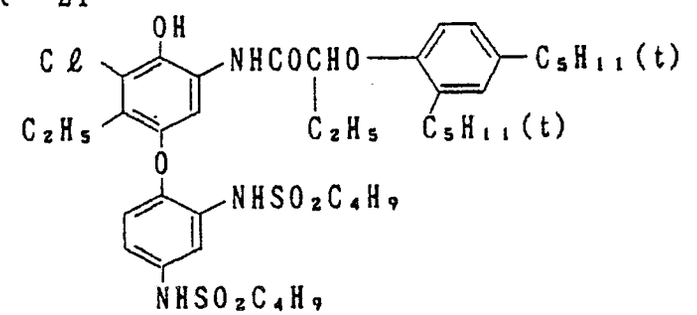

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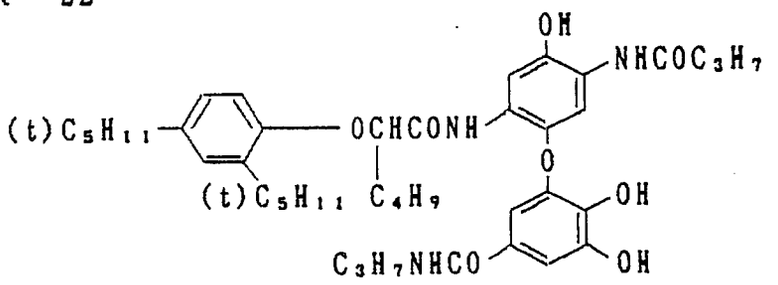

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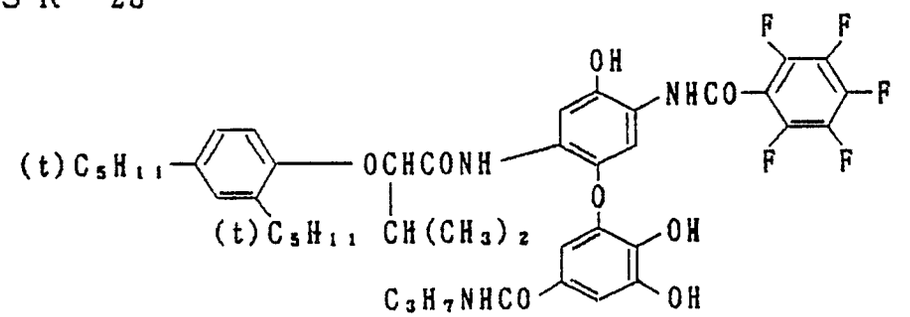

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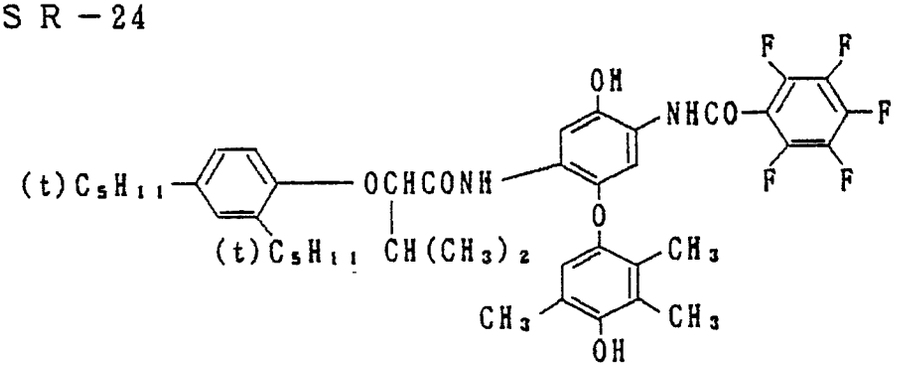

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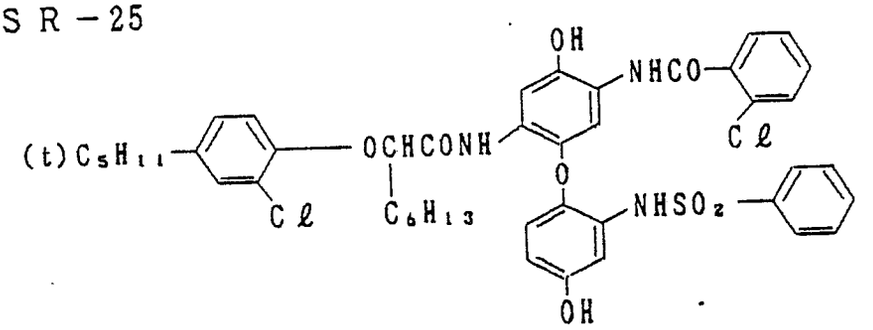

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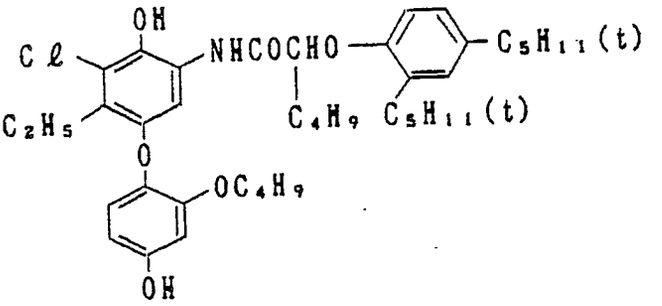

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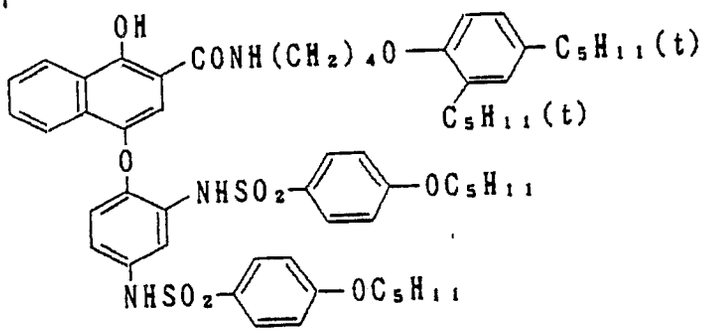

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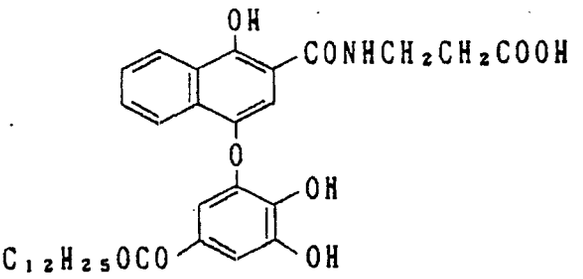

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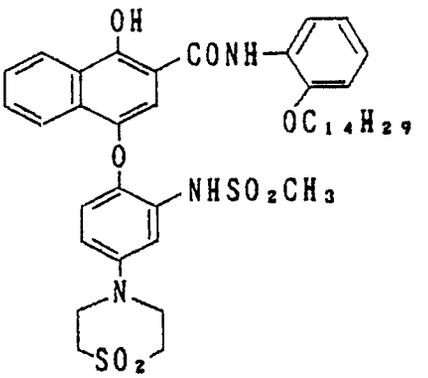

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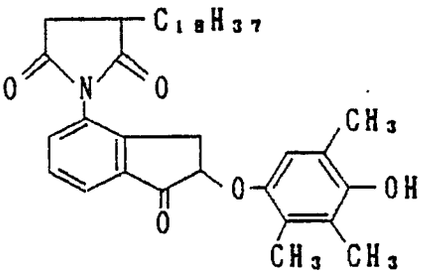

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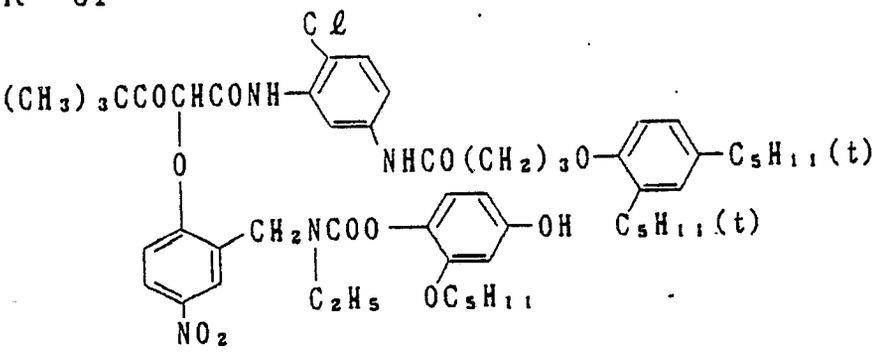
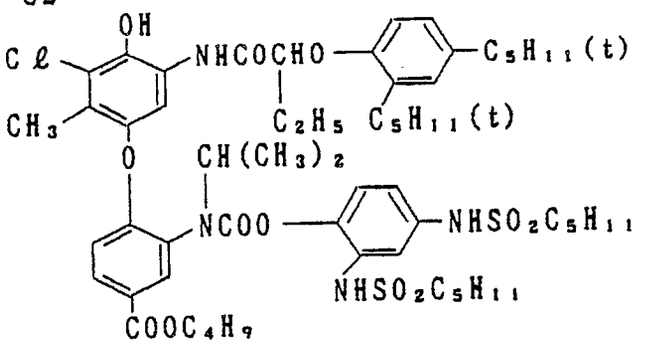
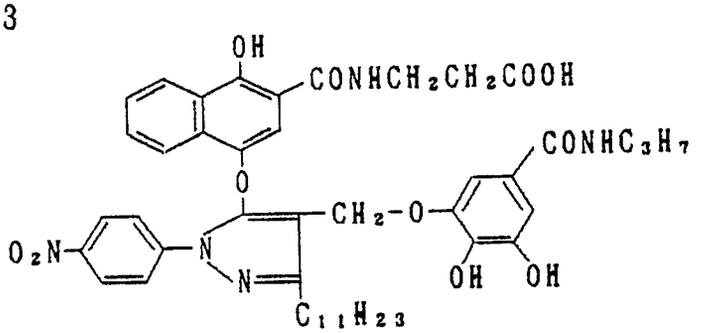


DSR-32



DSR-33



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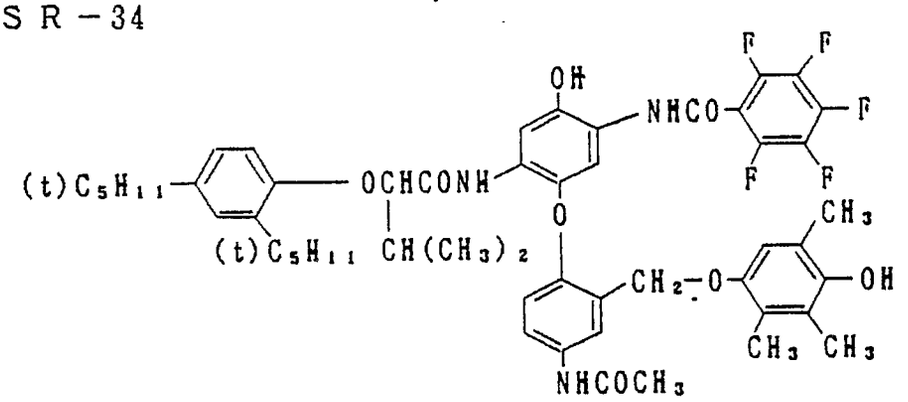

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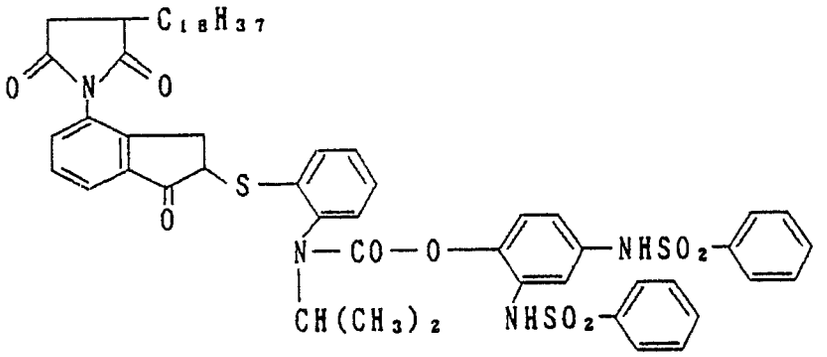

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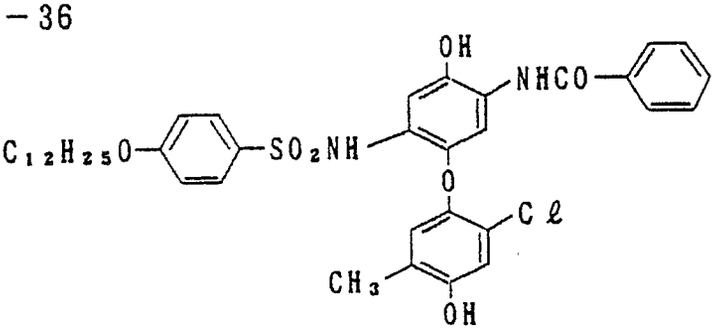
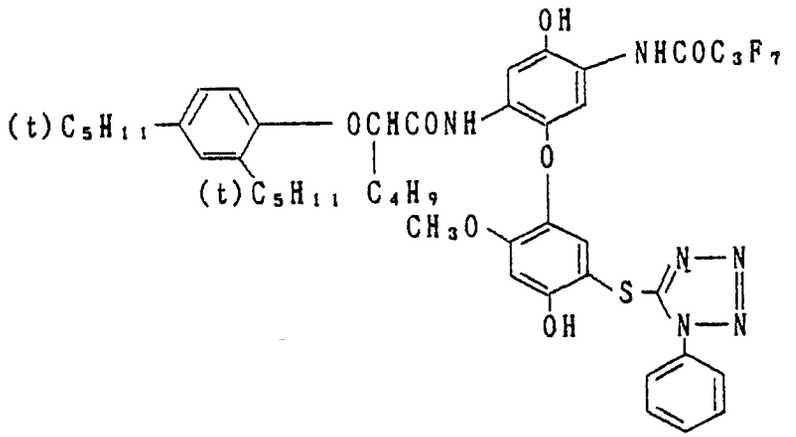
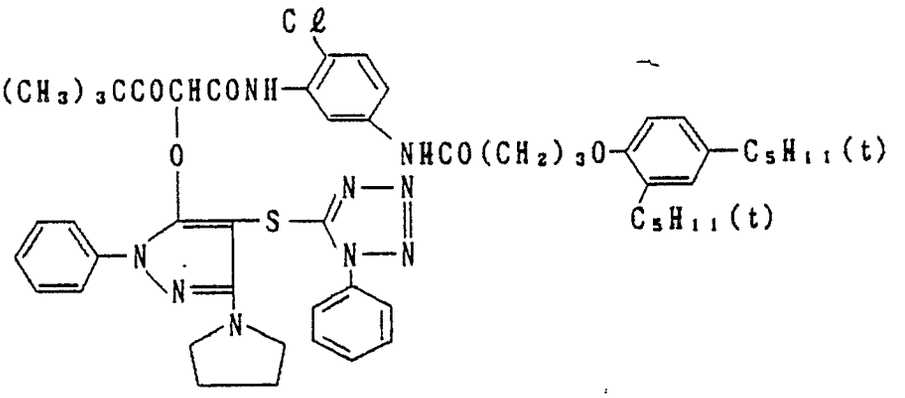


DSR-37



DSR-38



The light-sensitive material of this invention may be suitably applied to a variety of color photographic light-sensitive materials such as, for example, color photographic papers, direct positive papers, direct positive films and the like, which all are to be subjects for direct appreciation.

When the present invention is used to realize color photographic paper, a common arbitrary negative-type silver halide emulsion may be used. When the invention is used to prepare direct positive paper, preferably an unfogged surface-having internal latent image-type silver halide emulsion is used. This emulsion is used with the light-fogging method or the method in combination with a fog speck-forming agent. Such the light-sensitive material does not have its own color correction function just as color negative films do, so that it is unable to correct the doubling due to irregular absorptions owned by yellow, magenta and cyan color forming couplers, thus deteriorating the essential color reproduction, but the present invention displays its effect for such light-sensitive materials. Particularly for direct positive light-sensitive materials for direct photographing use unable to be adapted to the negative film-type color correction, the masking method utilizing the interimage effect according to this invention is very effective in the color reproduction.

In this invention, the DSR compound may be added to the light-sensitive silver halide emulsion layer and/or non-light-sensitive photographic component layer, but the addition of the compound to the light-sensitive silver halide emulsion layer is preferred.

Two or more kinds of the DSR compound may be contained in one and the same layer, or the same DSR compound may be contained in two or more different layers.

Normally, the DSR compound is used in an amount of preferably from $1x10^{-3}$ to 5 moles per mole of the silver contained in an emulsion layer, and more preferably from $1x10^{-2}$ to $5x10^{-1}$ mole.

In order to incorporate the DSR compound into the silver halide emulsion or other photographic component layer coating liquid, the DSR compound, if alkali-soluble, may be added in the form of an alkaline solution and, if oil-soluble, according to any of those methods as described in, e.g., U.S. Patent Nos. 3,322,027, 2,801,170, 2,801,171, 2,272,191 and 2,304,940, desirable to be dissolved into a high-boiling solvent, if necessary, in combination with a low-boiling solvent and then made into a finely dispersed liquid, which is then added to the silver halide emulsion or other photographic component layer coating liquid. In this instance, if necessary, other additives such as hydroquinone derivatives, ultraviolet absorbing agents, antidiscoloration agents and the like may be used. Two or more kinds of the DSR compound may be mixed to be used. Further, to detail the preferred method for adding the DSR compound in this invention, one or two or more kinds of the DSR compound, if necessary, along with other additives such as couplers, hydroquinone derivative, antidiscoloration agent, ultraviolet absorbing agent and the like, are dissolved into a high-boiling solvent such as one selected from the group of organic acid amides, carbamates, esters, ketones, urea derivatives, ethers, hydrocarbons and the like; particularly, di-n-butyl phthalate, tricresyl phosphate, triphenyl phosphate, diisooctyl azerate, di-n-butyl sebacate, tri-n-hexyl phosphate, N,N-diethyl-caprylamidobutyl, N,N-diethyl-laurylamide, n-pentadecyl-phenyl ether, dioctyl phthalate, n-nonylphenol, 3-pentadecylphenyl-ethyl ether, 2,5-di-sec-amylphenyl-butyl ether, monophenyl-di-o-chlorophenyl phosphate, fluoroparaffin, or the like, and/or a low-boiling solvent such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, butyl propionate, cyclohexanol, diethylene glycol monoacetate, nitromethane, carbon tetrachloride, chloroform, cyclohexanetetrahydrofuran, methyl alcohol, acetonitrile, dimethylformamide, dioxane, methylethyl ketone, or the like, and the solution is then mixed with an aqueous solution containing an anionic surface active agent such as an alkylbenzene sulfonate or alkylnaphthalene sulfonate and/or a nonionic surface active agent such as a sorbitansesquioleic acid ester or sorbitanmonolauric acid ester and/or a hydrophilic binder such as gelatin, and the obtained mixture liquid is then dispersed by means of a high-speed rotary mixer, colloid mill or ultrasonic disperser. And this dispersed product is then added to a silver halide emulsion or photographic component layer coating liquid.

Alternatively, the DSR compound may be dispersed by using a latex dispersing method. Latex dispersing methods and their effect are described in Japanese Patent O.P.I. Publication Nos. 74538/1974, 59943/1976 and 32552/1979, and Research Disclosure No. 14850, Aug. 1976, pp.77-79.

Suitable latexes for the above method are those homopolymers, copolymers and terpolymers of such monomers as, e.g., styrene, acrylates, n-butyl acrylate, n-butyl methacrylate, 2-acetacetoxyethyl methacrylate, 2-(methacryloyloxy)ethyltrimethylammonium methosulfate, sodium 3-(methacryloyloxy)-propan-1-sulfonate, N-isopropylacrylamide, N-[2-(2-methyl-4-oxopentyl)]acrylamide, 2-acrylamido-2-methyl-propansulfonic acid and the like.

The above DSR compound may be synthesized in accordance with any of those methods as disclosed in Japanese Patent O.P.I. Publication Nos. 138638/1982, 155537/1982, 171334/1982, 111941/1983, 53643/1986, 84646/1986, 86751/1986, 102646/1986, 102647/1986, 107245/1986, 113060/1986, and the like.

The compound or its precursor which is to be released corresponding to the density of an image at the time of development from the DSR compound to be used in this invention and which is to effect coupling reaction or oxidation-reduction reaction with the oxidation product of a color developing agent at the time of development, when present in a light-sensitive emulsion layer, restrains the dye-forming reaction (coupling reaction) according to the image density to thereby improve the image sharpness, i.e., to bring about a so-called intraimage effect, and on the other hand, when the released compound to scavenge the oxidation product of the color developing agent is diffused into other layers, the compound hinders the dye-forming reaction of the other layers according to the image density of the diffusing-source layer, bringing about a masking effect, so-called interimage effect, thus enabling to display two different image effects.

The DSR compound, as stated above, may be added to the silver halide emulsion layer and/or non-light-sensitive photographic layer; preferably to at least one silver halide emulsion layer. For example, when the compound is to be applied to an ordinary multilayer color photographic light-sensitive material comprising blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers, the compound may be incorporated into one or two or more of these layers.

At least one of the silver halide emulsion layers of the silver halide light-sensitive color photographic material of this invention contains a silver halide comprised substantially of silver chloride, silver chlorobromide or silver chloroiodobromide. This includes the case where the silver halide is a mixture in combination of silver chloride with silver bromide. The word 'substantially' herein implies that the containing of other silver halide constituent is allowed as long as it is in so small an amount as not to impede the functional effect of the above compound component; that is, to realize a rapid developability, the silver

halide is desirable to contain a chlorine atom as its halide component, and particularly desirable to be silver chlorobromide or silver chloroiodobromide containing at least 1% silver chloride.

The whole amount of the silver (coating weight of silver) of the light-sensitive silver halide emulsion layers of the silver halide light-sensitive color photographic material of this invention, although not particularly restricted, is preferably from 0.3 to 1.5 g/m^2. That is, in order to obtain an excellent image quality, the coating weight of silver is preferably not more than 1 g/m^2, while on the other hand, to obtain a high maximum density and a high sensitivity, the coating weight of silver is preferably not less than 0.3 g/m^2.

Where the present invention is applied to producing a color photographic paper, as its silver halide, negative-type silver halide grains are used, while where the invention is applied to realizing a direct positive light-sensitive material, internal latent image-type silver halide grains are suitably used. To refer to the silver halide grain to be used in a color photographic paper, its crystal may be either regular or twin or in other form, and those grains whose crystal is of an arbitrary [100] face-[111] face proportion may be used. Further, the crystal of these silver halide grains may be of either homogeneous structure from the inside through the outside or heterogeneous structure stratified with the inside and the outside (core/shell type). In addition, the silver halide may be of either the type of forming a latent image mainly on the grain surface or the type of forming it inside the grain. Further, planar silver halide grains may also be used.

The silver halide emulsion suitably usable in this invention is a monodisperse emulsion, which may be one prepared according to any of the conventionally known acidic method, neutral method or ammoniacal method.

Also, for example, the emulsion may also be prepared in the manner that seed grains are prepared by the acid method, and they are then grown up to a desired grain size by the ammoniacal method capable of growing them faster. When growing silver halide grains, it is desirable to control the pH and pAg of the reaction pot, and to pour and mix into the pot sequentially simultaneously silver ions and halide ions in amounts meeting the growth rate of silver halide grains as described in, e.g., Japanese Patent O.P.I. Publication No. 48521/1979.

The silver halide emulsion to be used in this invention may be chemically sensitized by active gelatin; a sulfur sensitizer such as an arylthiocarbamide, thiourea, cystine, etc.; a selenium sensitizer; a reduction sensitizer such as stannous chloride, thiourea dioxide, polyamine, etc.; a noble metal sensitizer, e.g., a gold sensitizer such as potassium aurithiocyanate, potassium chloroaurate, 2-aurothio-3-methylbenzothiazolium chloride, etc., or a water-soluble salt sensitizer such as of, e.g., ruthenium, palladium, platinum, rhodium, iridium, etc., particularly ammonium chloropalladate, potassium chloroplatinate, or sodium chloropalladate (some of these compounds function as sensitizers or antifoggants depending upon their amount used); these may be used alone or in arbitrary combination (e.g., in combination of gold sensitizer with sulfur sensitizer, gold sensitizer with selenium sensitizer, etc.).

The silver halide emulsion may be chemically ripened with the addition of a sulfur-containing compound thereto, and into the emulsion may be incorporated at least one hydroxytetrazaindene and at least one mercapto group-having nitrogen-containing heterocyclic compound before, during or after the chemical ripening.

The silver halide to be used in this invention, in order to be made sensitive to a desired wavelength region, may be optically sensitized by adding thereto an appropriate sensitizing dye in an amount of 5×10^{-8} to 3×10^{-3} mole per mole of silver halide. A variety of sensitizing dyes may be used alone or in combination of two or more of them. Those sensitizing dyes advantageously usable in this invention include the following:

Sensitizing dyes usable for a blue-sensitive silver halide emulsion layer include those sensitizing dyes as disclosed in, e.g., West German Patent No. 929,080, U.S. Patent Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 2,656,959, 3,672,897, 3,694,217, 4,025,349 and 4,046,572, British Patent No. 1,242,588, Japanese Patent Examined Publication Nos. 14030/1969 and 24844/1977. Typical sensitizing dyes for a green-sensitive silver halide emulsion layer include those cyanine dyes, merocyanine dyes and complex cyanine dyes as disclosed in, e.g., U.S. Patent Nos. 1,939,201, 2,072,908, 2,739,149 and 2,945,736, and British Patent No.505,979. And typical sensitizing dyes for a red-sensitive silver halide emulsion layer includ those cyanine dyes, merocyanine dyes and complex cyanine dyes as disclosed in, e.g., U.S. Patent Nos. 2,269,234, 2,270,378, 2,442,710, 2,454,629 and 2,776,280. Further, those cyanine dyes, merocyanine dyes and complex cyanine dyes as disclosed in U.S. Patent Nos. 2,213,995, 2,493,748 and 2,519,001, and West German Patent No. 929,080 may be advantageously used in a green-sensitive silver halide emulsion layer or red-sensitive silver halide emulsion layer.

These sensitizing dyes may be used alone or in combination. Combination of such sensitizing dyes is often used particularly for the purpose of supersensitization. Its typical examples are described in U.S.

Patent Nos. 2,688,545, 2,977,229, 3,397,060, 3,552,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862 and 4,026,707, British Patent Nos. 1,344,281 and 1,509,803, Japanese Patent Examined Publication Nos. 4936/1968 and 12375/1978, and Japanese Patent O.P.I. Publication Nos. 110618/1977 and 109925/1977.

The internal latent image-type silver halide emulsion to be used in applying this invention to a direct positive light-sensitive material will now be explained. Also in the case of a direct positive-type silver halide light-sensitive material, at least one of its silver halide emulsion layers has a silver halide comprised substantially of silver chloride, silver chlorobromide or silver chloroiodobromide, and such the emulsion includes those conversion-type silver halide emulsions by the conversion method as described in, e.g, U.S. Patent No. 2,592,250; those silver halide emulsions having internally chemically sensitized silver halide grains as described in U.S. Patent Nos. 3,206,316, 3,317,322 and 3,367,778; those silver halide emulsions having polyvalent metal ions-built-in silver halide grains as described in U.S. Patent Nos. 3,271,157, 3,447,927 and 3,531,291; those silver halide emulsions with doping agent-containing silver halide grains whose grain surface is weakly chemically sensitized as described in U.S. Patent No. 3,761,276; those core/shell-type silver halide emulsions by the stratification method as described in Japanese Patent O.P.I. Publication Nos. 8524/1975, 38525/1975 and 2408/1978; and those silver halide emulsions as described in Japanese Patent O.P.I. Publication Nos. 156614/1977, 127549/1980.

In this invention, when the internal image-type silver halide is used, the silver halide is particularly desirable to be one made of laminated-type grains.

Such the silver halide may be prepared in similar manner to ordinary laminated-type silver halides. For example, as is described in Japanese Patent O.P.I. Publication Nos. 8524/1975, 38525/1975, 60222/1978 and 1524/1980, and U.S. Patent No. 3,206,313, it may be prepared by a method wherein after forming silver chloride grains, a bromide is added to the grains to convert them into silver bromide grains, and further to the grains are added a halide and silver nitrate to make lamination thereover, or by a method wherein silver iodobromide grains are formed with a less excessive halide, and the grains are laminated thereon with silver chloride and then with silver bromide.

An internal image-type silver halide emulsion is used in this invention, to this emulsion may be added various photographic additives. For example, optical sensitizers usable in this invention include cyanines, merocyanines, three- or four-nucleus merocyanine, three- or four-nucleus cyanines, styryls, horopolacyanines, hemicyanines, oxonols and hemioxonols.

The internal image-type silver halide emulsion to be used in this invention may be subjected to supersensitization. Methods for supersensitization are described in, for example, the 'Review of Supersensitization' (Photographic Science and Engineering (PSE) vol.18, p.4418 (1974)).

The internal image-type silver halide emulsion to be used in this invention, in order to restrain its surface sensitivity as much low as possible and to provide a lower maximum density and more stable characteristics, may contain a commonly usable stabilizer such as, e.g., an azainden ring-having compound, mercapto group-having heterocyclic compound or the like.

The azaindene ring-having compound is preferably, e.g., 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene. As for the mercapto group-having heterocyclic compound, its nitrogen-containing heterocyclic ring represents a pyrazole ring, 1,2,4-triazole ring, 1,2,3-triazole ring, 1,3,4-thiadiazole ring, 1,2,3-thiadiazole ring, 1,2,4-thiadiazole ring, 1,2,5-thiadiazole ring, 1,2,3,4-tetrazole ring, pyridazine ring, 1,2,3-triazine ring, 1,2,4-triazine ring, 1,3,5-triazine ring, or the like, or a ring formed by the condensation of two or three of these rings such as, e.g., triazolotriazole ring, diazaindene ring, triazaindene ring, tetrazaindene ring, pentazaindene ring, etc., or phthalazinone ring, indazole ring or the like; and particularly preferred as the compound is 1-phenyl-5-mercaptotetrazole.

The silver halide emulsion layers of the light-sensitive material of this invention may contain couplers other than the foregoing respective DSR compounds, i.e., compounds capable of reacting with the oxidation product of a color developing agent to thereby form dyes.

As the above-mentioned couplers, a large variety of couplers including yellow couplers, magenta couplers and cyan couplers may be used with no particular restriction. These couplers may be either two-equivalent-type couplers or four-equivalent-type couplers. Further, diffusible dye-releasing-type couplers may also be used in combination with these couplers.

Useful couplers as the above yellow coupler include open-chain ketomethylene compounds and the so-called two-equivalent-type couplers including active site-o-aryl- substituted couplers, active site-o-acyl-substituted couplers, active site hydantoin compound-substituted couplers, active site urazole compound-substituted couplers, active site succinic acid imido compound-substituted couplers, active site fluorine-substituted couplers, active site chlorine or bromine-substituted couplers, active site-o-sulfonyl-substituted couplers and the like. Particular examples of the yellow coupler usable in this invention are found in U.S.

Patent Nos. 2,875,057, 3,265,506, 3,409,194, 3,551,155, 3,582,322, 3,725,072 and 3,891,445, West German Patent No. 1,547,868, West German OLS Patent Nos. 2,219,917, 2,261,361 and 2,414,006, British Patent No. 1,425,020, Japanese Patent Examined Publication No. 10783/1976, Japanese Patent O.P.I. Publication Nos. 26133/1972, 73147/1973, 102636/1976, 6341/1975, 123342,1975, 130442/1975, 21827/1976, 87650/1975, 82424/1977, 115219/1977 and 95346/1983.

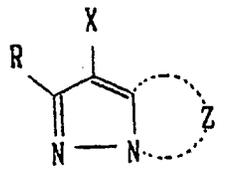
Magenta couplers usable in this invention include pyrazolone-type, pyrazolotriazole-type, pyrazolinobenzimidazole-type and indazolone-type compounds.

These magenta couplers may be not only four-equivalent-type but also two-equivalent-type couplers, and particular examples of the magenta coupler useful in this invention are found in U.S. Patent Nos. 2,600,788, 2,983,608, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,834,908 and 3,891,445, West German Patent No. 1,810,464, West German OLS Patent Nos. 2,408,665, 2,417,945, 2,418,959 and 2,424,467, Japanese Patent Examined Publication No. 6031/1965, Japanese Patent O.P.I. Publication Nos. 20826/1976, 58922/1977, 129538/1974, 74027/1974, 159336/1975, 42121/1977, 74028/1974, 60233/1975, 26541/1976 and 55122/1978, and Japanese Patent Application No. 110943/1980.

Among those magenta couplers listed hereinabove, pyrazoloazole type compound represented by the formula [M-I] may advantageously be used in the present invention:

The foregoing pyrazoloazole-type magenta coupler according to the present invention has the following Formula [M-I]:

Formula [M-I]



wherein Z is a group of non-metal atoms necessary to form a nitrogen-containing heterocyclic ring, provided that the ring to be formed by the Z may be allowed to have a substituent; X is a hydrogen atom or a group capable of being split off upon reaction with the oxidation product of a color developing agent; and R is a hydrogen atom or a substituent.

The substituent represented by the R, although not specially restricted, is typified by alkyl, aryl, anilino, acylamino, sulfonamido, alkylthio, arylthio, alkenyl, cycloalkyl and the like groups, and in addition, by a halogen atom and those groups including cycloalkenyl, alkinyl, heterocyclic, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl and heterocyclic thio groups, and spiro compound residue, cross-linked hydrocarbon compound residue and the like.

The alkyl group represented by the R is preferably a straight-chain or branched-chain alkyl group having from 1 to 32 carbon atoms.

The aryl group represented by the R is preferably a phenyl group.

The acylamino group represented by the R is preferably an alkylcarbonylamino group, arylcarbonylamino group or the like.

The sulfonamido group represented by the R is such as an alkylsulfonylamino group, arylsulfonylamino group, or the like.

The alkyl and aryl constituents of the alkylthio and arylthio groups are the same as the above alkyl and aryl groups, respectively, represented by the foregoing R.

The alkenyl group represented by the R is one having from 2 to 32 carbon atoms, and the cycloalkyl group is one having from 3 to 12 carbon atoms, and particularly preferably from 5 to 7 carbon atoms. The alkenyl group may be either straight-chain or branched-chain.

The cycloalkenyl group represented by the R is one having from 3 to 12 carbon atoms, and more preferably from 5 to 7 carbon atoms.

The sulfonyl group represented by the R is such as an alkylsulfonyl group, arylsulfonyl group or the like.

The sulfinyl group is such as an alkylsulfinyl group, arylsulfinyl group or the like.

The phosphonyl group is such as an alkylphosphonyl group, alkoxyphosphonyl group aryloxyphosphonyl group, arylphosphonyl group or the like.

The acyl group is such as an alkylcarbonyl group, arylcarbonyl group or the like.

The carbamoyl group is such as an alkylcarbamoyl group, arylcarbamoyl group or the like.

The sulfamoyl group is such as an alkylsulfamoyl group, arylsulfamoyl group or the like.

The acyloxy group is such as an alkylcarbonyloxy group, arylcarbonyloxy group or the like.

The carbamoyloxy group is such as an alkylcarbamoyloxy group, arylcarbamoyloxy group or the like.

The ureido group is such as an alkylureido group, arylureido group or the like.

The sulfamoylamino group is such as an alkylsulfamoylamino group, arylsulfamoylamino group or the like.

The heterocyclic group is preferably a 5- to 7-member heterocyclic group such as a 2-furyl group, 2-thienyl group, 2-pyrimidinyl group, 2-benzothiazolyl group or the like.

The heterocyclic oxy group is preferably one having a 5-to 7-member heterocyclic ring, such as a 3,4,5,6-tetrahydropyranyl-2-oxy group, 1-phenyltetrazole-5-oxy group or the like.

The heterocyclic thio group is preferably a 5- to 7-member heterocyclic thio group such as a 2-pyridylthio group, 2-benzothiazolylthio group, 2,4-diphenoxy-1,3,5-triazole-6-thio group or the like.

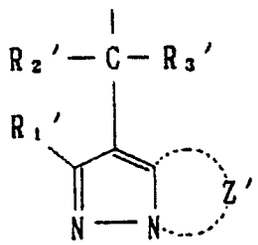
The siloxy group is such as a trimethylsiloxy group, triethylsiloxy group, dimethylbutylsiloxy group or the like.

The imido group is such as a succinic acid imido group, 3-heptadecyl-succinic acid imido group, phthalimido group, glutarimido group or the like.

The spiro compound residue is such as spiro[3.3]heptan-1-yl, or the like.

The cross-linked hydrocarbon compound residue is such as bicyclo[2.2.1]heptan-1-yl, tricyclo-[3.3.1.1^{3,7}]decan-1-yl, 7,7-dimethyl-bicyclo[2.2.1]heptan-1-yl, or the like.

The group represented by the X, which is capable of being split off upon reaction with the oxidation product of a color developing agent, is, for example, a halogen atom (such as chlorine, bromine, fluorine) or an alkoxy group, aryloxy group, heterocyclic oxy group, acyloxy group, sulfonyloxy group, alkoxycarbonyloxy group, aryloxycarbonyl group, alkyloxalyloxy group, alkoxyoxalyloxy group, alkylthio group, arylthio group, heterocyclic thio group, alkyloxythiocarbonylthio group, acylamino group, sulfonamido group, nitrogen-containing heterocyclic group combined by a nitrogen atom, alkyloxycarbonylamino group, aryloxycarbonylamino group, carboxyl group, or group having the formula:

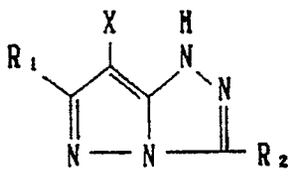


where R_1' is as defined in the foregoing R; Z' is as defined in the foregoing Z; R_2' and R_3' each is a hydrogen atom, an aryl, alkyl or heterocyclic group; and preferably a halogen atom, and more preferably a chlorine atom.

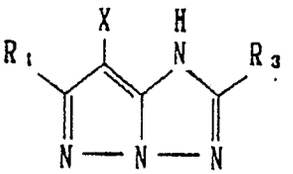
The nitrogen-containing heterocyclic ring formed by the Z or Z' is such as a pyrazole ring, imidazole ring, triazole ring or tetrazole ring, which each may have a substituent. Examples of the substituent include those represented by the foregoing R.

The compounds having Formula [M-I], more particularly, include those represented by, e.g:, the following Formulas [M-II] through [M-VII]:

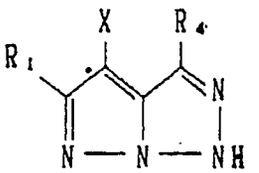
[M-II]



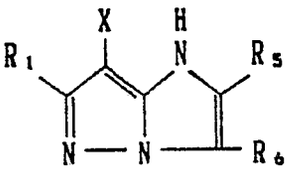
[M-III]



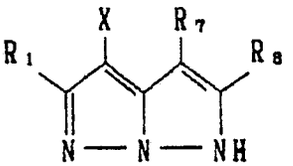
[M-IV]



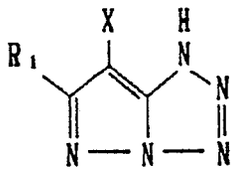
[M-V]



[M-VI]



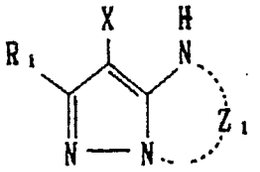
[M-VII]



In the above Formulas [M-II] through [M-VII], R_1 through R_8 and X are as defined in the foregoing R and X, respectively, wherein the R_5 and R_6 may form a ring together, examples of which ring include, e.g., a benzene ring.

Further, preferred among the compounds having Formula [M-I] are those having the following Formula [M-VIII]:

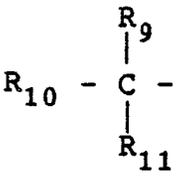
Formula [M-VIII]



wherein R_1, X and Z_1 are as defined in the R, X and Z, respectively, of Formula [M-I].

Particularly preferred among the magenta couplers having Formulas [M-II] through [M-VII] are those magenta couplers having Formula [M-II].

The most preferred as the substituent R or R_1 to the above-mentioned heterocyclic ring are those having the following Formula [M-IX]:



wherein R_9, R_{10} and R_{11} are as defined in the foregoing R.

Two out of the R_9, R_{10} and R_{11}, e.g., R_9 and R_{10}, may combine with each other to form a saturated or unsaturated ring such as, e.g., cycloalkene, cycloalkene, heterocyclic ring, and further the formed ring may also combine with the R_{11} to constitute a cross-linked organic hydrocarbon compound residue.

The preferred case of Formula [M-IX] is where (i) at least two of the R_9 through R_{11}, are alkyl groups, or (ii) one of the R_9 through R_{11}, e.g., the R_{11} is a hydrogen atom and the other two, both R_9 and R_{10}, combine together with the immediate carbon atom to form a cycloalkyl group.

Further, the case (i) is more preferably where two of the R_9 through R_{11} are alkyl groups and the other one is a hydrogen atom or an alkyl group.

Preferred as the substituent which the ring formed by the Z of Formula [M-I] or the ring formed by the Z_1 of Formula [M-VIII] may have or as the R_2 through R_8 of Formulas [M-II] through [M-VI] are those having the following Formula [M-X]:

Formula [M-X]

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

wherein R^1 is an alkylene group, R^2 is an alkyl group, cycloalkyl group or aryl group.

The alkylene group represented by the R^1 is an either straight-chain or branched-chain alkylene group of which the straight-chain portion has preferably not less than 2 carbon atoms, and more preferably from 3 to 6 carbon atoms.

The cycloalkyl group represented by the R^2 is preferably a 5- or 6-member cycloalkyl group.

The following are examples of the compound of this invention.

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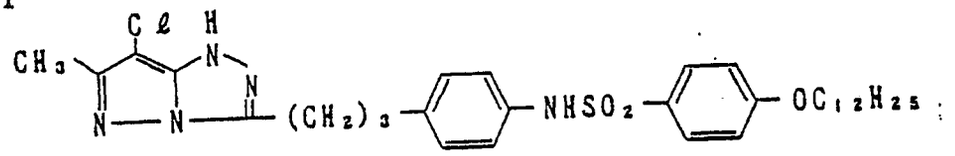

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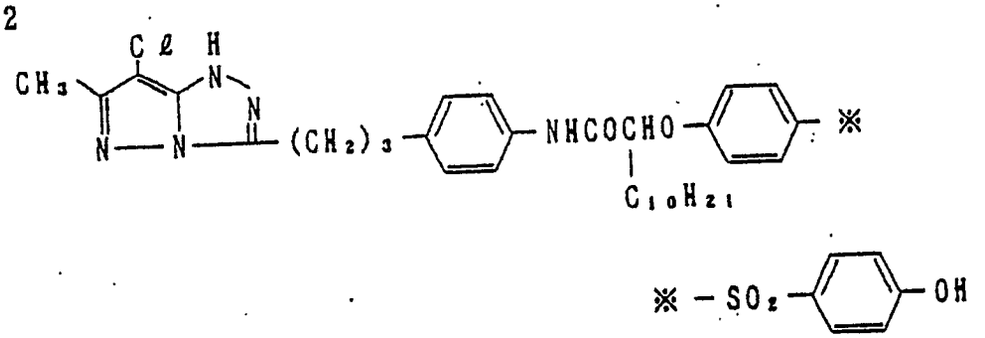

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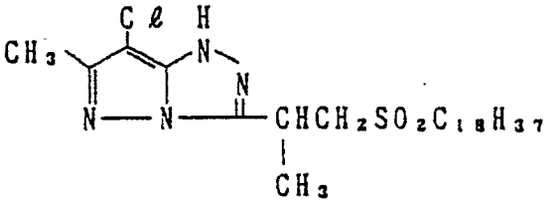

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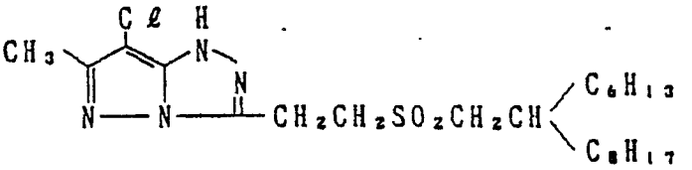

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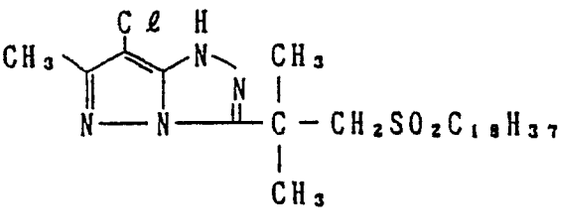

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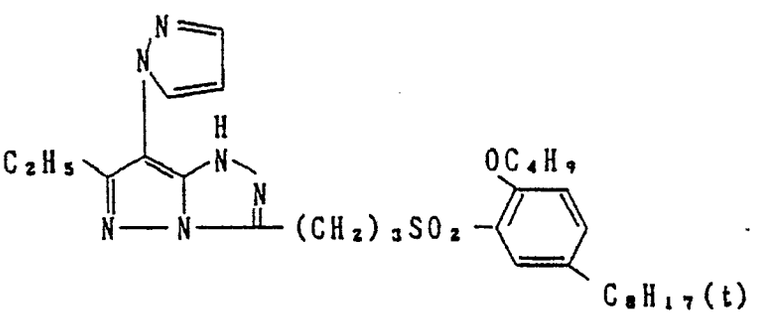

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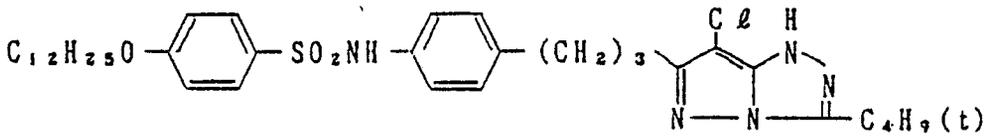

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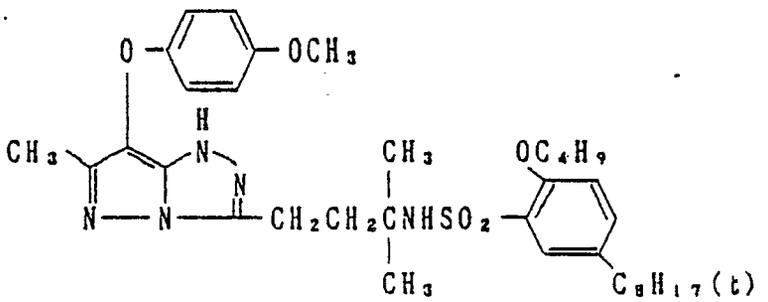

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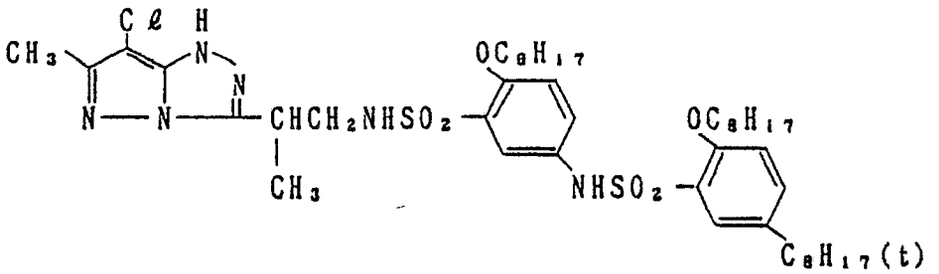

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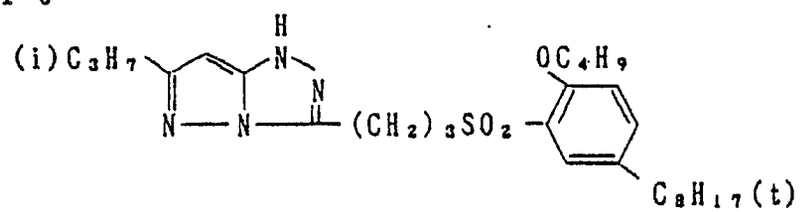

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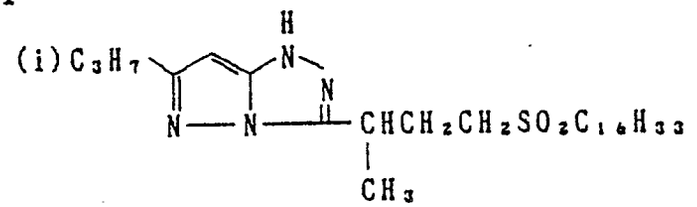

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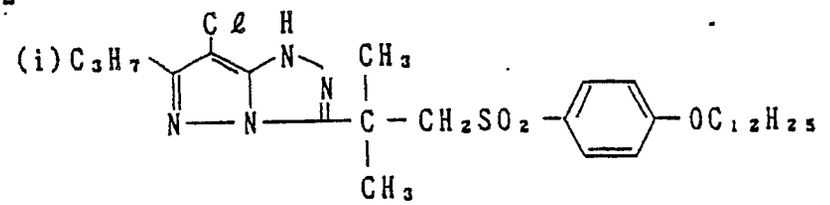

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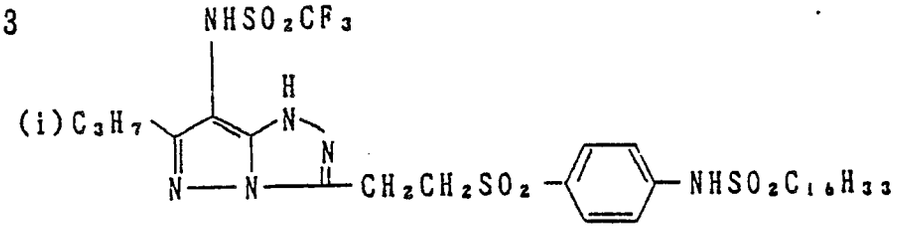

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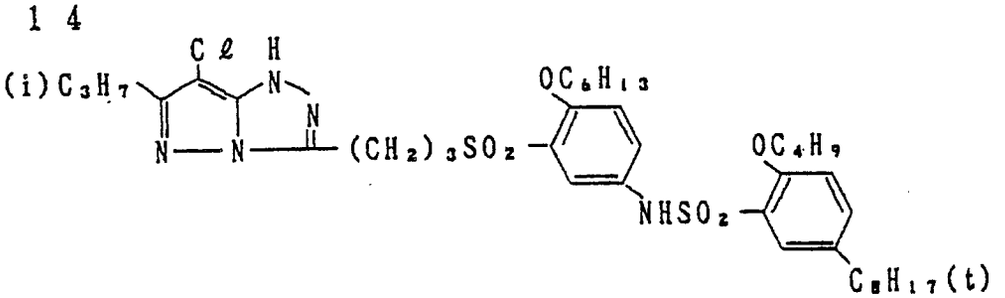

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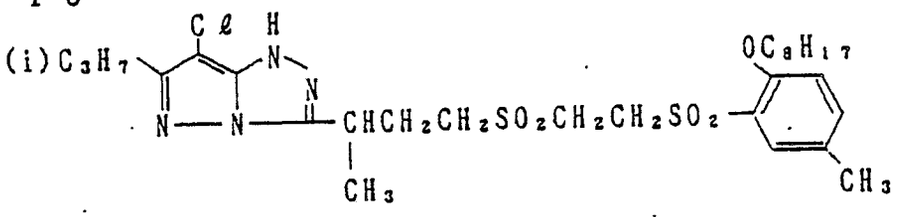

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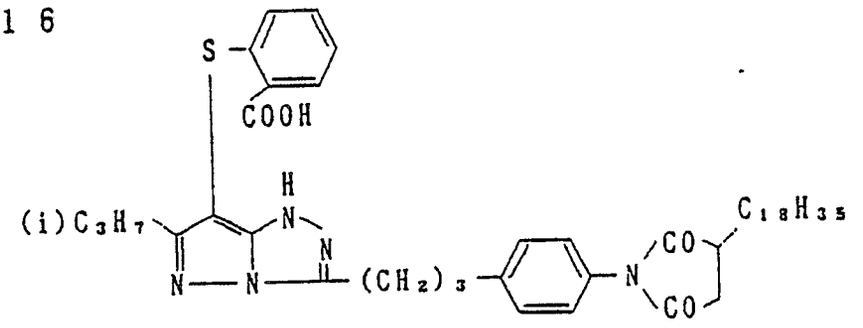

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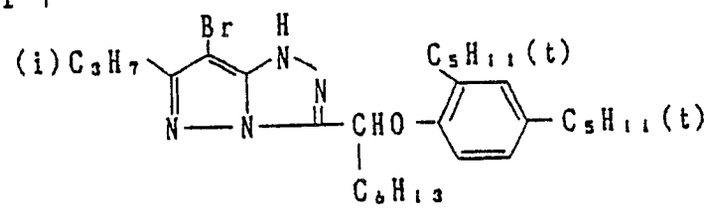

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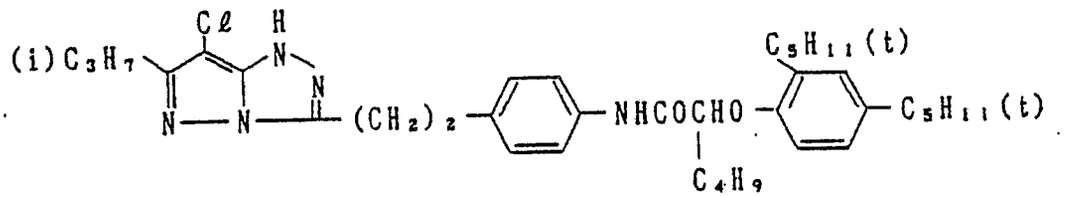

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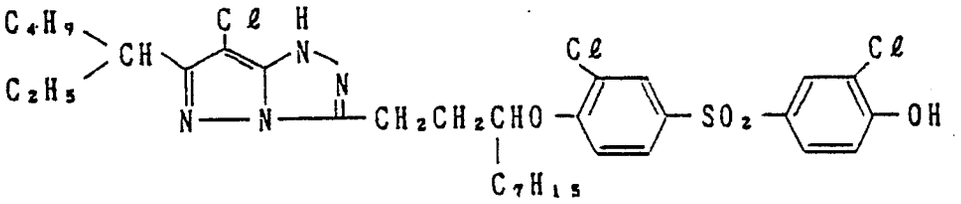

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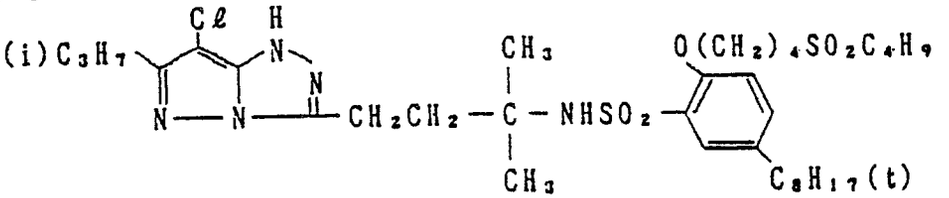

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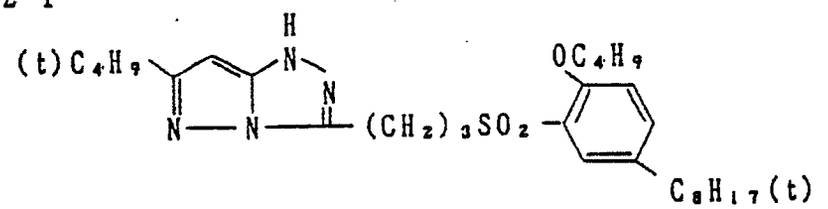

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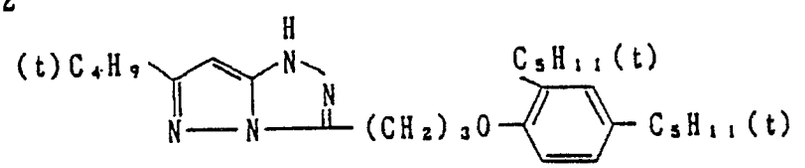

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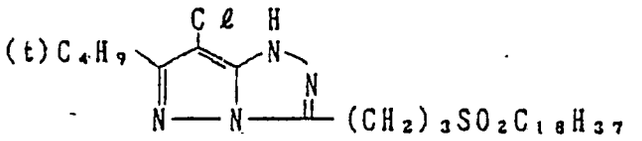

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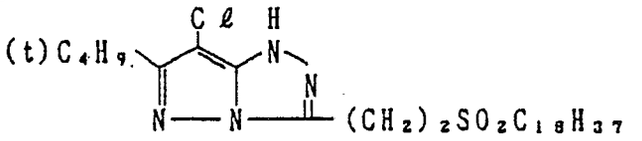

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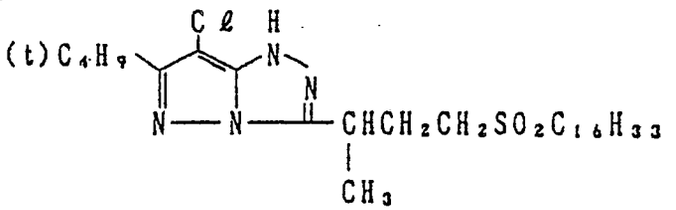

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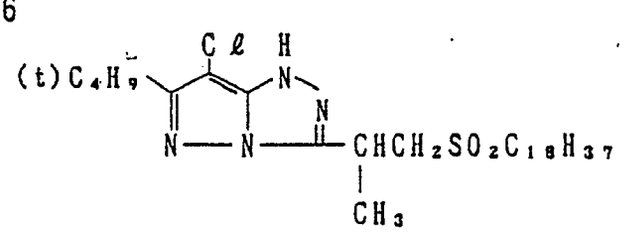

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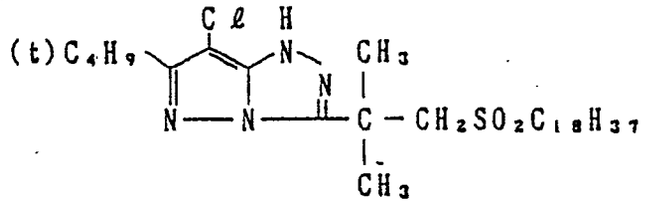

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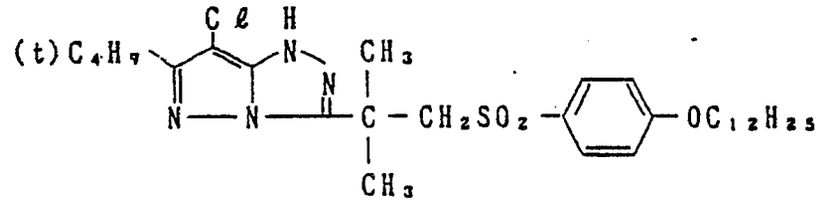

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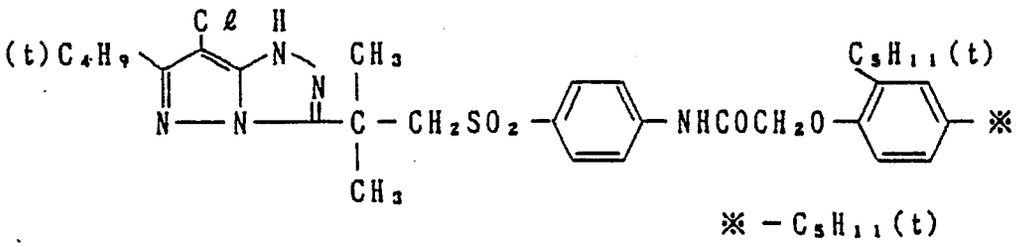

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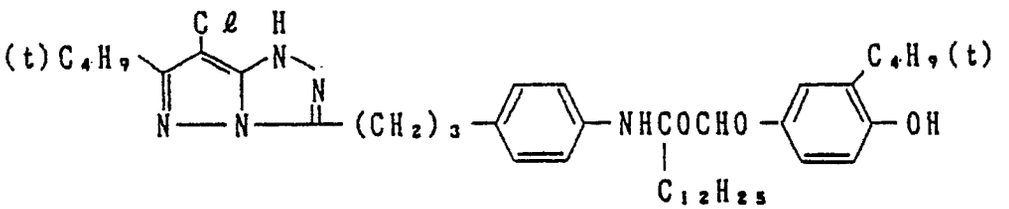

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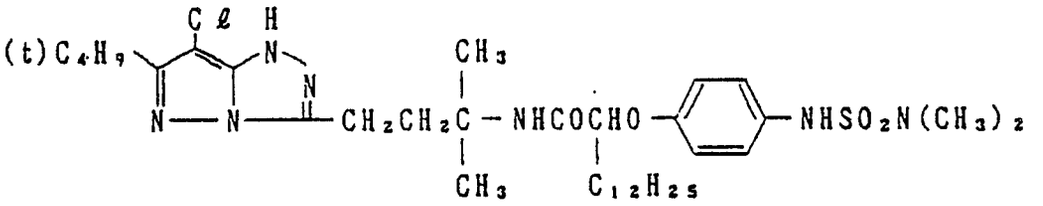

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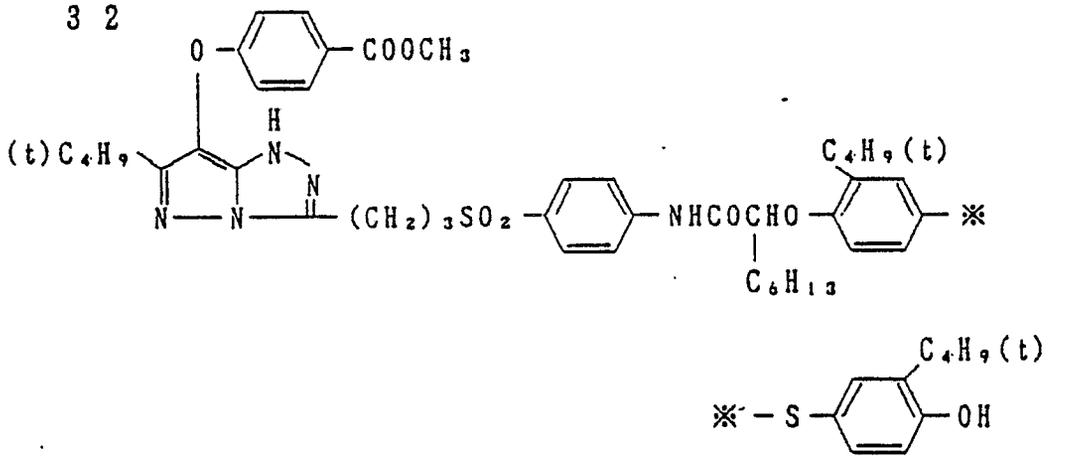

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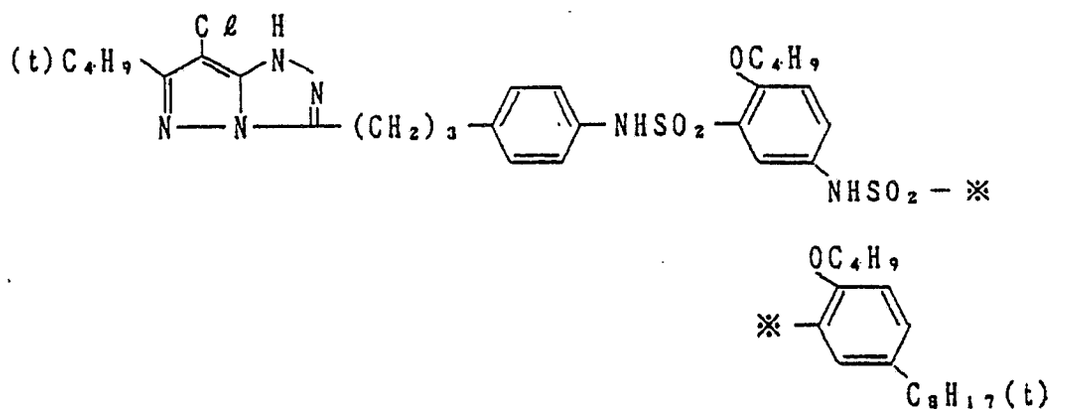

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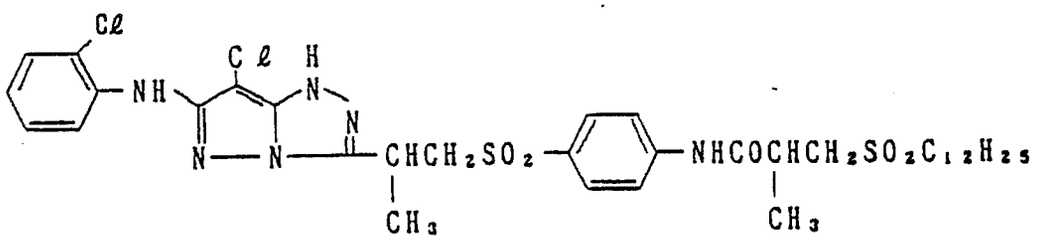

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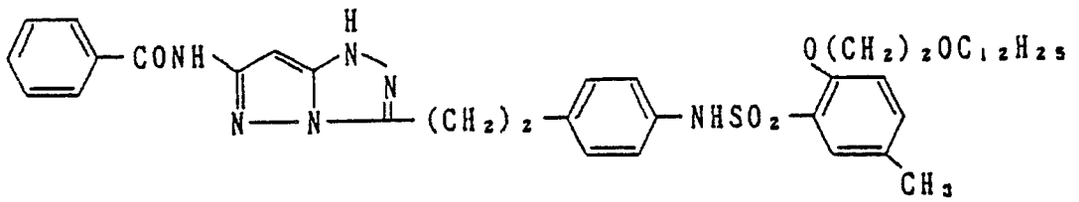

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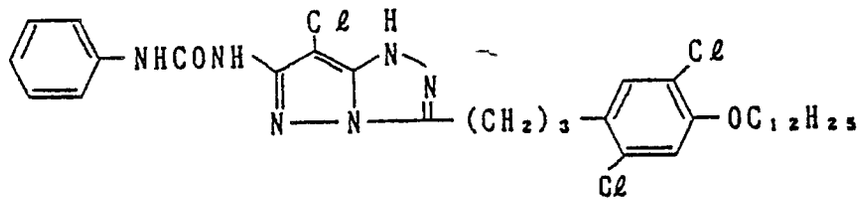

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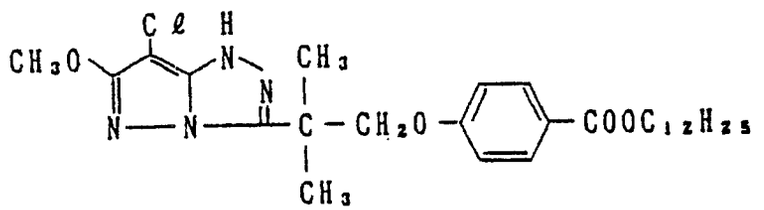

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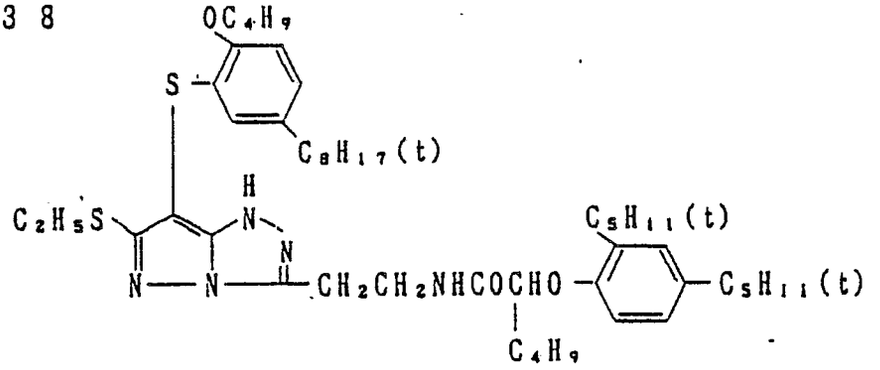

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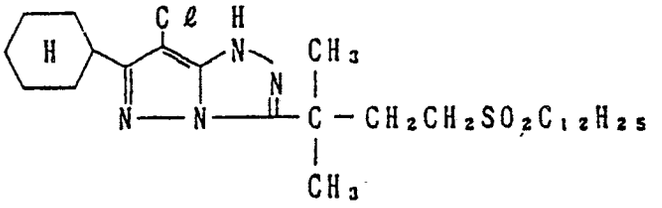

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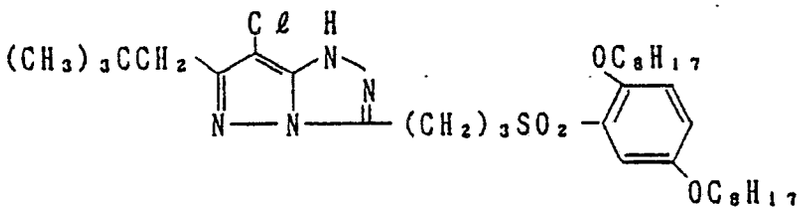

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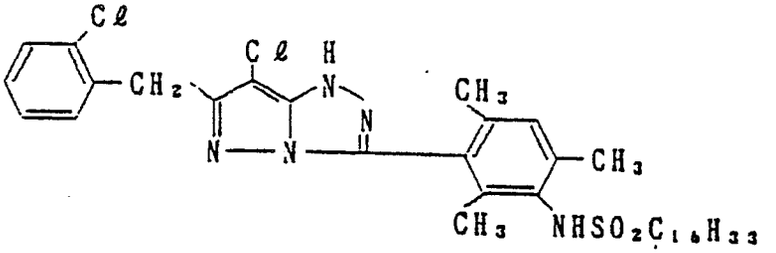

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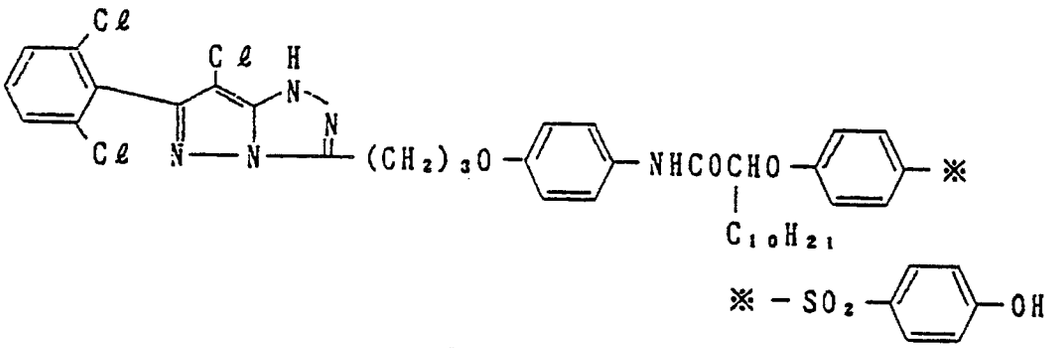

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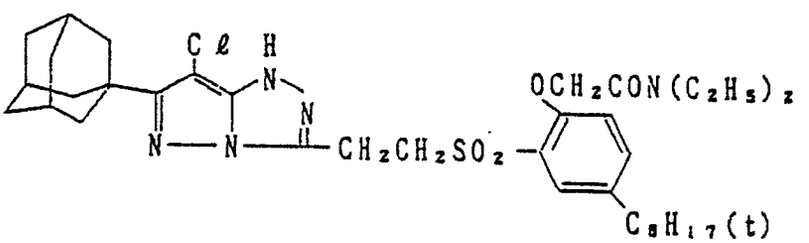

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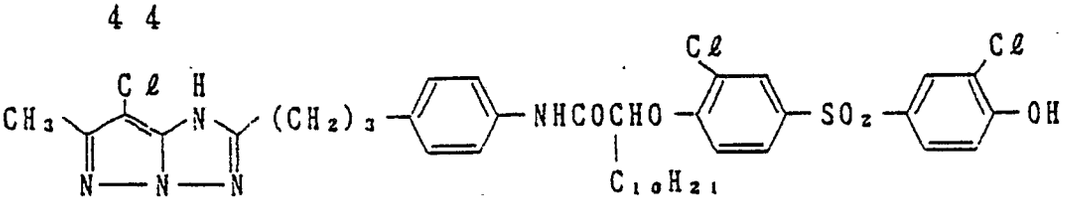

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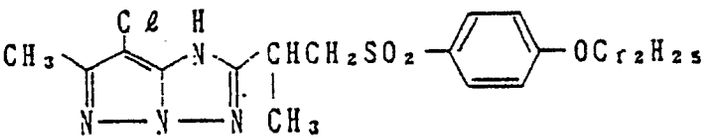

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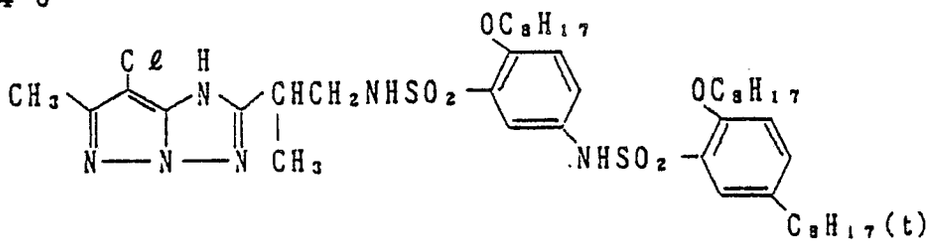

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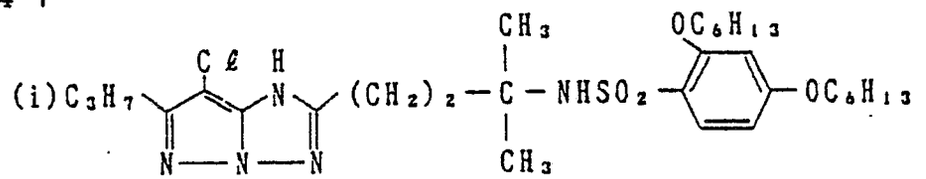

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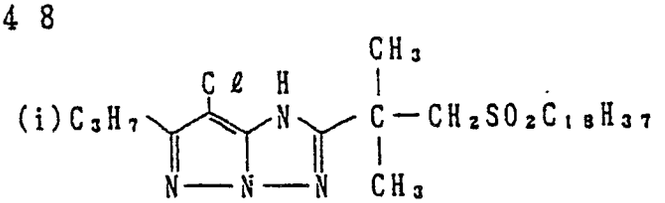

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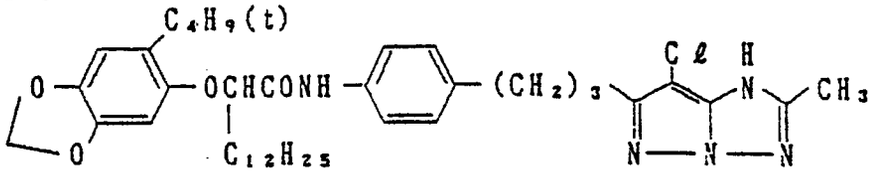

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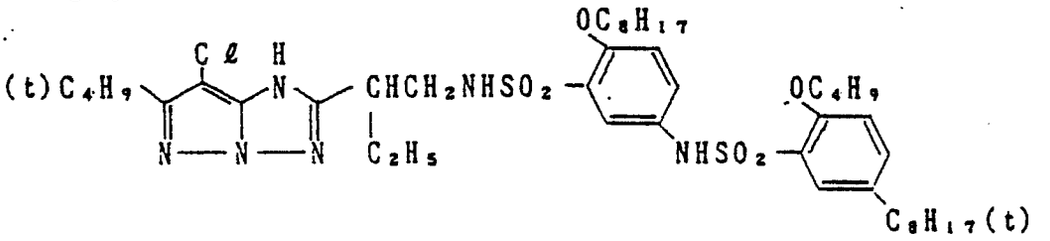

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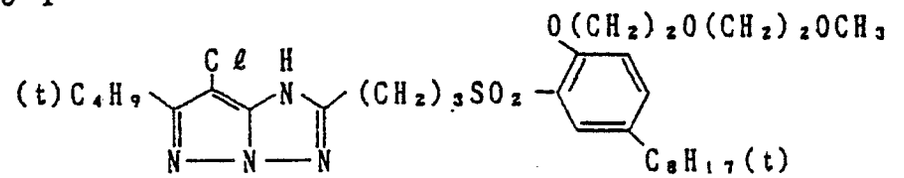

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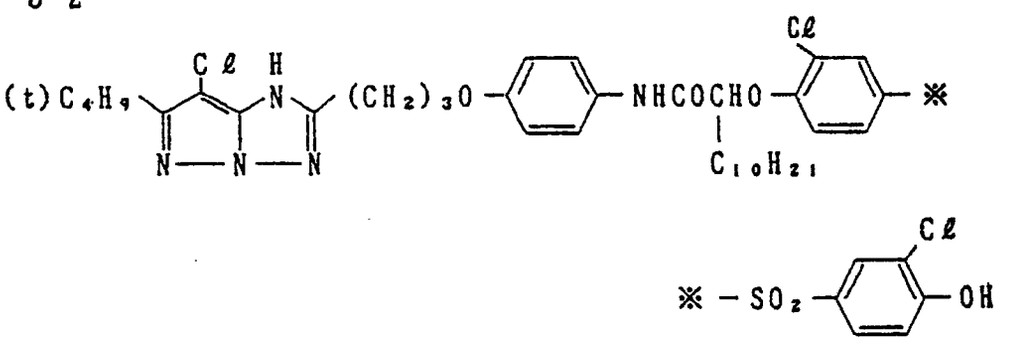

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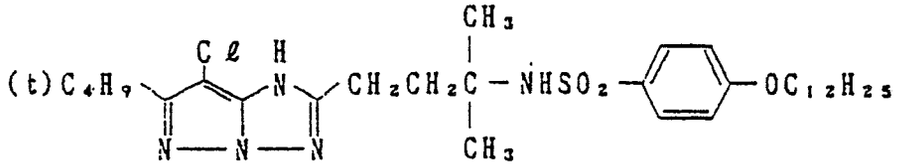

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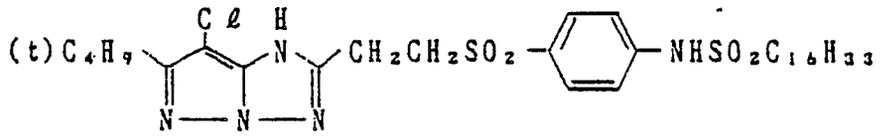

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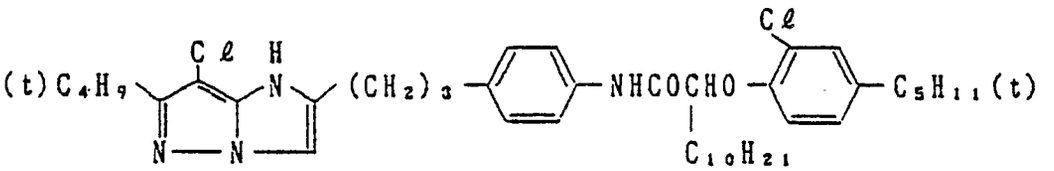

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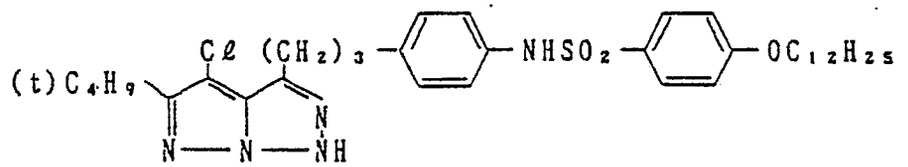

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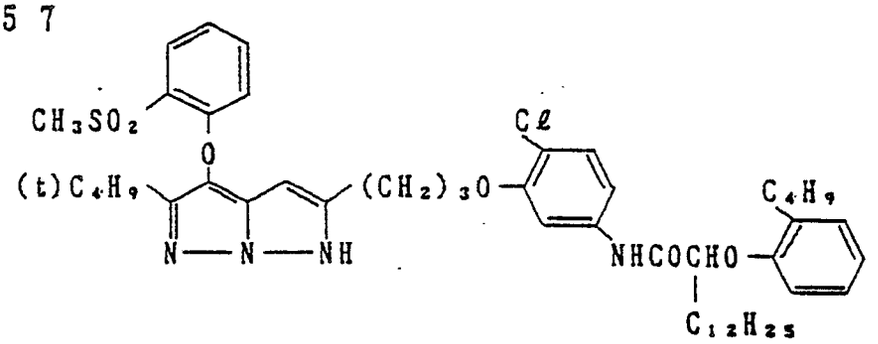

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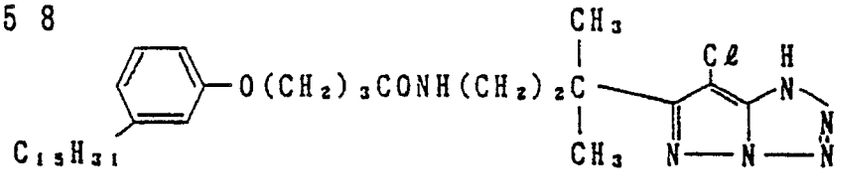

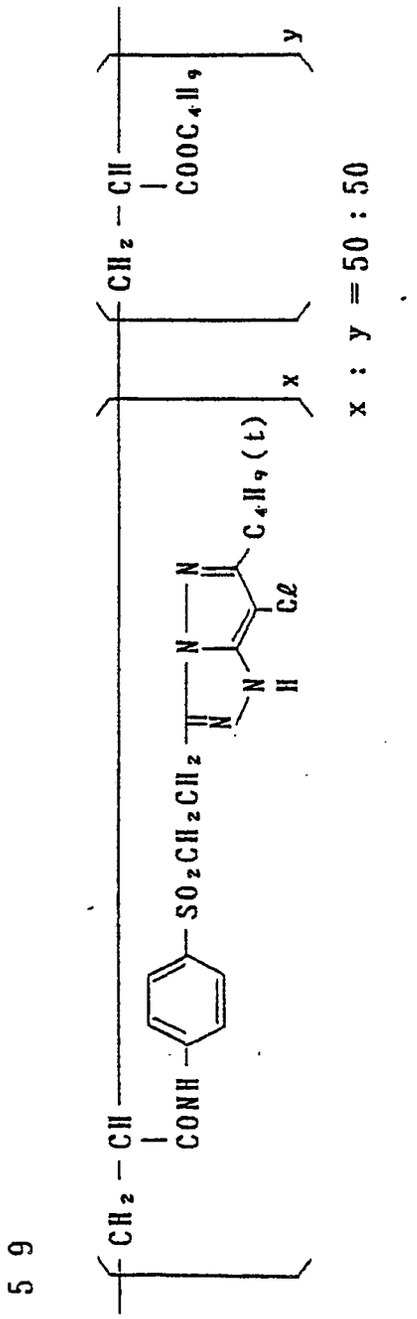

x : y = 50 : 50

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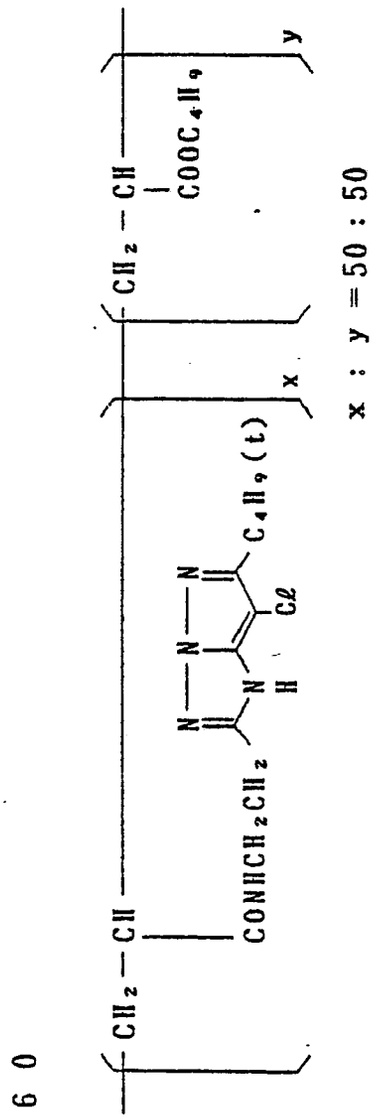

x : y = 50 : 50

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In addition to the above examples of the compounds according to this invention, other examples of the compounds usable in this invention also include those compounds Nos. 1 through 4, 6, 8 through 17, 19 through 24, 26 through 43, 45 through 59, 61 through 104, 106 through 121, 123 through 162, and 164 through 223 disclosed in pages 66 through 122 of Japanese Patent O.P.I. Publication No.9791/1986.

These couplers can be synthesized by making reference to the Journal of the Chemical Society, Perkin, I (1977), 2047-2052, 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 coupler of this invention may be used in the amount range of normally from $1x10^{-3}$ mole to mole per mole of silver halide, and more preferably from $1x10^{-2}$ mole to $8x10^{-1}$ mole.

The coupler of this invention may be used in combination with different other magenta coupler.

Useful cyan couplers applicable to this invention include, for example, phenol-type and naphthol-type couplers. And these cyan couplers, as in the foregoing yellow couplers, may be not only four-equivalent-type but also two-equivalent-type couplers. Particular examples of the cyan coupler are found in U.S. Patent Nos. 2,369,929, 2,434,272, 2,474,293, 2,521,908, 2,895,826, 3,034,892, 3,311,476, 3,458,315, 3,476,563, 3,583,971, 3,591,383, 3,767,411 and 4,004,929, West German OLS Patent Nos. 2,414,830 and 2,454,329, Japanese Patent O.P.I. Publication Nos. 59838/1973, 26034/1976, 5055/1973, 146827/1976, 69624/1977,

90932/1977 and 95346/1983.

The method of adding the above-mentioned coupler usable in this invention to the photographic component layers of this invention may be carried out by making reference to the method for the foregoing DSR compound, and the adding amount of the DSR compound, although not limited, is preferably from $1x10^{-3}$ to 5 moles per mole of silver, and more preferably from $1x10^{-2}$ to $5x10^{-1}$ moles.

The silver halide light-sensitive color photographic material of this invention may contain various photographic additives such as those antifoggant, stabilizer, ultraviolet absorbing agent, anti-color-stain agent, brightening agent, antidiscoloration agent, antistatic agent, hardening agent, surface active agent, plasticizer, wetting agent and the like as disclosed in, e.g., Research Disclosure No.17643.

In the silver halide light-sensitive color photographic material of this invention, the hydrophilic colloid for use in preparing its emulsion includes any arbitrary ones such as gelatin, derivative gelatin, graft polymers of gelatin with other high-molecular materials, proteins such as albumin, casein, etc., cellulose derivatives such as hydroxyethyl cellulose derivatives, carboxymethyl cellulose derivatives, etc., starch derivatives, and synthetic hydrophilic high-molecular materials including homo- or copolymers such as polyvinyl alcohol, polyvinyl imidazole, polyacrylamides, and the like.

The support of the silver halide light-sensitive color photographic material of this invention may be of any discretional one of various materials. In the case of a color photographic paper, its support may be of any material as long as it is of reflective type, such as, e.g., baryta paper, polyethylene-coated paper, polypropylene synthetic paper, reflective layer-coated or reflective sheet-combined transparent support such as, e.g., glass plates, cellulose acetate, cellulose nitrate, polyester film such as polyethylene terephthalate, etc., polyamide film, polycarbonate film, polystyrene film, and the like. A transparent support may of course be used. Materials as the transparent support include, for example, at need subbed polyethylene terephthalate film, polycarbonate film, polystyrene film, polypropylene film, cellulose acetate film, and the like. These support materials are arbitrarily selected to be used according to the purpose for which the light-sensitive material is to be used.

The coating of the silver halide emulsion layer and other photographic component layer of this invention may be carried out by using any of various coating methods such as the dipping coating, air doctor coating, curtain coating, hopper coating, and the like, and those simultaneous coating methods for coating two or more layers at the same time as disclosed in U.S. patent Nos. 2,761,791 and 2,941,898 may also be used.

In this invention, the coating positions of the respective emulsion layers may be discretionally determined. For example, in the case of a light-sensitive material for full-color photographic paper use, it is desirable to arrange a blue-sensitive emulsion layer, green-sensitive emulsion layer, and red-sensitive emulsion layer in the described order from the support side. Each of these light-sensitive silver halide emulsion layers may consist of two or more sub-layers.

In the light-sensitive material of this invention, it is discretional to provide, if necessary, an appropriate thickness-having intermediate layer, and further, various component layers such as filter layer, anticurl layer, protective layer, antihalation layer and the like, may be discretionarily provided in combination. To these component layers may be applied a hydrophilic colloid as its binder that can be used in the foregoing emulsion layer, and in such component layers may be incorporated various photographic additives that can be contained in the foregoing emulsion layer.

Regarding the processing of the photographic light-sensitive material of this invention, various processing methods may be used. A typical and common method comprises color development or fogging development, then bleach-fix processing and, if necessary, washing and/or stabilizing.

The color developer solution for use in processing the light-sensitive material of this invention is an aqueous alkaline solution containing a color developing agent, having a pH of preferably not less than 8, and more preferably from 9 to 12. As the color developing agent, an aromatic primary amine developing agent is commonly used, of which the aromatic ring has a primary amino group and which is a compound capable of developing a silver halide. Further, if necessary, to the developer solution may be added a precursor capable of forming such the compound. Further, in the case of processing the internal latent image-type light-sensitive material, a fogging agent (hereinafter described) may be added.

The above color developing agent is typified by p-phenylenediamine-type compounds. Suitable examples of the color developing agent include 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methoxy-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methoxy-4-amino-N-ethyl-N-β-methoxyethylaniline, 3-acetamido-4-amino-N,N-dimethylaniline, N-ethyl-N-β-[β-(β-methoxyethoxy)ethoxy]ethyl-3-methyl-4-aminoaniline, N-ethyl-N-β-(β-methoxy)ethyl-4-aminoaniline, and salts such as sulfates, hydrochlorides, sulfites, p-toluenesulfonates, and the like, of these compounds.

Further those as disclosed in, e.g., Japanese Patent O.P.I. Publication Nos. 64932/1973, 131526/1975 and 95849/1976, and Bent, the Journal of the Americaln Chemical Society, vol. 73, 3100-3152 (1951) may also be used as typical color developing agents.

The using amount of these aromatic primary amino compounds depends on how high the acitivity of a developer solution should be, but to raise the activity, the amount is desirable to be increased. Normally, the amount range is from 0.0002 mole/liter to 0.7 mole/liter. Depending upon purpose, two or more of such compounds may be discretionarily combined to be used; for example, 3-methyl-4-amino-N,N-diethylaniline and 3-methyl-4-amino-N-ethyl-N-β-methansulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methansulfonamidoethyl aniline and 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, and the like combination.

The color developer solution for use in developing the light-sensitive material of this invention may further contain various constituents usually used as additives including alkali agents such as, e.g., sodium hydroxide, sodium carbonate, etc., alkali metal sulfites, alkali metal hydrogensulfites, alkali metal thiocyanates, alkali metal halides, benzyl alcohol, water softening agents, thickening agents, development accelerators, and the like.

Further, additives other than the above ones to be added to the above color developer solution include, e.g., bromides such as potassium bromide, ammonium bromide, etc., alkali iodide, compounds for rapid processing use such as nitrobenzimidazole, mercaptobenzimidazole, 5-methyl-benzotriazole, 1-phenyl-5-mercaptotetrazole, etc., antistain agents, antisludge agents, preservatives, interimage effect accelerators, chelating agents, and the like.

Where the present invention is applied to a direct positive internal latent image-type silver halide light-sensitive photographic material, the principal process to form a direct positive image is usually performed in such manner that an in-advance-unfogged internal latent image-type silver halide light-sensitive photographic material is exposed imagewise, and then, after or while being subjected to fogging treatment, is surface-developed. The fogging treatment herein can be made by overall uniformly exposing the light-sensitive material to light or by using a fogging agent. In this instance, the overall and uniform exposure is desirable to be made after immersing or wetting an imagewise exposed internal latent image-type silver halide light-sensitive photographic material in a developer solution or some other aqueous solution. The light source to be used herein can be of any type as long as it is a light that falls under the range corresponding to the wavelength region to which the internal latent image-type silver halide light-sensitive photographic material is sensitive. The overall exposure may also be made by a high-illuminance light emission in a short period of time like electronic flash light or weak light emission in a long period of time. The overall exposure time may be varied according to the internal latent image-type silver halide light-sensitive photographic material to be used, developing conditions, the type of light source to be used and the like so that the best positive image can be finally obtained. As the above fogging agent, any diverse compounds may be used, and the fogging agent need only be present at the time of developing. For example, it may be present in either the internal latent image-type silver halide light-sensitive photographic material or a developer solution, or in a solution prior to the developer solution, but it is preferred to be contained in the internal latent image-type silver halide light-sensitive photographic material (particularly in its silver halide emulsion layers). The using amount of the fogging agent may be widely varied according to purposes. The preferred adding amount of the fogging agent, when adding to the silver halide emulsion layer, is from 1 to 1500 mg per mole of silver halide, and preferably from 10 to 1000 mg, while, when adding to a processing solution such as a developer solution, is from 0.01 to 5 g per liter, and preferably from 0.08 to 0.15 g per liter. Such fogging agents include those hydrazines as disclosed in, e.g., U.S. Patent Nos. 2,563,785 and 2,588,982, those hydrazides or hydrazone compounds as disclosed in U.S. Patent No. 3,227,552, those heterocyclic quaternary nitrogen compounds as disclosed in U.S. Patent Nos. 3,615,615, 3,718,470, 3,719,494, 3,734,738 and 3,759,901, and those acylhydrazionphenylthioureas as disclosed in U.S. Patent No. 4,030,925. These fogging agents may be used in combination. For example, Reseach Disclosure No. 15162 describes the combined use of a nonadsorption-type fogging agent with an adsorption-type fogging agent, and this is applicable also to this invention.

Useful examples of the fogging agents include hydrazine compounds such as hydrazine hydrochloride, phenylhydrazine hydrochloride, 4-methylphenylhydrazine hydrochloride, 1-formyl-2-(4-methylphenyl)-hydrazine, 1-acetyl-2-phenyl hydrazine, 1-acetyl-2-(4-acetamidophenyl)hydrazine, 1-methylsulfonyl-2-phenylhydrazine, 1-benzoyl-2-phenylhydrazine, 1-methylsulfonyl-2-(3-phenylsulfonamidophenyl)hydrazine, formaldehydephenylhydrazine, and the like.

When the present invention is applied to an internal latent image-type silver halide light-sensitive photographic material, as aforementioned, after being exposed imagewise, the light-sensitive material is overall exposed or developed in the presence of a fogging agent to thereby form a direct positive image, but the developing of the light-sensitive material may be made by an arbitrary method, and preferably by

the surface developing method. This surface developing method herein implies the processing in a developer solution which does substantially not contain a silver halide solvent.

In such the direct reversal processing, the exposed silver halide light-sensitive photographic material is processed in the foregoing color developer solution and a processing solution having fixability, whereby a positive image (actual image) corresponding to an orignal subject can be formed.

Subsequently, the processing method according to this invention will be explained, which is characterized by processing the aforementioned color photographic light-sensitive material in a procedure comprising the use of a bleach-fix bath.

In the processing method according to the present invention, the bleaching agent to be used in a bleach-fix bath is a compound of an organic acid, such as an aminopolycarboxylic acid, oxalic acid or citric acid, coordinated with metallic ions such as of cobalt or copper. Typical examples of the above aminopolycarboxylic acid includ:
ethylenediaminetetraacetic acid,
diethylenetriaminetetraacetic acid,
propylenediaminetetraacetic acid,
nitrilotriacetic acid,
iminodiacetic acid,
glycol-ether-diaminetetraacetic acid,
ethylenediaminetetrapropionic acid,
disodium ethylenediaminetetraacetate,
pentasodium diethylenetriaminepentaacetate, and
sodium nitrilotriacetate.

In the processing method of this invention, the bleach-fix bath is used preferably in a pH of 0.1 to 9.5, more preferably not less than 4.0, and most preferably not less than 5.0. The processing temperature is preferably not more than 80 °C, and more preferably not more than 55 °C in order to restrain the bath from evaporating. The processing time in the bath is preferably within 8 minutes, and more preferably within 6 minutes.

In the processing method of this invention, as the bleach-fix bath, a bleach-fix solution of a composition containing a small amount of a halogenated compound such as potassium bromide or of a composition containing to the contrary a large amount of a halogenated compound such as potassium bromide or ammonium bromide may be used, and further, a specific bleach-fix bath of a composition containing a bleaching agent in combination with a large amount of a halogenated compound such as potassium bromide may also be used.

As the halogenated compound, hydrochloric acid, hydrobromic acid, lithium bromide, sodium bromide, potassium iodide, sodium iodide, ammonium iodide or the like may also be used in addition to potassium bromide.

As the silver halide fixing agent to be contained in the bleach-fix bath to be used in the processing method of this invention, those compounds capable of reacting with a silver halide to form a water-soluble complex salt, which are commonly applied to ordinary fixing process, may be used which include thiosulfates such as, e.g., potassium thiosulfate, sodium thiosulfate, ammonium thiosulfate, etc., thiocyanates such as potassium thiocyanate, sodium thiocyanate, ammonium thiocyanate, etc., thiourea, thioether, high-bromide-content or high-iodide-content compounds, and the like. These fixing agents may be used in the soluble amount range of preferably not less than 5 g/liter, more preferably not less than 50 g/liter, and most preferably not less than 70 g/liter.

The bleach-fix bath applicable to the processing method of this invention may contain various additives along with the foregoing bleaching agent. The bath is desirable to contain as an additive for stabilizing the bleachability particularly alkali halide or ammonium halide such as, e.g., potassium bromide, sodium bromide, sodium chloride, ammonium bromide, potassium iodide, sodium iodide, ammonium iodide, or the like.

The bleach-fix bath applicable to the processing method of this invention may contain a pH buffer comprising boric acid, a borate such as borax, sodium hydroxide, carbonates such as sodium carbonate, potassium carbonate, etc., hydrogencarbonates such as sodium hydrogencarbonate, calcium hydrogencarbonate, etc., acetic acid or an acetate such as sodium acetate, ammonium hydroxide, or salts such as oxalates or phosphates, and these may be used alone or in combination of two or more of them. Further, the bath may contain a brightening agent or defoaming agent in combination with them, and may also contain a surfactant and fungicide in combination with the brightening agent and defoaming agent, and may further discretionarily contain preservatives such as hydroxyamine, hydrazine, sulfites, metabisulfites or sulfite addition products of aldehyde or ketone compounds; organic chelating agents such as acetylacetone,

phosphonocarboxylic acid, polyphosphoric acid, organic phosphonic acid, oxycarboxylic acid, polycarboxylic acid, dicarboxylic acid, aminopolycarboxylic acid, etc.; stabilizing agents such as nitroalcohol, nitrates, etc.; solubilizing agents such as triethanolamine, alkanolamine, etc.; antistain agents such as organic amines; other additives such as alkaliamines, polyethyleneoxides, etc.; and organic solvents such as methanol, dimethylformamide, dimethylsulfoxides, etc.

Different other suitable compounds to be added to the bleach-fix bath applicable to the processing method of this invention for accelerating the bleachability include tetramethylurea, phosphoric acid trisdimethylamide, ε-caprolactam, N-methylpyrolidone, N-methylmorpholine, tetraethylglycol-monophenyl ether, acetonitrile, glycolmonomethyl ether, and the like.

The processing method of this invention is a method in which the bleach-fix is desired to be made immediately after color developing, but after the color developing, a washing, linsing or stopping process is allowed to take place prior to the bleach-fix treatment. Most preferably, after the color developing, a prefixing process is to be inserted prior to the bleach-fix process. In this instance, the prefixing bath may contain a bleaching accelerator.

After the bleach-fix processing, stabilizing may take place without washing, or washing and then stabilizing may take place. Besides these processes, various other auxiliary processes such as hardening, neutralizing, black-and-white reduction, and reversal processes, and washing with a small amount of water, and the like may, if necessary, be additionally performed. Typical, suitable examples of the processing method are as follows:

(1) Color developing → bleach-fix → washing.
(2) Color developing → bleach-fix → washing with a small amount of water → washing.
(3) Color developing → bleach-fix → washing → stabilizing.
(4) Color developing → bleach-fix → stabilizing.
(5) Color developing → bleach-fix → first stabilizing → second stabilizing.
(6) Color developing → washing (or stabilizing) → bleach-stabilize → washing (or stabilizing).
(7) Color developing → prefixing → bleach-fix → washing.
(8) Color developing → prefixing → bleach-fix → stabilizing.
(9) Color developing → prefixing → bleach-fix → first stabilizing → second stabilizing.
(10) Color developing → stopping → bleach-fix → washing → stabilizing.

In order to have the invention display its effect more conspicuously, out of the above procedures, the processing methods (1), (2), (3), (4), (5) and (7) may be more suitably used.

The bleach-fix bath to be used in the processing method of this invention is desirable to contain various inorganic metal salts. These inorganic metal salts may be preferably added after being made into metal complex salts with chelating agents.

EXAMPLES

Examples of the present invention will be described in detail below, but the embodiment of the invention is not limited to the examples.

EXAMPLE 1

In this example, the invention was applied to a color photographic paper. On a both-side-polyethylene-coated paper support were coated the following layers in order from the support side, whereby a silver halide light-sensitive color photographic paper sample No.1 was prepared.

Layer 1

Layer containing 1.2 g/m^2 of gelatin, 0.32 g/m^2 (silver equivalent, the same shall apply hereinafter) of a blue-sensitive silver chlorobromide emulsion (containing 80 mole % silver bromide), and 0.80 g/m^2 of Yellow Coupler Y-1 dissolved into 0.50 g/m^2 of dioctyl phthalate.

Layer 2

Intermediate layer containing 0.70 g/m^2 of gelatin, 12 mg/m^2 of Antiirradiation Dye AI-1, and 6 mg/m^2 of AI-2.

Layer 3

Layer containing 1.25 g/m^2 of gelatin, 0.25 g/m^2 of a green-sensitive silver chlorobromide emulsion (containing 70 mole % silver bromide), and 0.74 g/m^2 of Magenta Coupler M-1 dissolved into 0.30 g/m^2 of dioctyl phthalate.

Layer 4

Intermediate layer containing 1.20 g/m^2 of gelatin.

Layer 5

Layer containing 1.2 g/m^2 of gelatin, 0.30 g/m^2 of a red-sensitive silver chlorobromide emulsion (containing 70 mole % silver bromide), and 0.45 g/m^2 of Cyan Coupler C-1 dissolved into 0.20 g/m^2 of dioctyl phthalate.

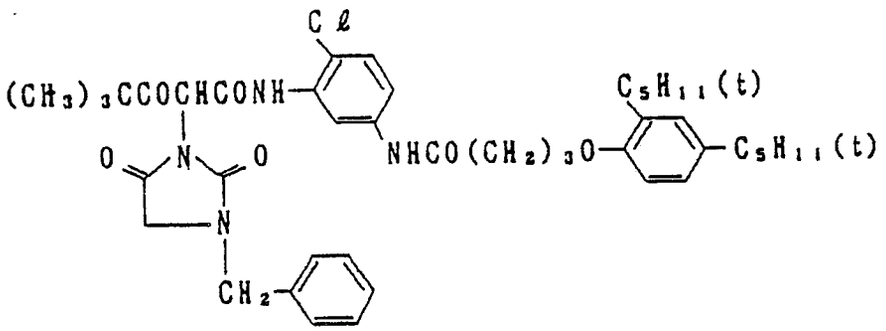
Layer 6

Layer containing 1.00 g/m^2 of gelatin and 0.30 g/m^2 of Ultraviolet Absorbing Agent UV-1 dissolved into 0.20 g/m^2 of dioctyl phthalate.

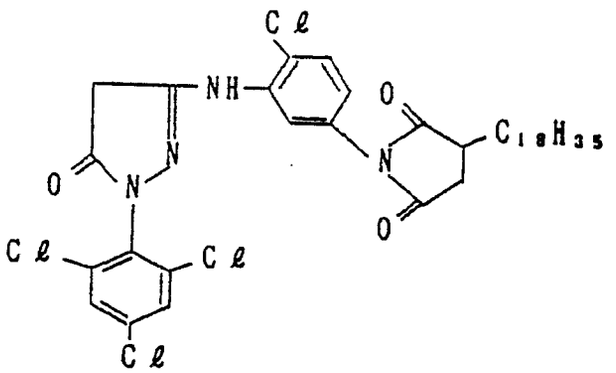
Layer 7

Layer containing 0.50 g/m^2 of gelatin.

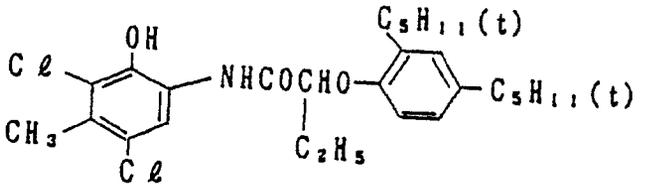
Y-1



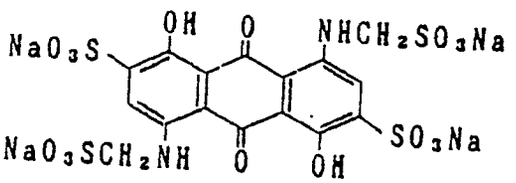
M-1



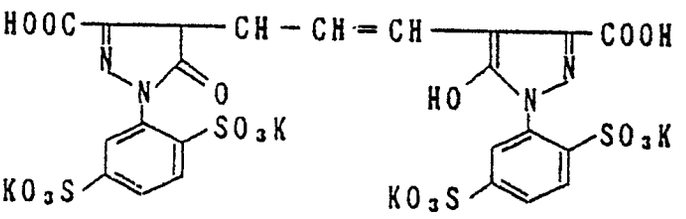
C-1



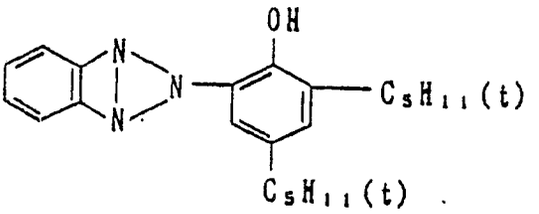
AI-1



AI-2



UV-1



In addition, a hardening agent sodium 2,4-dichloro-6-hydroxy-s-triazine was added to Layers 2, 4 and 7 so that its amount is 0.017 g per gram of the gelating of each of the layers.

Subsequently, Sample No.2 was prepared in the same manner as in Sample No.1 except that the amount of the magenta coupler of Layer 3 of Sample No.1 was changed to 0.59 g/m^2 and DSR-13 was added in an amount of 0.30 g/m^2.

The obtained light-sensitive material Samples No.1 and No.2 were subjected to the following test: Each of the samples was overall exposed to blue light and red light, and also exposed through an optical wedge to green light, and the exposed samples each was processed in the following procedure steps:

Processing steps

Color developing	(38° C)	3 min. 30 sec.
Bleach-fix	(38° C)	1 min. 30 sec.
Washing	(38° C)	1 min.
Drying	(60-80° C)	2 min.

The compositions of the respective solutions are as follows:

Color Developer Solution

Pure water	800 ml
Benzyl alcohol	15 ml
Hydroxyamine sulfate	2.0 g
Potassium bromide	1.5 g
Sodium chloride	1.0 g
Potassium sulfite	2.0 g
Triethanolamine	2.0 g
N-ethyl-N-β-methansulfonamidoethyl-3-methyl-4-aminoaniline sulfate	4.5 g
1-hydroxyethylidene-1,1-diphosphoninc acid (aqueous 60 % solution)	1.5 ml
Potassium carbonate	32.0 g
Whitex BB (aqueous 50 % solution) (brightening agent)	2.0 ml

Add pure water to make 1 liter.
Use 20 % potassium hydroxide or 10 % dilute sulfuric acid to adjust the pH to 10.1.

Bleach-Fix Bath

Pure water	550 ml
Iron(III)-ammonium ethylenediaminetetraacetate	65.0 g
Ammonium thiosulfate	85.0 g
Sodium hydrogensulfite	10.0 g
Sodium metabisulfite	2.0 g

Disodium ethylenediaminetetraacetate 20.0 g
Sodium bromide 10.0 g
Add pure water to make 1 liter.
Use aqueous ammonia or dilute sulfuric acid to adjust the pH to 7.0.

After the processing, each sample was measured with respect to its blue, green and red densities through interference filters having transmission maximums in 440 nm (blue region), 540 nm (green region) and 650 nm (red region), respectively.

The results are shown in figure 1 for Sample No.2 and in Figure 2 for Sample No.1. As has been mentioned, Figure 1 and Figure 2 show the results in the case of wedge exposure to green light and overall exposure to blue light and red light.

From Figure 1 it is apparent that as for Sample No.2 for this invention, the sample wherein its green-sensitive layer is color-formed shows that as the green density G increases, the red density R and blue density B become decreased, whereas in Sample No.1, the red density R and blue density B are hardly affected by the green density G. From the comparison of Figure 1 with Figure 2 it is understood that Sample No.2, which contains the DSR compound in its Layer 3, a green- sensitive layer, shows that the green color formation restrains the formation of red and blue colors, and therefore is a sample for this invention which provides an interlayer effect to other layers, whereby the sample displays an interimage effect. Due to this interimage effect, an excellent color reproducibility has been realized. (See also the following Example.)

EXAMPLE 2

In this example, the same Sample No.1 and Sample No.2 as used in Example 1 were used, and their color reproducibility from an original subject was examined visually: A color negative film (SAKURACOLOR SRV-100, manufactured by Konishiroku Photo Industry Co., Ltd.) and a camera (KONICA FT-1 MOTOR, manufactured by Konishiroku Photo Industry Co., Ltd.) were used to photograph a MACBETH Color Checker, and the film was then processed using Color Negative Processing Kit (CNK-4, manufactured by Konishiroku Photo Industry Co., Ltd.). The obtained negative image was printed on Sample No.1 and Sample No.2 to make 82mm x 117mm size prints by using a SAKURACOLOR Printer CL-P2000 (manufactured by Konishiroku Photo Industry Co., Ltd.), and the printed samples were processed in the same manner as in Example 1, whereby actual color prints were obtained. The printer's conditions in the printing were set for each sample so that the grey color on the color checker is truly reproduced on the print.

The obtained prints were examined and evaluated visually with respect to their color reproducibility. As a result, in Sample No.2 according to this invention, the blue and red of the color checker were especially vividly reproduced so close to the original colors, while Sample No.1 showed that its color reproducibility is no match for that of Sample No.1.

EXAMPLE 3

In the first place, three different silver halide emulsions Em-1 through Em-3 as shown in Table 1 were prepared according to the neutral method and by the simultaneously mixing process.

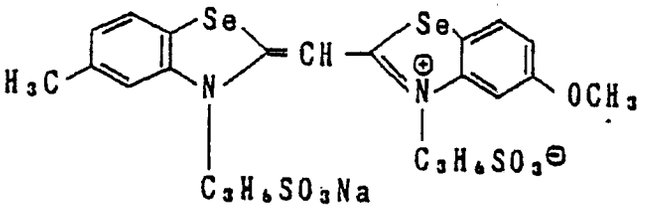
Table 1

Emulsion No.	AgCl %	AgBr %	Average grain size μ	Chemical sensitizer	Sensitizing dye
Em-1	100	0	0.67	Sodium thiosulfate *1	SD-1*3
Em-2	99.5	0.5	0.46	Chloroauric acid *2	SD-2*4
Em-3	99.5	0.5	0.43		SD-3*5

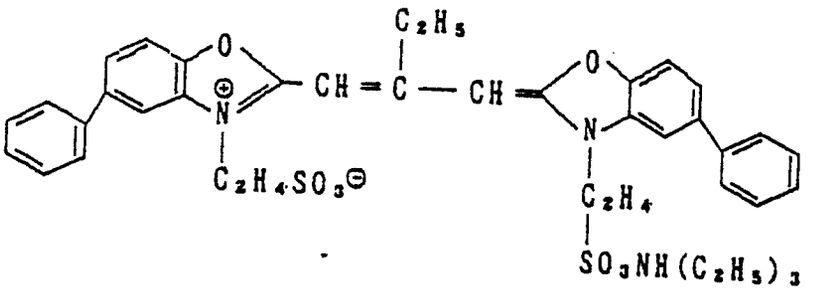
Note: *1 Added 2 mg per mole of silver halide
*2 Added 5×10^{-5} mole per mole of silver halide
*3 Added 0.9 millimole per mole of silver halide
*4 Added 0.7 millimole per mole of silver halide
*5 Added 0.2 millimole per mole of silver halide

After chemically sensitizing these silver halide emulsions, to each of the emulsions was added the following emulsion sensitizer STB-1 in an amount of 5×10^{-3} mole per mole of silver halide.

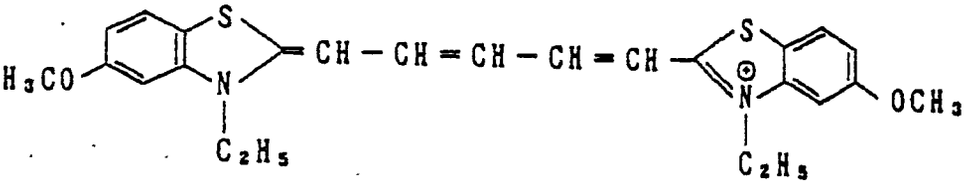
SD-1



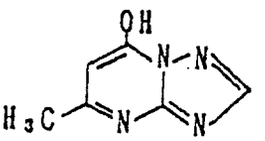
SD-2



SD-3



STB-1



Subsequently, the following Layers 1 through 7 were simultaneously coated on a both-side-polyethylene-coated paper support in order from the support side, whereby a silver halide light-sensitive photographic material Sample No.3 was prepared. Each added amount given below is a coating weight per m^2.

Layer 1

Layer containing 1.2 g of gelatin, 0.29 g (silver equivalent, the same shall apply hereinafter) of a blue-sensitive silver halide emulsion (Em-1), 0.75 g of Yellow Coupler Y-1, 0.3 g of Stabilizer ST-1 and 0.015 g of 2,5-dioctylhydroquinone HQ-1 dissolved into 0.3 g of dinonyl phthalate (DNP).

Layer 2

Layer containing 0.9 g of gelatin and 0.04 g of HQ-1 dissolved into 0.2 g of DOP (dioctyl phthalate).

Layer 3

Layer containing 1.4 g of gelatin, 0.2 g of a green-sensitive silver halide emulsion (Em-2), 0.9 millimole of a magenta coupler (M-1), 0.25 g of a photo-sensitizer ST-2, 0.01 g of HQ-1 dissolved into 0.3 g of DOP, and 6 mg of the following Filter Dye AI-2.

Layer 4

Layer containing 1.2 g of gelatin, 0.6 g of the following Ultraviolet Absorbing Agent UV-1 and 0.05 g of HQ-1 dissolved into 0.3 g of DNP.

Layer 5

Layer containing 1.4 g of gelatin, 0.20 g of a red-sensitive silver halide emulsion (Em-3), 0.50 g of Cyan Coupler C′-1, 0.13 g of DSR-21, 0.01 g of HQ-1 and 0.3 g of ST-1 dissolved into 0.3 g of DOP.

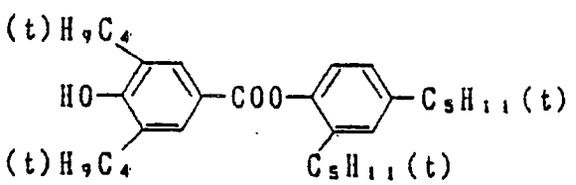
Layer 6

Layer containing 1.1 g of gelatin, 0.2 g of UV-1 dissolved into 0.2 g of DOP, and 5 mg of the following Filter Dye AI-1.

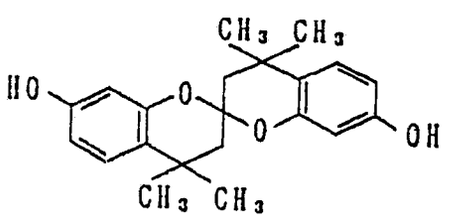
Layer 7

Layer containing 1.0 g of gelatin and 0.05 g of sodium 2,4-dichloro-6-hydroxytriazine.

ST-1



ST-2



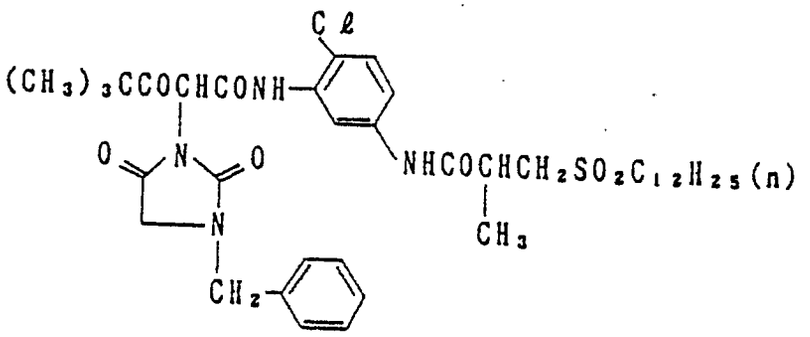
UV-1:

The same as the UV-1 of Example 1.

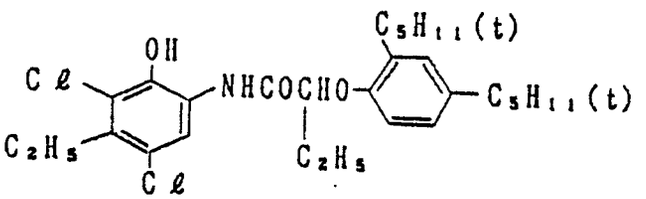
AI-1 and AI-2:

The same as the AI-1 and AI-2, respectively, of Example 1.

Y'-1



C'-1



The obtained Sample No.3 was overall exposed to blue light and green light by using a sensitometer KS-7 (manufactured by Konishiroku Photo Industry Co., Ltd.) and exposed through an optical wedge to red light. The exposed sample was then processed according to the following color developing procedure, and the processed sample was measured by means of an optical densitometer (PDA-65, manufactured by Konishiroku Photo Industry Co., Ltd.) with respect to the density (D) of each of the blue, green and red-sensitive emulsion layers, whereby characteristic curves were obtained. The measurement took place using interference filters having absorption maximums in 440 nm, 540 nm and 640 nm, respectively. The results are given in Figure 3.

Developing Process	Temperature	Time
Color developing	34.7±0.3°C	45 seconds
Bleach-fix	34.7±0.5°C	50 seconds
Stabilizing	30 - 34°C	90 seconds
Drying	60 - 80°C	60 seconds

Color Developer Solution

Pure water 800 ml
Triethanolamine 8 g
N,N-diethylhydroxyamine 5 g
Potassium chloride 2 g
N-ethyl-N-β-methansulfonamidoethyl-3-methyl-4-aminoaniline sulfate 5 g
Sodium tetrapolyphosphate 2 g
Potassium carbonate 30 g
Potassium sulfite 0.2g
Brightening agent (4,4'-diaminostilbenzylsulfonic acid derivative) 1 g
Add water to make 1 liter.
Adjust the pH to 10.2.

Bleach-Fix Bath

Iron(III)-ammonium ethylenediaminetetraacetate, dihydrated 60 g
Ethylenediaminetetraacetic acid 3 g
Ammonium thiosulfate (aqueous 70 % solution) 100 ml
Ammonium sulfite (aqueous 40 % solution) 27.5g
Use potassium carbonate or glacial acetic acid to adjust the pH to 5.7, and add water to make 1 liter.

Stabilizing Bath

5-Chloro-2-methyl-4-isothiazolin-3-one 1 g
1-Hydroxyethylidene-1,1-diphosphonic acid 2 g
Add water to make 1 liter, and use sulfuric acid or potassium hydroxide to adjust the pH to 7.0.

As is apparent from Figure 3, the sample having red-color formation by being exposed through an wedge to red light shows that as the red density R increases, the solid green density G and solid blue density B become decreased, and from this fact it is understood that Sample No.3, which contains the DSR compound in its Layer 5, a red-sensitive emulsion layer, has its green and blue color formation restrained by its red color formation, and thus it is a sample for this invention to give an interlayer effect to other layers, whereby the sample brings about an interimage effect. This interimage effect enables to attain an excellent color reproducibility, and this was ascertained by a separate experiment that was performed in the same manner as in Example 2.

EXAMPLE 4

This example is to embody the present invention in a direct positive silver halide light-sensitive photographic material.

In this example, internal latent image-type silver halide emulsions were prepared in the following manner:

Preparation of Emulsion S

To 750 ml of an aqueous 2.0 % inert gelatin solution kept at 50°C, with stirring, were added the following Solution A1 and Solution B simultaneously in pouring manner spending 3 minutes. The produced emulsion, after being ripened for 25 minutes, had its excessive salts removed therefrom by the precipitation-washing process, and was then redispersed, and to this were added Solution C1 and Solution D1. After 10 minutes, its excessive water-soluble salts were again removed, and a small amount of gelatin was added to the emulsion to disperse the silver halide grains.

Preparation of Emulsion L

To 750 ml of an aqueous 1.5 % inert gelatin solution kept at 60°C, with stirring, were added Solution A2 and Solution B simultaneously in pouring manner spending 15 minutes. After being ripened for 40 minutes, the produced emulsion had its excessive salts removed therefrom by the precipitation-washing process, and was then redispersed, and to this were added 10 mg of hypo and then Solution C2 and Solution D2. After 10 minutes, again its excessive water-soluble salts were removed and a small amount of gelatin was added to the emulsion to disperse the silver halide grains.

Preparation of Emulsion M

To 750 ml of an aqueous 2.0 % inert gelatin solution kept at 50°C, with stirring, were added Solution A3 and Solution B simultaneously in pouring manner spending 5 minutes. After 25-minute ripening. the emulsion had its excessive salts removed therefrom by the precipitation-washing process, and was then redispersed, and to this were added Solution C1 and Solution D2. After 10 minutes. again its excessive water-soluble salts were removed, and a small amount of gelatin was added to the emulsion to disperse the silver halide grains.

Solution A1:

Pure water	2000 ml
NaCl	35 g (60 mole %)
NH_4Br	109.6 g (80 mole %)
KI	0.8 g

Solution A2:

Pure water	1000 ml
NaCl	26.3 g (103 mole %)
NH_4Br	109.6 g (80 mole %)
KI	0.8 g (0.5 mole %)

Solution A3:

Pure water	1000 ml
NaCl	38.8 g
KBr	12 g

Solution B:

Pure water 1200 ml
$AgNO_3$ 170 g

Solution C1:

Pure water 1000 ml
NaCl 60 g (103 mole %)
NH_4Br 6.9 g (5.0 mole %)

Solution C2:

Pure water 1000 ml
NaCl 31.6 g

Solution D1:

Pure water 1000 ml
$AgNO_3$ 70 g

Solution D2:

Pure water 1000 ml
$AgNO_3$ 80 g

To these three different emulsions were added sensitizing dyes, couplers and the like as in the following manner and then coated, whereby a multilayer color light-sensitive material was prepared.

Red-sensitive emulsion layer (Layer 1)

To each of Emulsions S and M were added Sensitizing Dyes D-3 and D-4, Stabilizers T-1 and T-2, Surface Active Agent S-2, and further a protect-dispersed coupler liquid containing dibutyl phthalate, ethyl acetate, Surface Active Agent S-2, 2,5-dioctylhydroquinone, and Cyan Couplers C-1 and C-2.

Gelatin was added to the respective emulsions and they were mixed and coated so that the gamma value was 1.5.

First intermediate layer (Layer 2)

A gelatin solution containing a protect-dispersed liquid comprising dioctyl phthalate, 2,5-dioctylhydroquinone, ultraviolet absorbing agent Tinuvin 328 (product of Ciba Geigy) and Surface Active Agent S-1 was prepared, and the liquid was coated so that the coating weight of the Tinuvin was 0.15 g/m^2.

Green-sensitive emulsion layer (Layer 3)

To each of Emulsions S and M were added Sensitizing Dye D-2, Stabilizers T-1 and T-2, Surface Active Agent S-2, and further a protect-dispersed coupler liquid containing dibutyl phthalate, ethyl acetate, 2,5-dioctylhydroquinone, Surface Active Agent S-1 and Magenta Coupler M-1.

Gelatin and Hardening Agent H-1 were added to the emulsions, and they were mixed and coated so that the gamma value was 1.5.

Second intermediate layer (Layer 4)

A layer having the same composition as that of the first intermediate layer. The layer was coated so that the coating weight of the Tinuvin was 0.2 g/m^2.

Yellow filter layer (Layer 5)

A colloidal silver coating liquid containing a yellow colloidal silver prepared by being oxidized in the presence of an alkaline weak reducing agent (after neutralization, the weak reducing agent was removed by the noodle washing method), dioctyl phthalate, ethyl acetate, Surface Active Agent S-1, 2,5-dioctylhydroquinone, Surface Active Agent S-2 and Hardening Agent H-1 was coated so that the coating weight of the colloidal silver was 0.15 g/m^2.

Third intermediate layer (Layer 6)

The same as the first intermediate layer.

Blue-sensitive emulsion layer (Layer 7)

To each of Emulsions L, S and M were added Sensitizing Dye D-1, Stabilizers T-1 and T-3, Surface Active Agent S-2, and a protect-dispersed coupler liquid containing dibutyl phthalate, ethyl acetate, 2,5-dioctylhydroquinone, Surface Active Agent S-1, and Yellow Coupler Y-1.

Gelatin and Hardening Agent H-1 were added to these emulsions, and they were mixed and coated so that the gamma value was 1.5.

Third intermediate layer (Layer 8)

A liquid having the same composition as that of the first intermediate layer was coated so that the coating weight of the Tinuving 328 was 0.35 g/m^2.

Protective layer (Layer 9)

A gelatin solution containing colloidal silica, Coating Aid S-2 and Hardening Agents H-2 and H-3 was coated so that the coating weight of the gelatin was 1.0 g/m^2.

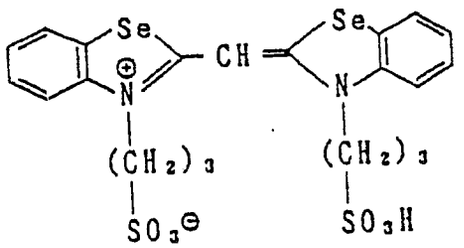
The Layers 1 through 9 were coated simultaneously and then dried on a surface-treated polyethylene-laminated paper support.

The thus prepared sample was regarded as Sample No.11. Also, Sample No.12 was prepared in the same manner as in Sample No.11 except that the coating weight of the green-sensitive emulsion layer (Layer 3) of Sample No.11 was increased by 5 % on the whole, and 10 mole % of the Magenta Coupler M-1 was replaced by Exemplified Compound DSR-14.

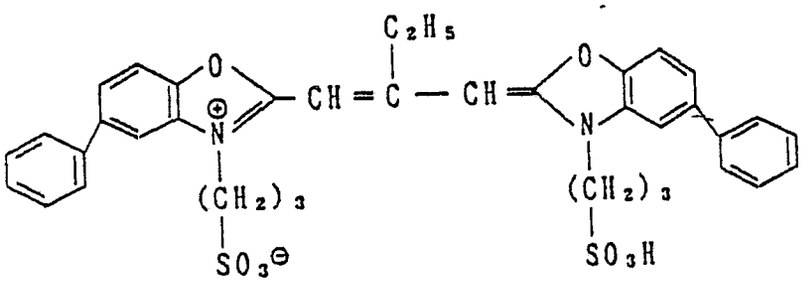
In addition, Sample No.13 was prepared in the same manner as in Sample No.11 except that the coating weight of the red-sensitive emulsion layer (Layer 1) of Sample No.11 was increased by 8 % on the whole, and 15 mole % of the Cyan Coupler C-2 was replaced by SDR-24.

Further, Sample No.14 was prepared in the same manner as in Sample No.11 except that the coating weight of the Layer 3 of Sample No.11 was increased by 5 % on the whole, 10 mole % of the Magenta Coupler M-1 was replaced by DSR-14, the coating weight of the Layer 1 was increased by 8 % on the whole, and 15 mole % of the Cyan Coupler C-2 was replaced by DSR-24.

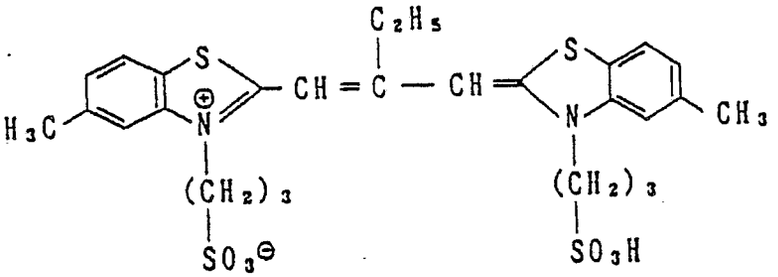
D-1



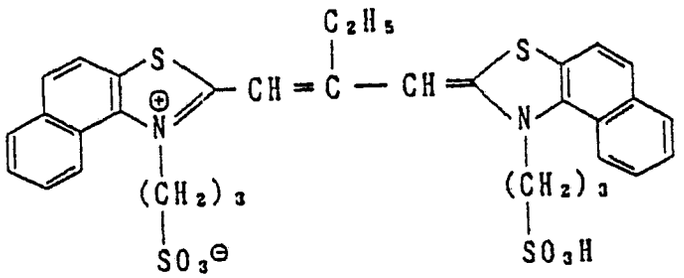
D-2



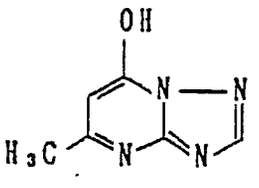
D-3



D-4



T-1



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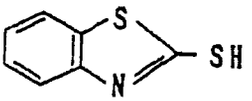

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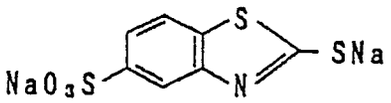
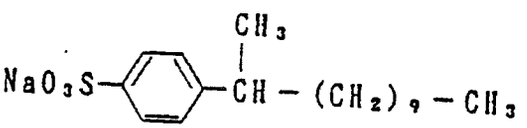
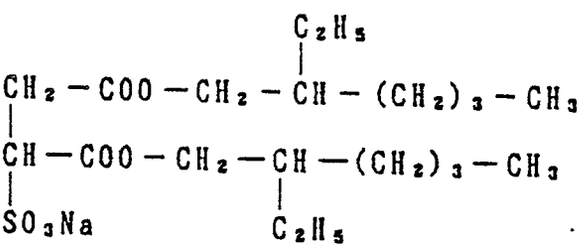


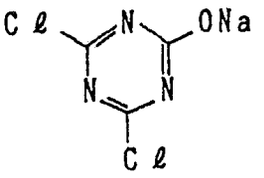
S-1



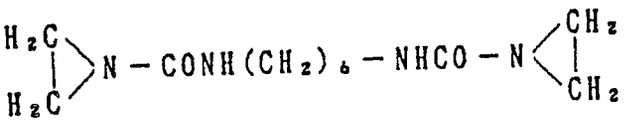
S-2



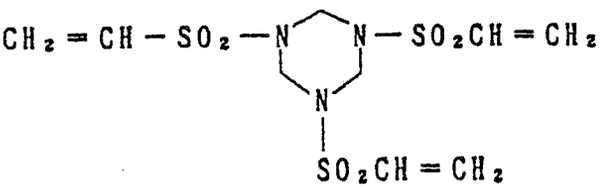
H-1



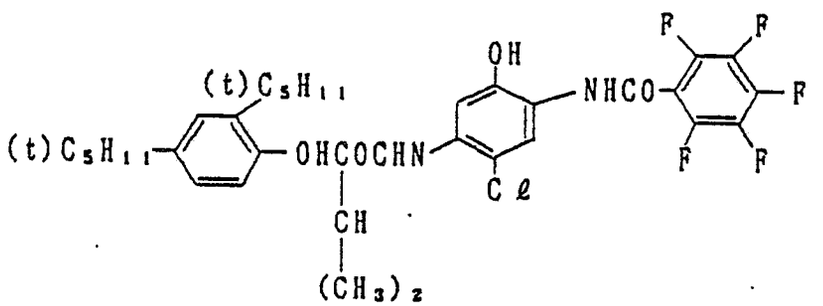
H-2



H-3



C-2



The thus prepared Samples No.11 and No.12 were exposed through an optical wedge to green light. The exposed samples were processed in the following procedure, and the samples' characteristic curves for their formed blue, green and red colors were obtained; Figure 4 and Figure 5 show the results of Samples No.11 and No.12, respectively, exposed through wedge to green light. By comparison of Figure 4 with Figure 5, it is understood that in Sample No.11, containing no DSR compound, the blue density B and red density R are not affected by the change in the green density G, so that little interimage effect is seen from the green-sensitive layer to other layers, whereas in Sample No.12, containing the DSR compound in its green-sensitive layer, as the green density G increases, the blue density B and red density R become lowered, thus displaying an interimage effect.

Similar tests took place also for Samples No.13 and No.14. As a result, they showed the same

tendency.

The developing process that was used in the above tests is as follows:

Processing steps	Temperature	Time
Immersing (in color dev. sol.)	38°C	8 sec.
Fogging exposure	--	10 sec. at 1 lux
Color developing	38°C	2 min.
Bleach-fix	35°C	60 sec.
Stabilizing	25-30°C	1 min. 30 sec.
Drying	75-80°C	1 min.

Color Developer Solution

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
3-Methyl-4-amino-N-ethyl-N-(β-methansulfonamidoethyl)-aniline sulfate 5.5 g
Brightening agent (4,4'-diaminostilbenzosulfonic acid derivative) 1.0 g
Potassium hydroxide 2.0 g
Add water to make 1 liter.
Adjust the pH to 10.20.

Bleach-Fix Bath

Ferric-ammonium ethylenediaminetetraacetate, dihydrated 60 g
Ethylenediaminetetraacetic acid 3 g
Ammonium thiosulfate (70 % solution) 100 ml
Ammonium sulfite (40 % solution) 27.5 ml
Use potassium carbonate or glacial acetic acid to adjust the pH to 7.1, and add water to make 1 liter.

Stabilizing Bath

5-Chloro-2-methyl-4-isothiazolin-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 (28 % solution) 2.0 g
Sodium nitrilotriacetate 1.0 g
Water to make 1 liter.
Use ammonium hydroxide or sulfuric acid to adjust the pH to 7.0.

The stabilizing bath is of a double-bath countercurrent system.

EXAMPLE 5

In this example, the same Samples No.11 through No.14 as in Example 4 were used, and their color reproducibilities to an original subject were evaluated visually. The foregoing light-sensitive material Samples No.11 through No.14 were used to make copies of the foregoing MACBETH Color Checker by using a Konicolor 7 Copier (color copying machine, manufactured by Konishiroku Photo Industry Co., Ltd.). In each sample, the processed image's speed-γ (gamma) balance was adjusted by the filter in advance set in the copying apparatus so that the neutral color can be fully reproduced.

A Comparison by eye between the original MACBETH Color Checker and each of the obtained copies was made, and as a result, it has now been found that Sample No.12 according to this invention, as compared to Sample No.11, is excellent in the red, purple and blue color reproducibilities which are considerably close to those of the original, and shows remarkably vivid reproduction particularly in the red color. Sample No. 13 is closer in the purple, blue and cyan color reproductions to the original, while Sample No.14 is significantly improved on the red, violet, blue and cyan color reproductions.

EXAMPLE 6

In this example, the processing method of this invention was applied to color photographic paper. The following layers were coated on a both-side-polyethylene-laminated paper support in order from the support side, whereby a silver halide light-sensitive color photographic material Sample No.15.

Layer 1

Layer containing 1.2 g/m^2 of gelatin, 0.32 g/m^2 (silver equivalent, the same shall apply hereinafter) of a blue-sensitive silver chlorobomide emulsion (containing mole silver bromide), 0.80 g/m^2 of Yellow Coupler Y-1 dissolved into 0.50 g/m^2 of dioctyl phthalate.

Layer 2

Intermediate layer containing 0.70 g/m^2 of gelatin, 12 mg/m^2 of Antiirradiation Dye AI-1 and 6 mg/m^2 of AI-2.

Layer 3

Layer containing 1.25 g/m^2 of gelatin, 0.25 g/m^2 of a green-sensitive silver chlorobromide emulsion (containing 70 mole % silver bromide), 0.62 g/m^2 of Magenta Coupler M-1 dissolved into 0.30 g/m^2 of dioctyl phthalate, and 0.03 g/m^2 of Compound DIR-1.

Layer 4

Intermediate layer containing 1.20 g/m^2 of gelatin.

Layer 5

Layer containing 1.20 g/m^2 of gelatin, 0.30 g/m^2 of a red-sensitive silver chlorobromide emulsion (containing 70 mole % silver bromide), and 0.45 g/m^2 of Cyan Coupler C-1 dissolved into 0.20 g/m^2 of dioctyl phthalate.

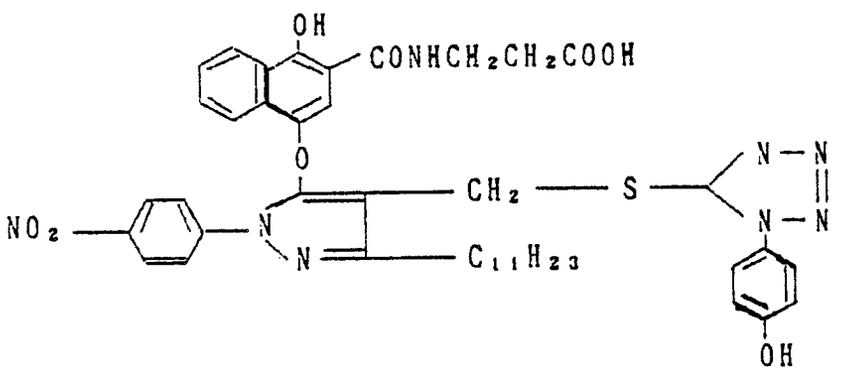
Layer 6

Layer containing 1.00 g/m^2 of gelatin and 0.30 g/m^2 of Ultraviolet Absorbing Agent UV-1 dissolved into 0.20 g/m^2 of dioctyl phthalate.

Layer 7

Layer containing 0.50 g/m^2 of gelatin.

DIR-1



In addition, sodium 2,4-dichloro-6-hydroxy-s-triazine as a hardening agent was added to Layers 2, 4 and 7 so that its amount was 0.017 g per gram of the gelatin of each layer.

Further, Sample No.16 was prepared in the same manner as in Sample No.15 except that the coating weight of the Layer 3 of Sample No.15 was increased by 15 % on the whole except DIR-1, and 30 % of the Magenta Coupler M-1 was replaced by Exemplifed Compound DSR-13.

The obtained Samples No.15 and No.16 each was exposed through an optical wedge and then processed in the same manner as in Example 1.

Each of the processed samples was measured with respect to the fog f, gamma γ and maximum density D_M. The obtained characteristics values are as shown in the following table. Also, in order to investigate the residual amount of silver in the D_M portion, its density measurement was made with infrared rays (λ = 1000 nm) to thereby examine the infrared density $D\lambda$ = 1000nm.

Sample No.	Layer	Fog f	Gamma γ	Maximum density D_M	Infrared density $D_{\lambda=1000nm}$
Sample 15 (comparative)	B	0.05	1.8	1.5	0.21
	G	0.04	2.6	2.3	
	R	0.02	2.2	2.0	
Sample 16 (invention)	B	0.05	2.8	2.3	0.03
	G	0.03	3.0	2.5	
	R	0.03	2.7	2.2	

As is apparent from the above data, in Sample No.15, which uses the DIR compound, both D_M and γ are low on the whole, which means that the development was restrained on the whole. And the infrared density at $D_\lambda = 1000nm$ is as high as 0.21, which implies that silver retention occurred.

In contrast, in Sample No.16 for this invention, the infrared density is as low as 0.03, which means that no residual silver was present, and both D_M and γ are high, which implies that the development was not restrained.

On the other hand, both Samples No.15 and No.16 each was exposed overall to red light and also exposed through an wedge to green light, and each exposed sample was processed in the same manner as the above. The processed samples were measured for their densities through interference filters having transmission maximums in a red region of 650 nm and green region of 540 nm respectively. The results are shown in Figure 6 for Sample No.15 and in Figure 7 for Sample No.16. By comparison between Figure 6 and Figure 7, an interimage effect to some extent is seen in comparative Sample No.15, but the interimage effect that as the green density decreases, the red density becomes increased is remarkable in Sample No.16 for this invention.

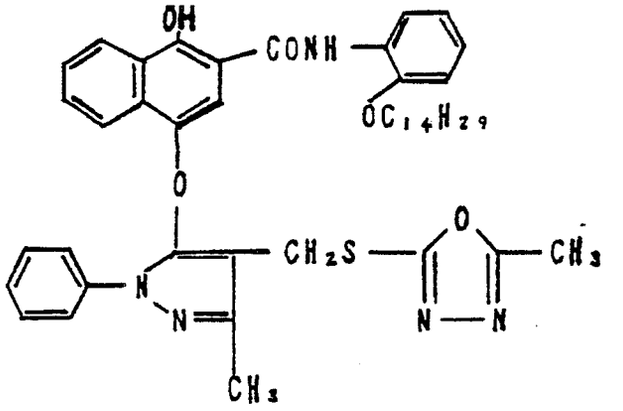
As is apparent from the above results, in Sample No.15, which uses a DIR coupler, an interimage effect to some extent is seen, but the development is retarded on the whole, and thus no adequate D_M and γ are obtained, whereas in Sample No. 16 for this invention, which uses a DSR coupler, both D_M and γ are high, displaying an interimage effect.

EXAMPLE 7

This example embodies the processing method of this invention as the processing method for a direct positive silver halide light-sensitive photographic material.

In this example, the same Sample No.11 as in Example 4 was first prepared, and also Sample No.17 was prepared in the same manner as in Sample No.11 except that the coating weight of the Layer 1 of Sample No.11 was increased by 10 % on the whole, and the following DIR Coupler DIR-2 was added in an amount of 0.03 mole % per mole of silver. Further, Sample No. 18 was prepared in the same manner as in the foregoing Sample No.3 except that the coating weight of the Layer 1 of the Sample No.11 was increased by 10 % on the whole, and the Cyan Coupler C-2 corresponding to 30 mole % of the whole cyan couplers (Cyan Couplers C-2 and C-2) was replaced by DSR-24.

DIR-2



Each of the thus prepared Samples No.11, No.17 and No.18 was exposed through an optical wedge to light, and then subjected to color development in the same manner as in Example 4. The processed pieces of Samples No.11, No.17 and No.18 were each measured with respect to the D_M portion with infrared rays having a wavelength of 1000 nm. The results are as given in the following table. The higher the infrared density $D_\lambda = 1000nm$, the larger the amount of residual silver.

Comparative Sample No.11, which contains no functional materials such as DIR and DSR compounds at all, has a low infrared density and satisfactory desilvering ability, but naturally lacks function by functional materials. On the other hand, Sample No.17, which contains DIR Coupler DIR-2, is significantly inferior in the desilvering ability, whereas Sample No.18 according to this invention, although it contains the DSR compound, is as satisfactory in the desilvering ability as Sample No.11.

Sample No.	Infrared density $D_{\lambda=1000nm}$	
11	0.03	Comparative
17	0.12	Comparative
18	0.03	Invention

EXAMPLE 8

Emulsions EM-4 through EM-6 were prepared in quite the same manner as in the foregoing Emulsions Em-1 through EM-3 in Example 3 except that the silver halide compositions were varied as shown in the following Table 2:

Table 2

Emulsion No.	AgCl %	AgBr %	Average grain size μ	Chemical sensitizer	Spectral sensitizing dye
Em-4	0	100	0.67	Sodium thiosulfate *1	SD-1*3
Em-5	0	100	0.46	Chloro-auric acid *2	SD-2*4
Em-6	0	100	0.43		SD-3*5

*1 Added 2 mg per mole of silver halide.

*2 Added 5×10^{-5} mole per mole of silver halide.

*3 Added 0.9 millimole per mole of silver halide.

*4 Added 0.7 millimole per mole of silver halide.

*5 Added 0.2 millimole per mole of silver halide.

To each of these emulsions, after their chemical sensitization, was added the following Sensitizer STB-1 in an amount of 5×10^{-3} mole per mole silver halide.

Sample No.19 was prepared in quite the same manner as in the foregoing Sample No.3 except that Em-4 through Em-6 were used in place of the Em-1 through Em-3, respectively. Each of Samples No.3 and No.19 was exposed through an optical wedge to green light and also to white light by using a Sensitometer KS-7 (manuractured by Konica Corporation), and then processed in the same manner as in Example 3. The processed samples were subjected to sensitometry tests with use of green light, and then the gamma values at the time of the exposure to green light were compared. The results are shown in Table 3.

Table 3

Sample No.	γ_G *6	γ_N *7	IIE *8	Remarks
3	2.71	2.42	1.12	Invention
19	2.53	2.41	1.05	Comparison

*6 Inclination of the sensitometry curve between the formed color density points of 0.3 and 0.8 when exposed to green light.

*7 Inclination of the sensitometry curve between the formed color density points of 0.3 and 0.8 when exposed to white light.

*8 IIE = γ_G / γ_N

As is apparent from Table 3, Sample No.19, which uses the emulsions (Em-4 through Em-6) containing silver bromide that is outside this invention, shows a smaller IIE than that of Sample No.3, which uses both silver chloride and silver bromide, and thus cannot be expected to show any improved color reproduction.

As has been mentioned above, this invention enables to largely improve the color reproducibility of a

light-sensitive material, and thus to provide an excellent color reproducibility-having color photographic light-sensitive material.

The processing method according to this invention display the effect that silver retention hardly occurs at the time of processing, and an image excellent in the graininess, sharpness and color reproducibility can be obtained.

EXAMPLE 9

Firstly, Emulsions Em-1 through Em-3 were prepared in the same manner as in the foregoing Example 3.

<Preparation of a silver halide light-sensitive color photographic material>

Subsequently, the following Layers 1 through 7 were simultaneously coated on a both-side-polyethylene-laminated paper support in order from the support side, whereby a silver halide light-sensitive color photographic material Sample No.1 was prepared. (The adding amount of each photographic component is hereinafter given in the form of a coating weight per m^2 of the light-sensitive material in the following example.)

Layer 1

Layer containing 1.2 g of gelatin, 0.29 g (silver equivalent) of a blue-sensitive silver halide emulsion (Em-1), and 0.3 g of dinonyl phthalate (DNP) into which are dissolved 0.75 g of Yellow Coupler Y′-1 and 0.3 g of Photo-Stabilizer ST-1 and 0.015 g of 2,5-dioctylhydroquinone (HQ-1).

Layer 2

0.9 g of gelatin and 0.04 g of HQ-1 dissolved into 0.2 g of dioctyl phthalate (DOP).

Layer 3

Layer containing 1.4 g of gelatin, 0.2 g of a green-sensitive silver halide emulsion (Em-2), 0.9 millimole of Magenta Coupler M-1, 0.25 g of Photo-Stabilizer ST-2, 0.01 g of HQ-1 dissolved into 0.5 g of DOP, and 6 mg of Filter Dye AI-1.

Layer 4

Layer containing 1.2 g of gelatin and 0.6 g of DNP into which are dissolved 0.6 g of Ultraviolet Absorbing Agent UV-1 and 0.05 g of HQ-1.

Layer 5

Layer containing 1.4 g of gelatin, 0.20 g of a red-sensitive silver halide emulsion (Em-3), and 0.3 g of DOP into which are dissolved the foregoing exemplified Cyan Coupler C′-1 and exemplified Cyan Coupler C-2, 0.01 g of HQ-1 and 0.3 g of ST-1.

Layer 6

Layer containing 1.1 g of gelatin, 0.2 g of UV-1 dissolved into 0.2 g of DOP, and 5 mg of Filter Dye AI-2.

Layer 7

Layer containing 1.0 g of gelatin and 0.05 g of sodium 2,4-dichloro-6-hydroxytriazine.

Further, in the same manner as in Sample No.1 were prepared Sample No.2 except that 0.13 g of exemplifed Compound DSR-21 of this invention was added to Layer 5: Sample No.2 except that the Magenta Coupler M-1 of Layer 3 was replaced by the same mole of exemplified Magent Coupler No.10 represented by Formula [M-I]; and Samples No.4 through No.6 except that the DSR compound and the magenta coupler were replaced as shown in Table 2.

Each sample thus obtained was exposed through an optical wedge to green light and white light by using a Sensitometer KS-7 (manufactured by Konishiroku Photo Industry Co., Ltd.), and then processed in the same processing solutions and in the same manner as in Example 3, and after that, was subjected to sensitometry tests with use of green light, and comparison between the gamma (γ) values obtained when exposed to green light and when exposed to white light took place.

The obtained results are collectively shown in Table 2. As is apparent from Table 2, Samples No.2, No.4, No.5 and No.6, which each contains DSR compound, have larger IIE values than those of Samples No.1 and No.3, which contain no DSR compound, and thus it is obvious that the former samples have an interimage effect.

By comparison of Samples No.2, No.4, No.5 and No.6, it is apparent that the samples containing the magenta coupler of this invention have larger IIE values and are more satisfactory in the color reproduction.

Table 2

Sample No.	Magenta coupler	DSR compound	γ_G *6	γ_N *7	IIE*8	Remarks
1	M-1	--	2.70	2.63	1.03	Comparative
2	M-1	DSR-21	2.71	2.42	1.12	Comparative
3	No.10	--	2.92	2.84	1.03	Comparative
4	No.10	DSR-21	2.94	2.52	1.17	Invention
5	No.10	DSR-22	2.99	2.49	1.20	Invention
6	No.26	DSR-21	3.10	2.47	1.26	Invention

*6 Inclination of the sensitometry curve between the formed color density points of 0.3 and 0.8 when exposed to green light.

*7 Inclination of the sensitometry curve between the formed color density points of 0.3 and 0.8 when exposed to white light.

*8 $IIE = \gamma_G/\gamma_N$

EXAMPLE 10

The above Samples No.1 through No.6 were evaluated in respect of their color reproduciblity in the following manner:

First, a color negative film (SAKURACOLOR SR V-100, manufactured by Konishiroku Photo Industry Co., Ltd.) and a camera (Konica FT-1 MOTOR, manufactured by Konishiroku Photo Industry Co., Ltd.) were used to photograph a MACBETH Color Checker. The film was then processed using a color negative processing kit (CNK-4, manufactured by Konishiroku Photo Industry Co., Ltd.), and the obtained negative image was printed by a SAKURACOLOR Printer CL-P2000 (manufactured by Konishiroku Photo Ind. Co., Ltd.) onto 82mm x 117mm size sheets of Samples No.1 through No.6, which were then processed in the same manner as in Example 3, whereby actual color prints for visual evaluation were obtained. The printer conditions in making prints were set so that the grey part of the Color Checker is truly reproduced on each print.

The color reproduciblity of each print was evaluated. The results are collectively shown in Table 3.

Table 3

Sample No.	Color reproducibility						Remarks
	Blue	Green	Red	Yellow	Magenta	Cyan	
1	C	C	C	C	C	C	Comparative
2	B	B	C	C	C	B	Comparative
3	B	C	B	C	B	B	Comparative
4	A	B	B	B	B	A	Invention
5	A	B	B	B	B	A	Invention
6	A	B	B	B	B	A	Invention

A: Excellent
B: Good
C: Inferior (in hue, chroma)

As is apparent from Table 3, Sample No.1, which uses the non-invention magenta coupler alone, shows no color reproducibility improvement at all in all the blue, green, red, yellow, magenta and cyan colors. Sample No.2, which contains the DSR compound of this invention, shows color reproducibility improvement in the blue, green and cyan colors. And Sample No.3, which contains the magenta coupler of this invention, shows color reproducibility improvement in the blue, red, magenta and cyan colors, but shows little improvement in other colors.

In contrast, Samples No.4 through No.6, which contain both DSR compound and magenta coupler of this invention, show color reproducibility improvement in any colors.

EXAMPLE 11

This example comprises the application of the present invention to a direct positive silver halide light-sensitive photographic material. In this example, internal latent image-type silver halide emulsions S, M and L were first prepared in the same manner as in Example 4.

The three different emulsions were used, and sensitizers, couplers and the like were added as shown below, and the following Layers 1 through 9 were coated simultaneously on a surface-treated polyethylene-laminated paper support and then dried, whereby a direct positive-type multilayer color light-sensitive material was prepared.

Red-sensitive emulsion layer (Layer 1)

To each of Smulsions S and M were added Sensitizing Dyes D-3 and D-4, Stabilizers T-1 and T-2, and a protect-dispersed coupler liquid containing dibutyl phthalate, ethyl acetate, Surface Active Agent S-2, 2,5-dioctylhydroquinone and Cyan Couplers C-1 and C-2.

Gelatin was added to these emulsions, and the emulsions were mixed and coated so that the gamma value was 1.5.

First intermediate layer (Layer 2)

A gelatin liquid containing a protect-dispersed liquid comprising dioctyl phthalate, 2,5-dioctyl-hydroquinone, Ultraviolet Absorbing Agent Tinuving 328 (product of Ciba Geigy), and Surface Active Agent S-1 was prepared, and then coated so that the coating weight of the Tinuvin was 0.15 g/m^2.

Green-sensitive emulsion layer (Layer 3)

To each of Emulsions S and M were added Sensitizing Dye D-2, Stabilizers T-1 and T-2, Surface Active Agent S-2, and a protect-dispersed coupler liquid containing dibutyl phthalate, ethyl acetate, 2,5-dioctyl-hydroquinone, Surface Active Agent S-1 and exemplified Compound No.10 as a magenta coupler having Formula (M-I).

Gelatin and Hardening Agent H-1 were added to the emulsions, and the emulsions were mixed and coated so that the gamma value was 1.5.

Second intermediate layer (Layer 4)

A layer having the same composition as that of the foregoing first intermediate layer was coated so that the coating weight of Tinuvin 328 was 0.2 g/m^2.

Yellow filter layer (Layer 5)

A liquid containing yellow colloidal silver prepared by being oxidized in the presence of an alkaline weak reducing agent (after neutralization, the weak reducing agent was removed by the noodle-washing method), dioctyl phthalate, ethyl acetate, Surface Active Agent S-1, 2,5-dioctylhydroquinone, Surface Active Agent S-2, and Hardening Agent H-1 was coated so that the coating weight of the colloidal silver was 0.15 g/m^2.

Third intermediate layer (Layer 6)

The same as the first intermediate layer.

Blue-sensitive silver halide emulsion layer (Layer 7)

To each of Emulsions L, S and M were added Sensitizing Dye D-1, Stabilizers T-1 and T-3, Surface Active Agent S-3, and a protect-dispersed coupler liquid containing dibutyl phthalate, ethyl acetate, 2,5-dioctylhydroquinone, Surface Active Agent S-1 and Yellow Coupler Y-2.

Gelatin and Hardening Agent H-1 were added to these emulsions, and they were mixed and coated so that the gamma value was 1.5.

4th intermediate layer (Layer 8)

A layer having the same composition as that of the first intermediate layer was coated so that the coating weight of Tinuving 328 was 0.35 g/m^2.

Protective layer (Layer 9)

A gelatin solution containing colloidal silica, Coating Aid S-2 and Hardening Agents H-2 and H-3 was coated so that the coating weight of the gelatin was 1.0 g/m^2.

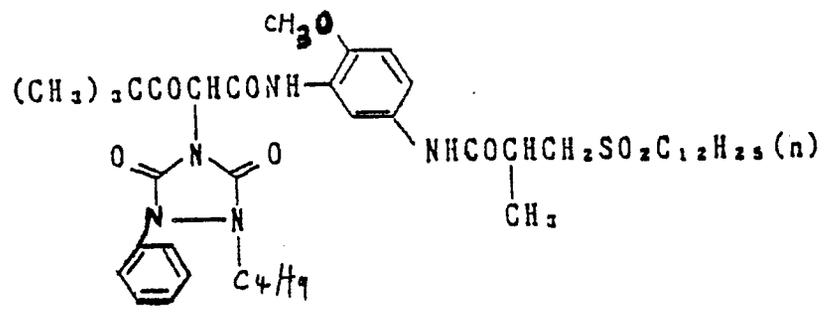
The sample thus prepared was regarded as Sample No.7. Also, Sample No.8 was prepared in the same manner as in Sample No.7 except that the coating weight of the green-sensitive layer of Layer 3 of Sample No.7 was increased by 5 % on the whole, and 10 mole % of the exemplified Magenta Coupler No.10 was replaced by DSR Compound DSR-14.

And, Sample No.9 was also prepared in the same manner as in Sample No.7 except that the coating weight of the red-sensitive emulsion layer of Layer 1 was increased by 8 % on the whole, and 15 mole % of the Cyan Couplers C-1 and C-2 was replaced by DSR Compound DSR-21.

Further, Sample No.10 was prepared also in the same manner as in Sample No.7 except that the coating weight of the whole Layer 3 was increased by 5 %, 10 mole % of the exemplified Magenta Coupler No.10 was replaced by DSR Compound DSR-14, the coating weight of the whole Layer 1 was increased by 8 %, and 15 mole % of the Cyan Couplers C-1 and C-2 was replaced by DSR Compound DSR-21.

Still further, the DSR compound and magenta coupler were replaced as shown in Table 4, whereby Samples No.11 through No.16 were prepared.

Y-2



Samples No.7 and No.8 were each exposed through an optical wedge to green light, and then processed in the same processing solutions and in the same manner as in the foregoing Example 4. In this instance, the relations between the densities R, G and B and log E were as shown in Figure 8 and Figure 9.

When Sample No.8 for this invention was exposed through an wedge, as is shown in Figure 9, as the green density increases, the red and blue densities become decreased, so that it is apparent that the interimage effect from the orthochromatic layer, i.e., green-sensitive layer, is brought to the blue-sensitive layer (regular layer) and red-sensitive layer (pachromatic layer).

On the other hand, comparative Sample No.7, even when exposed through an wedge, did not show any interimage effect as shown in Figure 8.

Each of Samples No.7 through No.16 was used to make copies of MACBETH Color Checker by being exposed, developed and fixed by means of a KONICACOLOR 7 (color copying apparatus, manufactured by Konishiroku Photo Industry Co., Ltd.).

Each image's speed-gamma value balance after completion of the above photographic processing was adjusted by the filter in advance set inside the copying apparatus so that the neutral reproduction can be completely carried out.

The color reproducibility of each copy was evaluated. The evaluation results are as shown in Table 4.

As is apparent from Table 4, Sample No.7, which uses the magenta coupler of this invention, shows improved red and magenta color reproduciblities as compared to Sample No.16, which uses a non-invention magenta coupler, but its improved level is hard to be considered adequate. In contrast, Sample No.8, which uses the magenta coupler of this invention and contains the DSR compound of this invention in its green-sensitive layer, and Sample No.9, which contains the DSR compound of this invention in its red-sensitive layer, show that they enable to obtain satisfactory color reproducibility for almost every color.

Further, Samples No.10 through No.15, which use the magenta coupler of this invention and contain the DSR compound of this invention in their green-sensitive and red-sensitive layers, show that they enable to obtain very excellent color reproducibility for every color.

Table - 4

Sample No.	Magenta coupler (ex. cpd. of Formula [M-I] or comparative coupler	DSR cpd. of Layer 3	DSR cpd. of Layer 1	Color reproducibility						Remarks
				Blue	Green	Red	Yellow	Magenta	Cyan	
7	No.10	—	—	C	C	B	C	B	C	Comparative
8	No.10	DSR-14	—	B	C	A	B	B	B	Invention
9	No.10	—	DSR-21	B	B	B	B	B	A	Invention
10	No.10	DSR-14	DSR-21	A	B	A	B	B	A	Invention
11	No.26	DSR-14	DSR-26	A	B	A	B	B	A	Invention
12	No.46	DSR-20	DSR-23	A	B	A	B	B	A	Invention
13	No.22	DSR-20	DSR-22	A	B	A	B	B	A	Invention
14	No.48	DSR-14	DSR-24	A	B	A	B	B	A	Invention
15	M-1	DSR-14	DSR-24	B	B	C	C	C	B	Comparative
16	M-1	—	—	C	C	C	C	C	C	Comparative

A: Excellent, B: Good, C: Inferior (in hue, chroma)

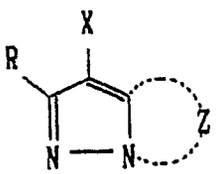
Claims

1. A silver halide light-sensitive color photographic material comprising a support and, provided thereon, a plurarity of light-sensitive silver halide emulsion layers including at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer, wherein at least one of the silver halide emulsion layers contains a silver halide consisting essentially of silver chloride, silver chlorobromide or silver chloroiodobromide, and at least one layer of the above silver halide emulsion layers contains a compound which is, during development, capable of releasing a compound selected from the group consisting of one which is capable of undergoing a coupling reaction with the oxidation product of a developing agent, one which is capable of reducing the oxidation product of a developing agent and one which is a precursor of either the compound which is capable of undergoing a coupling reaction with the oxidation product of a developing agent or the compound which is capable of reducing the oxidation product of a developing agent.

2. The silver halide light-sensitive color photographic material of claim 1, wherein at least one of the silver halide emulsion layers contains a direct positive type silver halide emulsion.

3. The silver halide light-sensitive color photographic material of claim 2, wherein the direct positive type silver halide emulsion contains internal latent image-type silver halide crystals.

4. The silver halide light-sensitive color photographic material of claim 1, wherein said photographic material contains a magenta dye-forming coupler represented by formula [M-I];



[M-I]

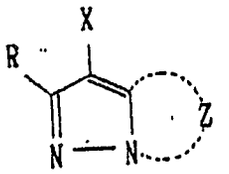
wherein, Z represents a group of non-metal atoms necessary to complete a nitrogen-containing heterocyclic group which may have a substituent; X is a hydrogen atom or a group which is, upon reaction with the oxidized product of a color developing agent, capable of being split off; and R is a hydrogen atom or a substituent.

5. A method of processing a silver halide light-sensitive color photographic mayerial comprising a step of imagewise exposing a silver halide light-sensitive color photographic material comprising a support and, provided thereon, a plurarity of light-sensitive silver halide emulsion layers including at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer, wherein at least one of the silver halide emulsion layers contains a silver halide consisting essentially of silver chloride, silver chlorobromide or silver chloroiodobromide, and at least one layer of the above silver halide emulsion layers contains a compound which is, during development, capable of releasing a compound selected from the group consisting of one which is capable of undergoing a coupling reaction with the oxidation product of a developing agent, one which is capable of reducing the oxidation product of a developing agent and one which is a precursor of either the compound which is capable of undergoing a coupling reaction with the oxidation product of a developing agent or the compound which is capable of reducing the oxidation product of a developing agent; a step of developing said exposed color photographic material with a solution containing a color developing agent:, and a step of processing said developed color photographic material with a bleach-fixing solution.

6. The methof of claim 5, wherein at least one of the silver halide emulsion layers contains a direct positive type silver halide emulsion.

7. The method of claim 6, wherein the direct positive type silver halide emulsion contains internal latent image-type silver halide crystals.

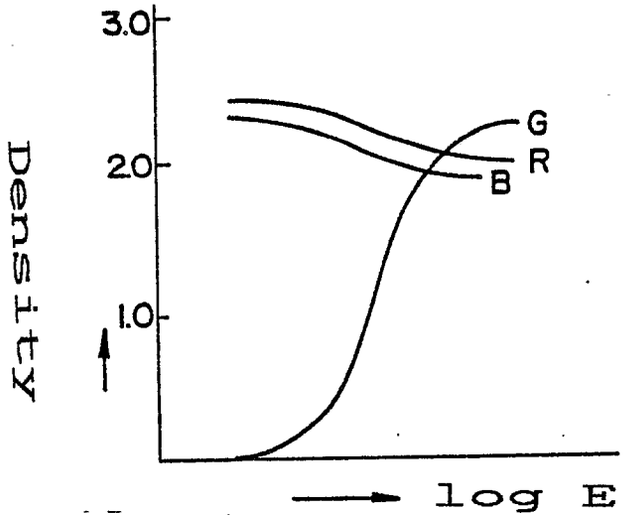
8. The method of claim 5, wherein said photographic material contains a magenta dye-forming coupler represented by formula [M-I];



[M-I]

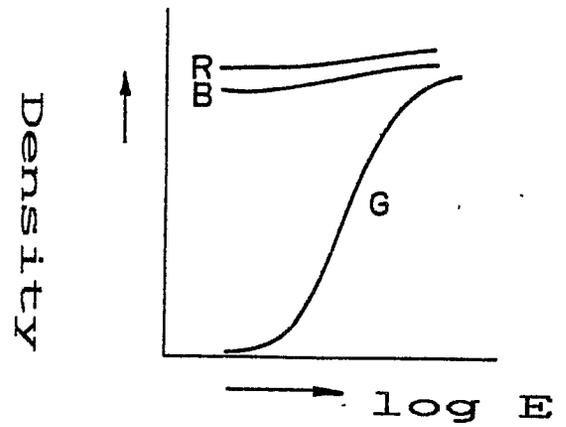
wherein, Z represents a group of non-metal atoms necessary to complete a nitrogen-containing heterocyclic group which may have a substituent; X is a hydrogen atom or a group which is, upon reaction with the oxidized product of a color developing agent, capable of being split off; and R is a hydrogen atom or a substituent.

Fig. 1



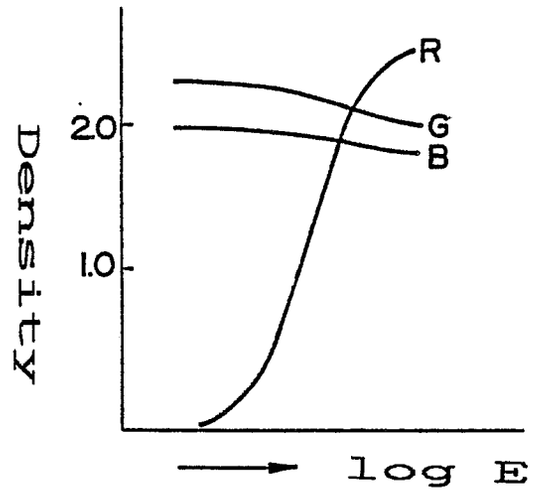
Sample No. 2
Exposure:
Blue: Uniform
Green: Wedge
Red: Uniform

Fig. 2



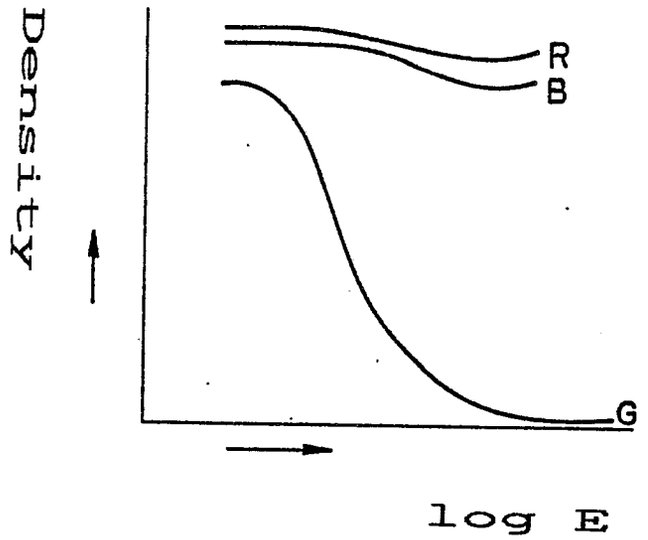
Sample No. 1
(Comparative)
Exposure:
Blue: Uniform
Green: Wedge
Red: Uniform

Fig. 3



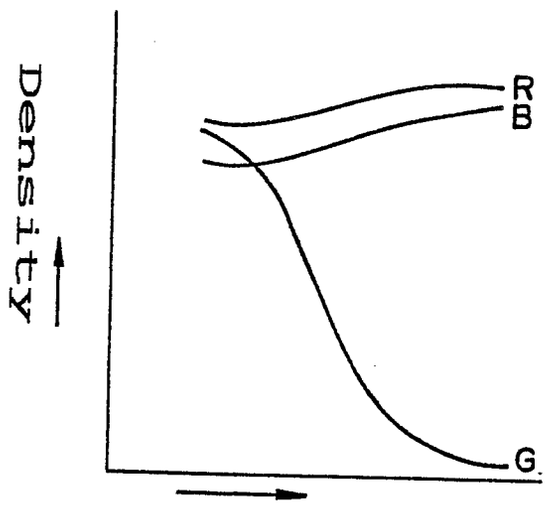
Sample No. 3
Exposure:
Blue: Uniform
Green: Uniform
Red: Wedge

Fig. 4



Sample No. 11
Exposure:
Blue: Uniform
Green: Wedge
Red: Uniform

Fig. 5



Sample No. 12
Exposure:
Blue: Uniform
Green: Wedge
Red: Uniform

Fig. 6

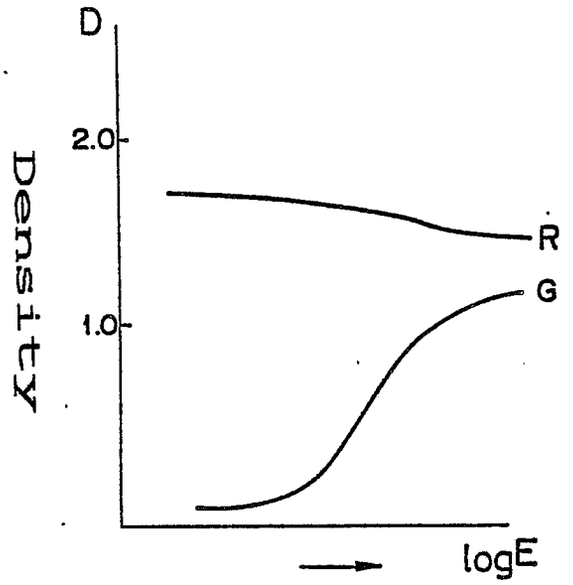


Fig. 7

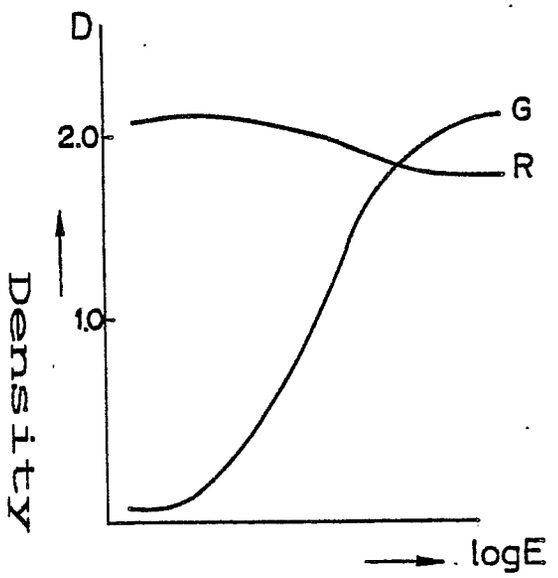
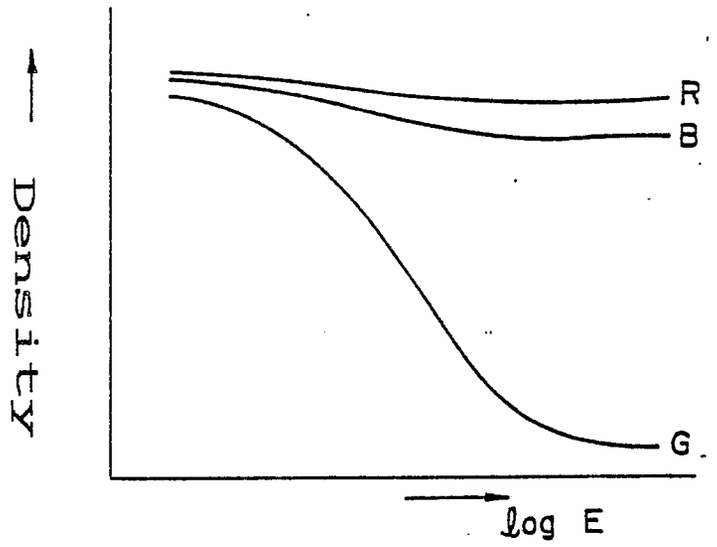
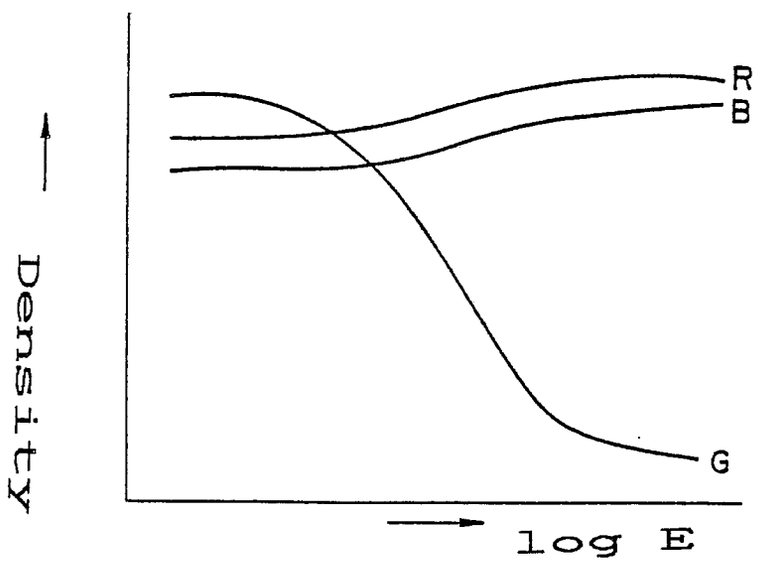


Fig. 8



Sample No. 7
(Comparative)
Exposure:
Blue: Uniform
Green: Wedge
Red: Uniform

Fig. 9



Sample No. 8
(Invention)
Exposure:
Blue: Uniform
Green: Wedge
Red: Uniform