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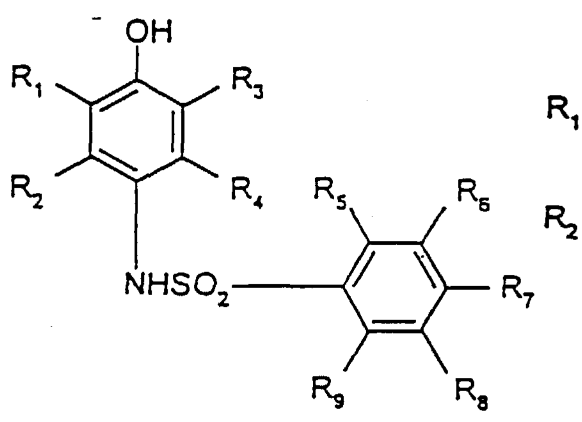
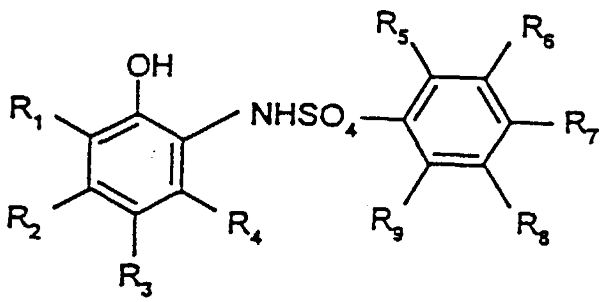
(54) Silver halide photographic light-sensitive material

(57) There is disclosed a silver halide photographic light-sensitive material which comprises at least a compound of the formula (1) or (2):

formula (1)



formula (2)



wherein R_1 to R_9 each are a hydrogen atom, a halogen atom, or a substituent having 4 or less carbon atoms or an I/O value of 1 or more; but in formula (1), R_2 and/or R_4, and R_5 and/or R_9, each are a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom; and in formula (2), R_4, and R_5 and/or R_9 each are a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom; and when R_1 and R_2, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, and R_8 and R_9 each are a substituent, except a hydrogen atom, the two of each of the combinations may independently bond together to form a ring. This light-sensitive material is excellent in discrimination and raw stock storability.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a silver halide photographic light-sensitive material, in particular to a silver halide photographic light-sensitive material excellent in the discrimination for an image formed and raw stock storability.

BACKGROUND OF THE INVENTION

[0002] The photographic process, in which silver halides are used, is conventionally most widely used, since it is excellent in photographic characteristics, such as sensitivity and gradation adjustment, in comparison with another photographic process, for example, electrophotography and diazo photography. The silver halide photographic process is still vigorously investigated because the highest image quality as, in particular, color hard copies can be obtained.

[0003] In recent years, from the image-formation processing method of light-sensitive materials in which silver halides are used, a system that can give an image easily and quickly by using, for example, an instant photographic system having a built-in developing solution or a dry-process heat development processing using heating or the like, has been developed in place of the conventional wet process. With respect to heat-development light-sensitive materials, "Shashin Kogaku No Kiso (Hi-ginen Shashin-hen)", published by Corona Co., p. 242, describes them, which is only directed to the black-and-white image formation method for dry silver as a representative.

[0004] As heat-development color light-sensitive materials, recently, products called PICTROGRAPHY and PICTROSTAT (trade names) have been marketed by Fuji Photo Film Co., Ltd. This easy, quick processing method uses a redox compound having a preformed dye linked (hereinafter referred to as a coloring material), to carry out the color image formation. On the other hand, as the method for the color image formation for photographic light-sensitive materials, one in which a coupling reaction of a coupler with the oxidized product of a developing agent is used, is most popular. Many ideas on heat development color light-sensitive materials that employ that method are disclosed and filed as patent applications, for example, in US-A-3 761 270, US-A-4 021 240, JP-A-59-231539 ("JP-A" means unexamined published Japanese patent application) and JP-A-60-128438. Further, JP-A-9-146247, JP-A-9-146248, and JP-A-9-204031 disclose color light-sensitive materials for photographing (shooting) wherein a processing material containing a base precursor is used, and processing by heating is carried out, in the presence of a small amount of water.

[0005] In the above-described heat-development light-sensitive materials, there are points that need improving because, for example, the processing time is long, it takes time from the exposure to the output, and the processor becomes large-sized. Further, the discrimination of images needs improving.

[0006] Generally, in heat-development light-sensitive materials, the built-in reducing agent (or the developing agent) reduces the silver halide in the development processing, which is a first step to initiate an image-forming reaction. In order to quicken this, first, a method is conceivable wherein the reducing agent is made hydrophilic, to accelerate its reaction with the silver halide in the aqueous phase. However, when this method is used for usual heat-development light-sensitive materials, the reducing agent moves between layers during processing, which allows unpreferable reactions to inevitably take place, such as causing mixing of colors. In order to obviate this, a method is conceivable wherein a hydrophilic reducing agent is used as an auxiliary developing agent in combination with a lipophilic reducing agent, so that electron transfer will occur between them, thereby increasing the development rate. This idea is known in the art, and its application to heat-development light-sensitive materials is described, for example, in JP-A-1-138556.

[0007] However, generally the reducing agent increased in hydrophilicity and improved in silver developability has the problem that it is poor in stability and is easily oxidized with oxygen in the air, to be decreased, during raw stock storage. As an auxiliary developing agent particularly excellent in silver developability, a 1-phenyl-3-pyrazolidinone derivative is known in the art, but this compound is not satisfactorily stable as a built-in developing agent. The inventors of the present invention have been searching for compounds that solve these problems. It has been found under these circumstances that sulfonamidophenols, as described, for example, in US-A-4 021 240, JP-A-60-128438, and JP-A-8-220717, are compounds excellent in discrimination and raw stock storability when they are built into light-sensitive materials. The performance of the sulfonamidophenols as a reducing agent has been investigated in various ways. As a result, it has been found that these compounds are compounds that have satisfactory raw stock storability, even when they are increased in hydrophilicity, as a built-in developing agent, to improve the silver developability. However, since, for the sulfonamidophenols, the oxidized product of the developing agent after the silver development is poor in stability, the oxidized product of the developing agent is hydrolyzed at the developed part, thereby producing developed silver whose quantity is more than the theoretical quantity. It has been found that, as a result, a problem arises that color contamination owing to silver images takes place.

SUMMARY OF THE INVENTION

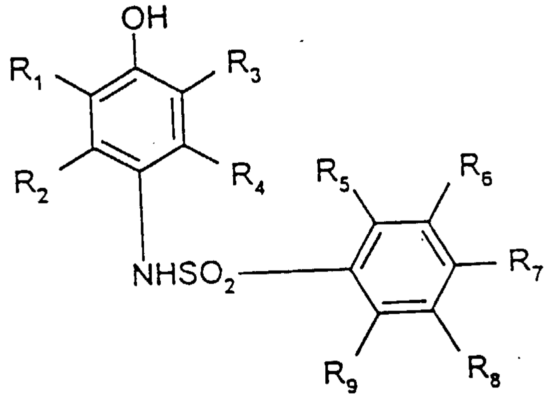
[0008] An object of the present invention is to provide a silver halide photographic light-sensitive material excellent in discrimination and raw stock storability.

[0009] Other and further objects, features, and advantages of the invention will appear more fully from the following description.

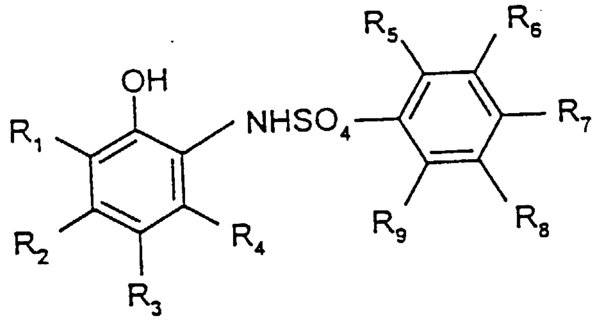
DETAILED DESCRIPTION OF THE INVENTION

[0010] The above object of the present invention has been attained by a silver halide photographic light-sensitive material which comprises at least a compound represented by the following formula (1) or (2):

formula (1)



formula (2)



wherein R_1 to R_9 each represent a hydrogen atom, a halogen atom, or a substituent having 4 or less carbon atoms or an I/O value of 1 or more; but in formula (1), R_2 and/or R_4, and R_5 and/or R_9, each represent a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom; and in formula (2), R_4, and R_5 and/or R_9 each represent a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom; and when R_1 and R_2, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, and R_8 and R_9 each represent a substituent, except a hydrogen atom, the two of each of the combinations may independently bond together to form a ring.

[0011] Hereinbelow, preferable modes of the present invention are described in detail.

[0012] First, the compounds represented by formula (1) or (2) are described in detail.

[0013] The compounds represented by formula (1) or (2) represent reducing agents (developing agents) collectively called sulfonamidophenols. In formulas, R_1 to R_9 each represent a hydrogen atom, a halogen atom, or a substituent having 4 or less carbon atoms or an I/O value of 1 or more. The term I/O value means a parameter representing the scale of the lipophilicity and the hydrophilicity of a compound or a substituent, and it is described in detail in "Yuki Gainen-zu" (written by Koda Yoshiki; published by Sankyo Shuppan, 1984). "I" denotes inorganic nature, and "O" denotes organic nature. The larger the I/O value is, the higher the inorganic nature is. Here, specific examples of I/O values are described. The O value is 20 per carbon atom. Representative examples of the I value are 200 for an -NHCO- group, 240 for an $-NHSO_2-$ group, and 60 for a -COO- group. For instance, in the case of $-NHCOC_5H_{11}$, the number of carbon atoms is 6, the O value is 20 x 6 = 120, and I = 200, so that $I/O \fallingdotseq 1.67$, and therefore $I/O > 1$.

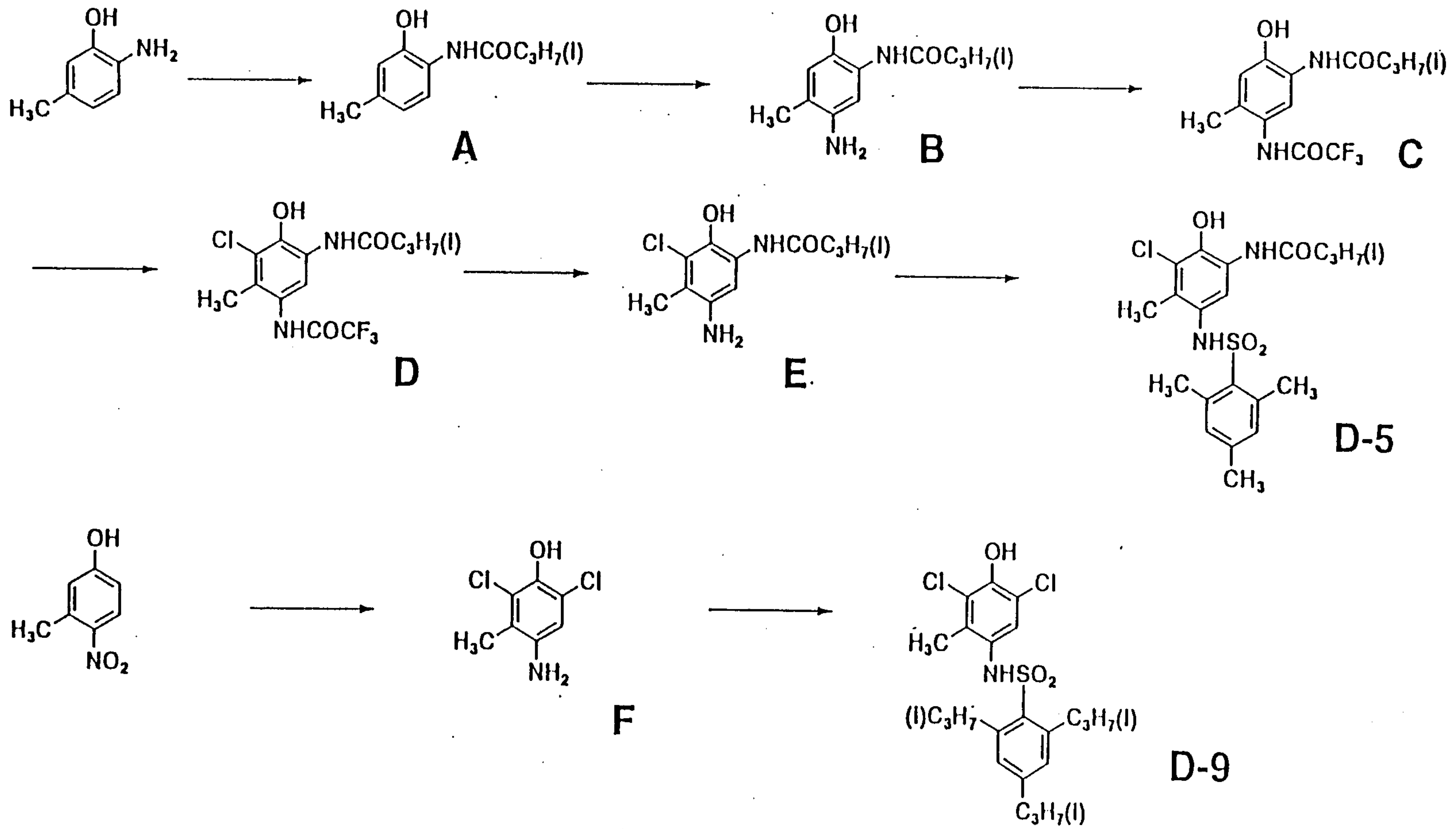
[0014] The compound for use in the present invention is a compound substituted by a substituent whose I/O value is 1 or more and preferably 12 or less, or the number of carbon atoms is 4 or less, and it is characterized by hydrophilicity. A specific example of the substituent is, for example, a halogen atom (e.g. chlorine and bromine), an alkyl group (e.g. methyl, ethyl, isopropyl, n-butyl, and t-butyl), an aryl group (e.g. 3-methanesulfonylamynophenyl), an alkylcarbonamido group (e.g. acetylamino, propionylamino, and butyroylamino), an arylcarbonamido group (e.g. benzoylamino), an alkylsulfonamido group (e.g. methanesulfonylamino and ethanesulfonylamino), an arylsulfonamido group (e.g. benzenesulfonylamino and toluenesulfonylamino), an alkoxy group (e.g. methoxy and ethoxy), an aryloxy group (e.g. 4-methanesulfonylaminophenoxy), an alkylthio group (e.g. methylthio, ethylthio, and butylthio), an arylthio group (e.g. 4-methanesulfonylaminophenylthio), an alkylcarbamoyl group (e.g. methylcarbamoyl, dimethylcarbamoyl, ethylcarbamoyl, diethylcarbamoyl, dibutylcarbamoyl, piperidinocarbamoyl, and morpholinocarbamoyl), an arylcarbamoyl group (e.g. phenylcarbamoyl, methylphenylcarbamoyl, ethylphenylcarbamoyl, and benzylphenylcarbamoyl), a carbamoyl group, an alkylsulfamoyl group (e.g. methylsulfamoyl, dimethylsulfamoyl, ethylsulfamoyl, diethylsulfamoyl, dibutylsulfamoyl, piperidinosulfamoyl, and morpholinosulfamoyl), an arylsulfamoyl group (e.g. phenylsulfamoyl, methylphenylsulfamoyl, ethylphenylsulfamoyl, and benzylphenylsulfamoyl), a sulfamoyl group, a cyano group, an alkylsulfonyl group (e.g. methanesulfonyl and ethanesulfonyl), an arylsulfonyl group (e.g. phenylsulfonyl, 4-chlorophenylsulfonyl, and p-toluenesulfonyl), an alkoxycarbonyl group (e.g. methoxycarbonyl, ethoxycarbonyl, and butoxycarbonyl), an aryloxycarbonyl group (e.g. phenoxycarbonyl), an alkylcarbonyl group (e.g. acetyl, propionyl, and butyloyl), an arylcarbonyl group (e.g. benzoyl and alkylbenzoyl), or an acyloxy group (e.g. acetyloxy, propionyloxy, and butyloyloxy).

[0015] Further, in formula (1), R_2 and/or R_4, and R_5 and/or R_9, each represent a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom; and in formula (2), R_4, and R_5 and/or R_9 each represent a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom.

[0016] When R_1 and R_2, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, and R_8 and R_9 each represent a substituent, except a hydrogen atom, the two of each of the combinations may independently bond together to form a ring.

[0017] The compounds represented by formula (1) or (2) can be synthesized by combining, stepwise, methods widely known in the field of organic synthesis chemistry. Examples of the stepwise synthetic method are described below by illustrating synthesis schemes of the below-mentioned Exemplified Compounds.

Route for synthesizing Exemplified Compounds



《Synthesis of Exemplified Compound D-5》

1) Synthesis of Compound A

[0018] 766 g (5 mol) of 6-amino-m-cresol and 2,000 ml of acetonitrile were charged into a 5-liter three-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a mechanical agitator, and they were stirred at room temperature. At that time, the solution was in the form of a non-uniform slurry. When 791 g (5 mol) of isobutyric anhydride was added thereto over 30 min, the temperature rose gradually until it reached 60 °C, finally, and the solution became uniform, finally. When the rising of the temperature stopped, crystals of the product began to precipitate in the flask. After stirring for one hour further, the contents were poured into 15 liters of a 10% brine, and the precipitated crystals were filtered through a Nutsche, under reduced pressure. After the crystals were washed with 2 liters of distilled water, they were dried. The crystals were so pure that they could be used in the next step as they were. Thus, 928 g of crystals of Compound A were obtained (yield: 96%).

2) Synthesis of Compound B

[0019] 193 g (1 mol) of Compound A was charged into a 10-liter beaker, and 500 ml of methanol and an aqueous solution of 120 g (30 mol) of sodium hydroxide dissolved in 500 ml of water were added thereto. This solution was continually stirred with the temperature kept at 0 °C or less. On the other hand, 216 g (1.25 mol) of sulfanilic acid was dissolved completely in an aqueous sodium hydroxide solution (an aqueous solution of 50 g of sodium hydroxide dissolved in 400 ml of water). 300 ml of concentrated hydrochloric acid was added thereto, to form a solution in the form of a slurry. While this liquid was stirred vigorously with the temperature kept at 0 °C or less, a solution of 93 g (1.35 mol) of sodium nitrite dissolved in 200 ml of water was added gradually, to produce a diazonium salt. At that time, the reaction was allowed to take place while ice was added appropriately, so that the temperature would be kept at 0 °C or less. The diazonium salt prepared in this way was added gradually to the above solution of Compound A that was kept stirred. At that time, again, the reaction was allowed to take place while ice was added appropriately, so that the temperature would be kept at 0 °C or less. With the addition, the solution assumed the red color of an azo dye. After completion of the addition, the reaction was allowed to proceed for 30 min further at 0 °C or less, and upon recognition of the disappearance of the raw material, 750 g (4.5 mol) of a powder of sodium hydrosulfite was added thereto. When this solution was heated to 50 °C, reduction of the azo group took place, with vigorous bubbling. When the bubbling subsided and the liquid was decolored, to become a yellowish transparent liquid, the solution was cooled gradually to 10 °C. From the time of about the start of the cooling, crystals began to deposit gradually. The deposited crystals were filtered, and the crude crystals were recrystallized from a mixed solvent of methanol and water, to obtain 162 g of crystals of Compound B (yield: 78%).

3) Synthesis of Compound C

[0020] 833 g (4 mol) of Compound B and 2,000 ml of acetontrile were charged into a 5-liter three-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a mechanical agitator, and they were stirred at room temperature. At that time, the solution was in the form of a non-uniform slurry. When 840 g (4 mol) of trifluoroacetic anhydride was added thereto over 30 min, the temperature rose gradually. It was cooled appropriately with an ice bath, so that the rise in the temperature would be up to 45 °C. After completion of the addition, the solution became uniform. When the rise of the temperature stopped, crystals of the product began to precipitate in the flask. After stirring for one hour further, the contents were poured into 15 liters of a 10% brine, and the deposited crystals were filtered through a Nutsche, under reduced pressure. After the crystals were washed with 2 liters of distilled water, they were dried. The crystals were so pure that they could be used in the next step as they were. Thus, 1,132 g of crystals of Compound C were obtained (yield: 93%).

4) Synthesis of Compound D

[0021] 913 g (3 mol) of Compound C and 2,500 ml of dichloromethane were charged into a 5-liter three-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a mechanical agitator, and they were stirred at room temperature. At that time, the solution was in the form of a non-uniform slurry. When 540 g (4 mol) of sulfuryl chloride was added thereto over 30 min, the temperature rose gradually; then a gas was given off, and at the same time reflux was started. After completion of the addition, when the reaction was allowed to proceed for 2 hours further under reflux, the generation of the gas stopped. At that time the solution remained in the non-uniform state. After stirring for one hour further, the internal temperature was lowered to room temperature, and the contents were poured into 10 liters of n-hexane. The deposited crystals were filtered through a Nutsche, under reduced pressure, and after the crystals were washed with 2 liters of n-hexane, they were dried. The crystals were so pure that they could be used in the next step as they were. Thus, 940 g of crystals of Compound D were obtained (yield: 89%).

5) Synthesis of Compound E

[0022] 224 g of potassium hydroxide and 1,200 ml of water were charged into a 3-liter three-necked flask equipped with a condenser, a thermometer, a dropping funnel, a nitrogen introduction pipe, and a mechanical agitator, and the potassium hydroxide was dissolved completely. While nitrogen was passed through the solution, 678 g (2 mol) of Compound D, in the form of a powder, was added gradually thereto, and after completion of the addition, the internal temperature was elevated to 60 °C. At that time, the solution changed from a non-uniform slurry to a uniform solution. After stirring for 2 hours further, the internal temperature was lowered to room temperature, and, when 200 ml of acetic acid was added, crystals deposited. The deposited crystals were filtered through a Nutsche, under reduced pressure. After the crystals were washed with cold distilled water, they were recrystallized from a methanol/water mixed solvent, to obtain 403 g of crystals of Compound E (yield: 83%).

6) Synthesis of Exemplified Compound D-5

[0023] 971 g (4 mol) of Compound E and 2,800 ml of acetontrile were charged into a 5-liter three-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a mechanical agitator, and they were stirred at room temperature. At that time, the solution was in the form of a non-uniform slurry. When 875 g (4 mol) of a powder of mesitylenesulfonyl chloride was added thereto over 10 min, the temperature rose gradually. It was cooled appropriately with an ice bath, so that the rise in the temperature would be up to 30 °C. After completion of the addition, it was cooled with an ice bath, so that the internal temperature would be 15 °C or less, and then 324 ml (4 mol) of pyridine was added, dropwise, over 10 min. After completion of the addition, the reaction was allowed to proceed for 2 hours at room temperature, with stirring. After a while, crystals of the product began to deposit in the flask. After completion of the reaction, the contents were poured into 20 liters of a 3% aqueous hydrochloric acid solution, and the deposited crystals were filtered through a Nutsche, under reduced pressure. After the crystals were washed with 4 liters of distilled water, they were recrystallized from an acetonitrile/water mixed solvent, to obtain 1,564 g of crystals of Exemplified Compound D-5 (yield: 92%).

⟨⟨Synthesis of Exemplified Compound D-9⟩⟩

1) Synthesis of Compound F

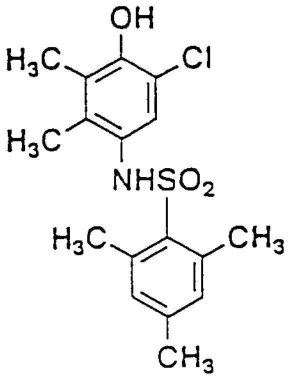
[0024] 153 g (1 mol) of 4-nitro-m-cresol and 1,000 ml of methanol were charged into a 5-liter three-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a mechanical agitator, and they were stirred at room temperature. At that time, the solution was in the form of a non-uniform slurry. 2 liters of an aqueous sodium hypochlorite solution (available chlorine: 5%) was added thereto, dropwise, with care taken so that the internal temperature did not exceed 50 °C. At the time of the addition, the color of the solution turned reddish-brown. After completion of the addition, when 500 g (3 mol) of a powder of sodium hydrosulfite was added gradually, reduction of the nitro group took place, with vigorous bubbling. At that time, care had to be taken that the internal temperature did not exceed 60 °C and bubbling did not become too vigorous. When the bubbling stopped and the liquid was decolored, to become a yellowish transparent liquid, the solution was cooled gradually to 10 °C. From about the time of the start of the cooling, crystals deposited gradually. The deposited crystals were filtered, and the crude crystals were recrystallized from a mixed solvent of methanol and water, to obtain 142 g of crystals of Compound F (yield: 74%).

2) Synthesis of Exemplified Compound D-9

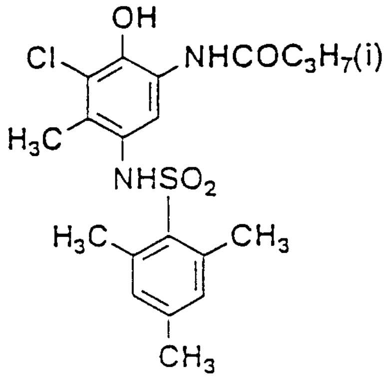
[0025] 768 g (4 mol) of Compound F, 1,500 ml of acetontrile, and 1,100 ml of N,N-dimethylacetamide (DMAc) were charged into a 5-liter three-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a mechanical agitator, and they were stirred at room temperature. At that time, the solution became uniform. When 1,212 g (4 mol) of a powder of triisopropylbenzenesulfonyl chloride was added thereto over 10 min, the temperature rose gradually. It was cooled appropriately with an ice bath, so that the rise in the temperature would be up to 30 °C. After completion of the addition, it was cooled with an ice bath, so that the internal temperature would be 15 °C or less, and then 324 ml (4 mol) of pyridine was added, dropwise, over 10 min. After completion of the addition, the reaction was allowed to proceed for 2 hours at room temperature, with stirring. After completion of the reaction, the contents were poured into 20 liters of a 3% aqueous hydrochloric acid solution, and the deposited crystals were filtered through a Nutsche, under reduced pressure. After the crystals were washed with 4 liters of distilled water, they were recrystallized from a mixed solvent of methanol and water, to obtain 1,669 g of crystals of Exemplified Compound D-9 (yield: 91%).

[0026] Specific examples of the compounds represented by formula (1) or (2) are shown below, which of course are not meant to limit the present invention.

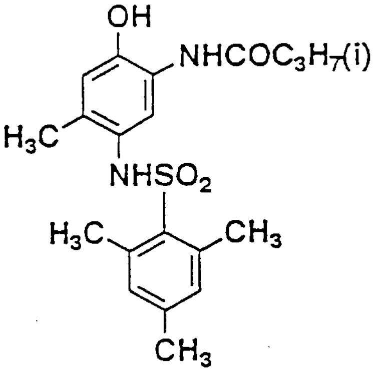
D-1



D-5



D-2



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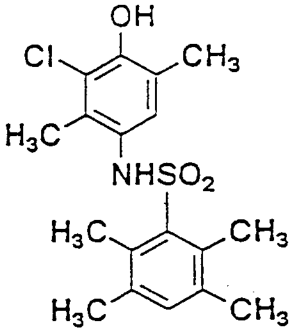

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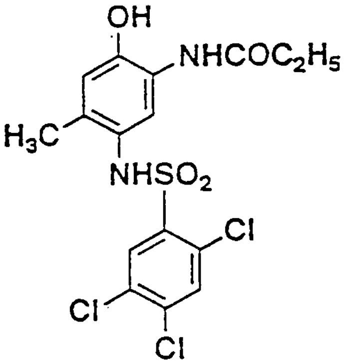

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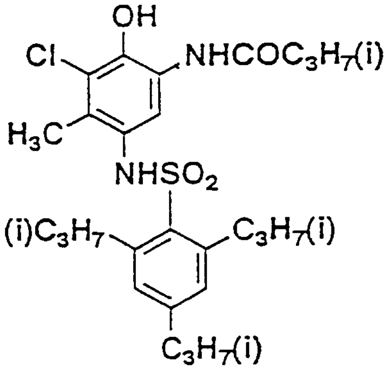

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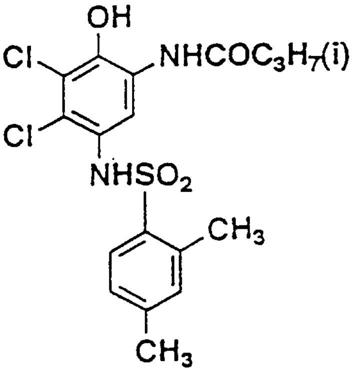

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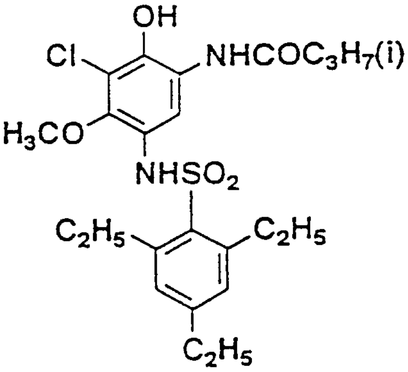
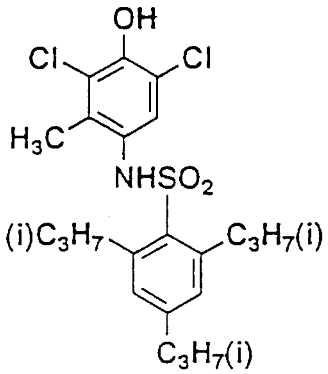


D-9



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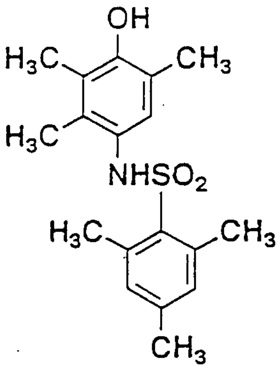

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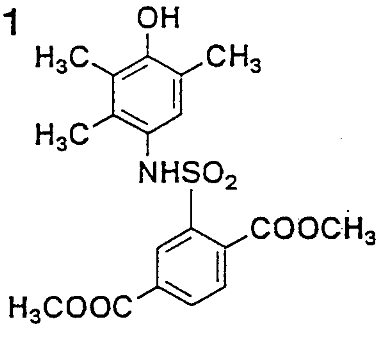

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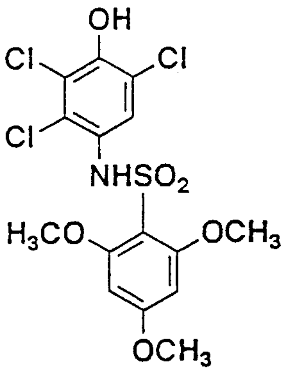

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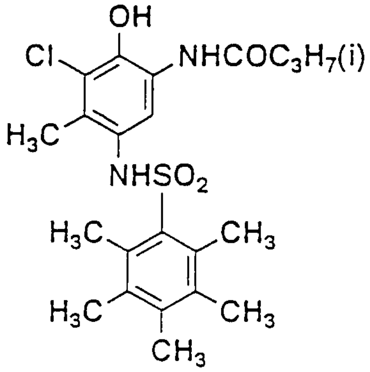
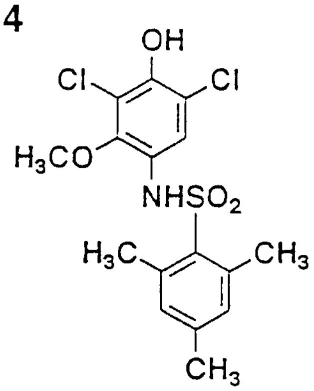
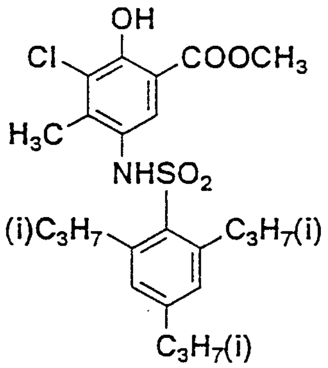


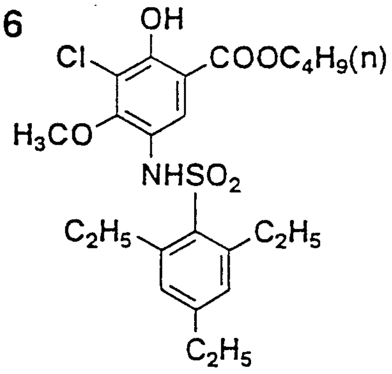
D-14



D-15



D-16



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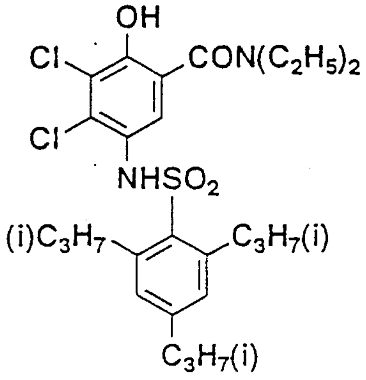

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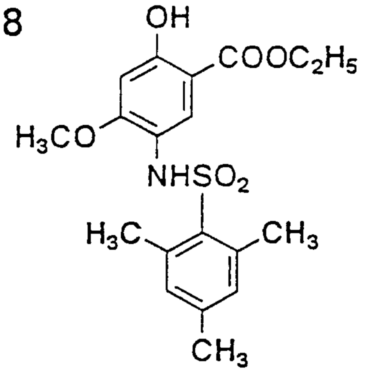

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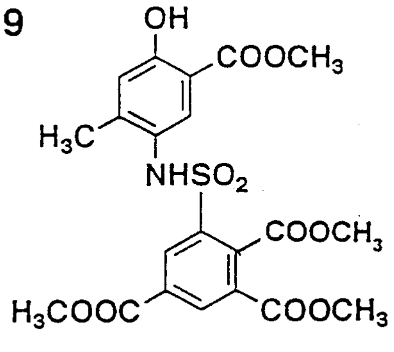

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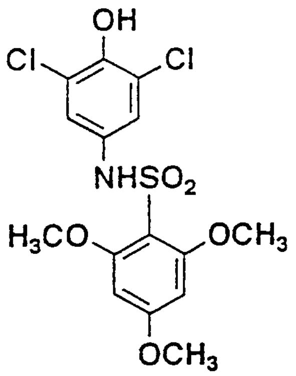

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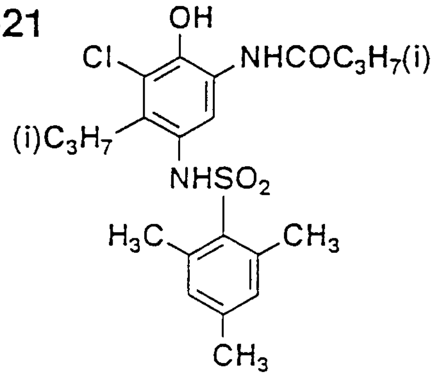

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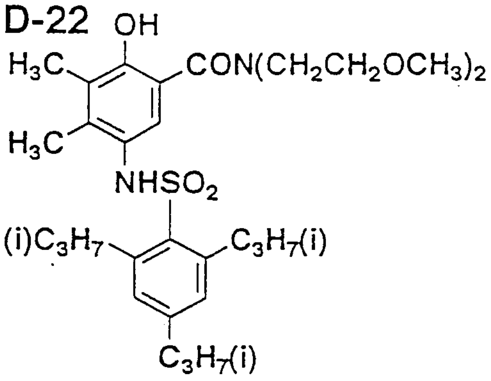

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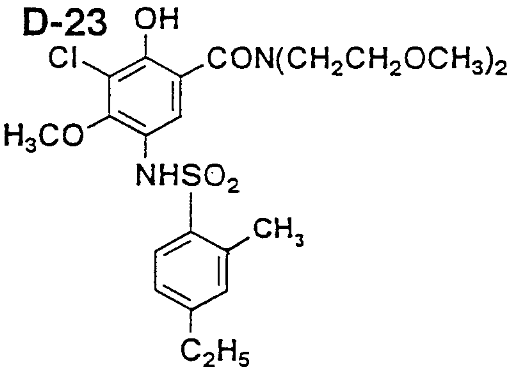

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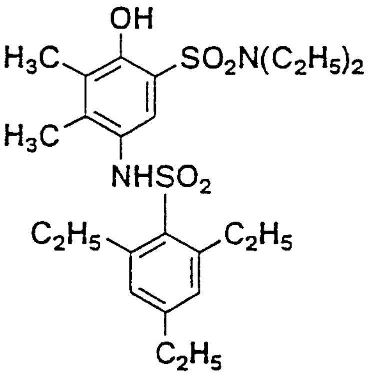

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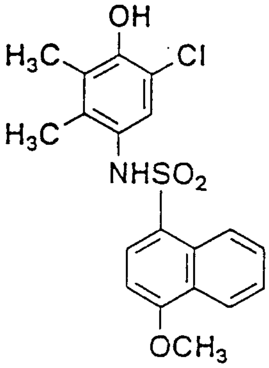

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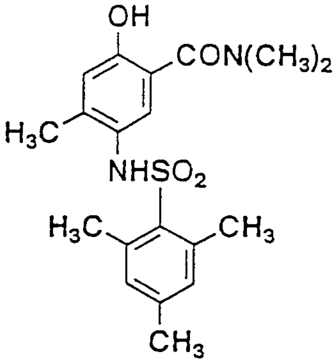

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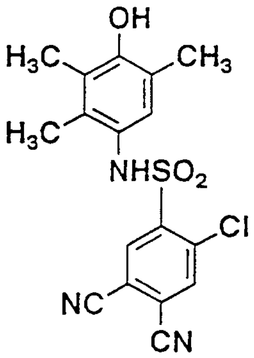

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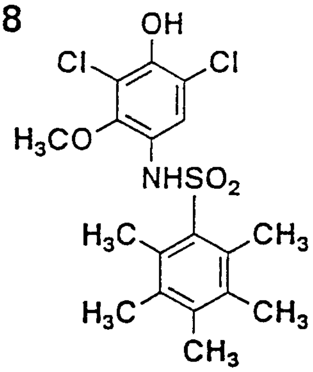

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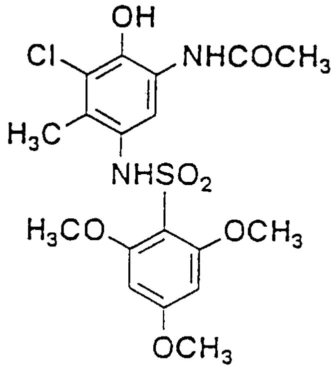

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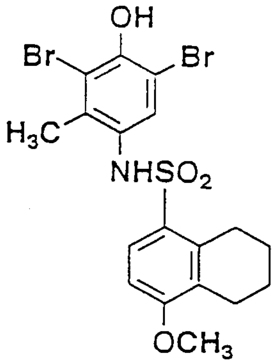

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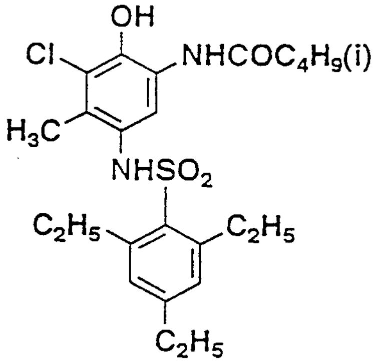

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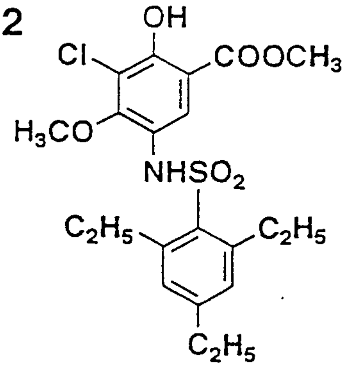

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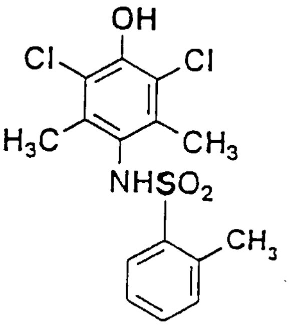

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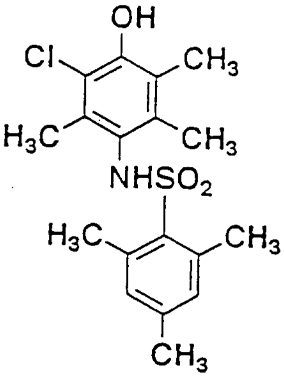

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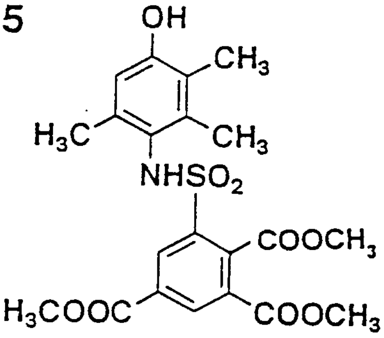

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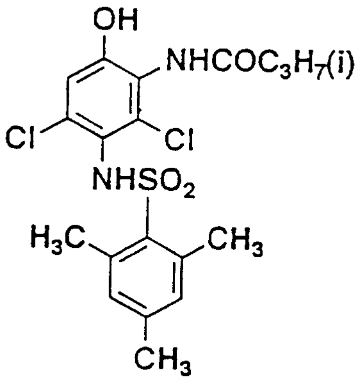

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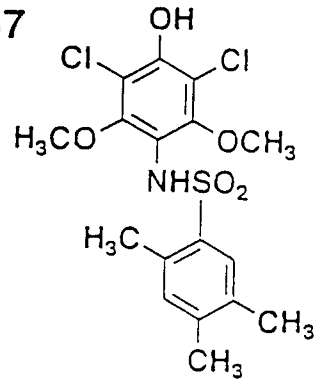

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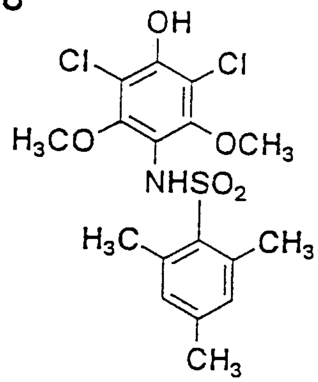

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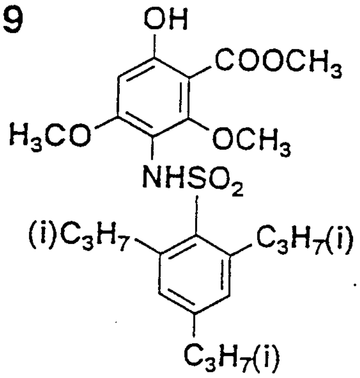

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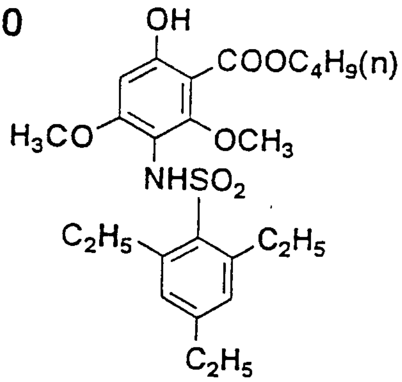

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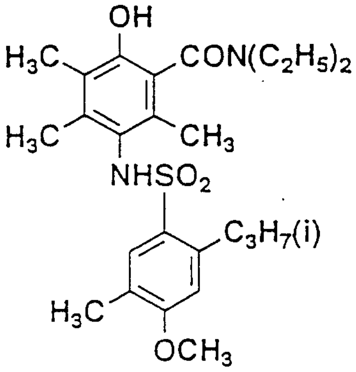

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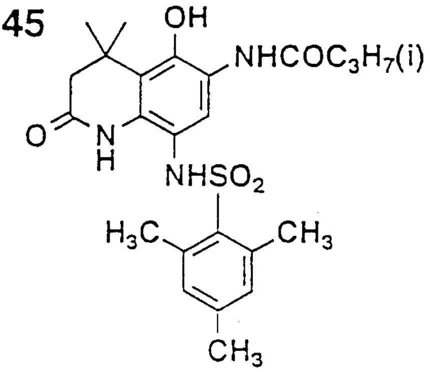

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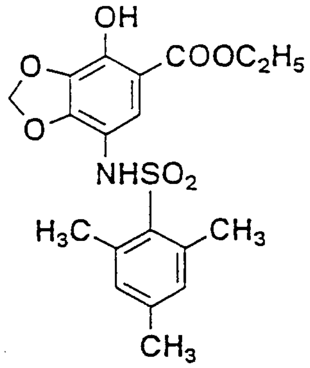

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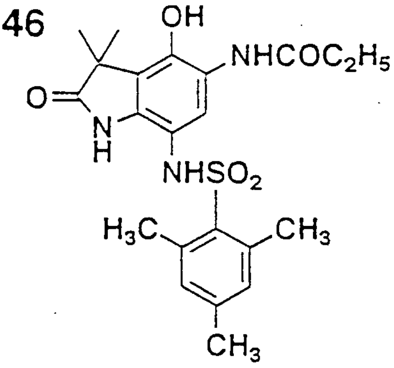

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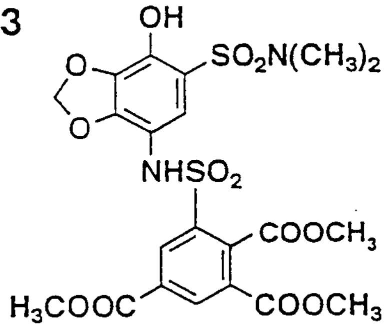

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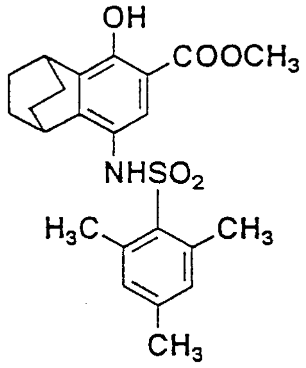

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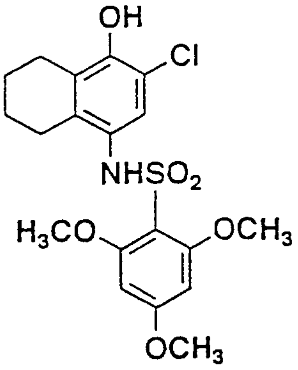

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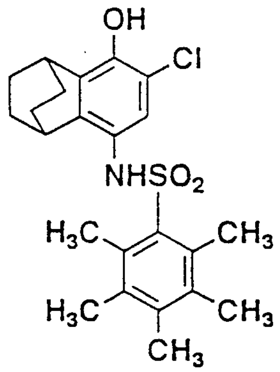

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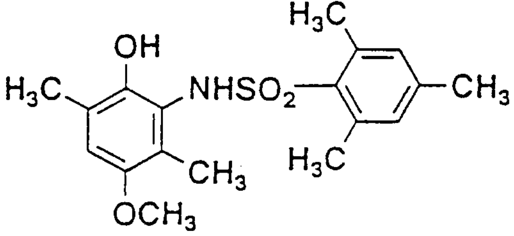

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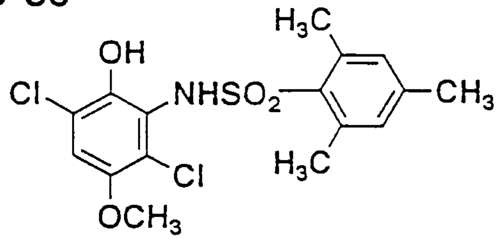

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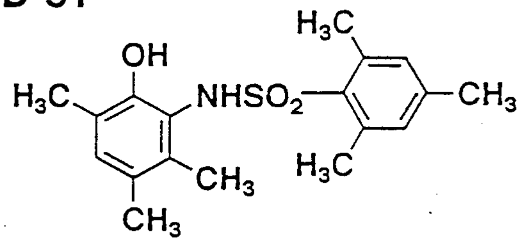

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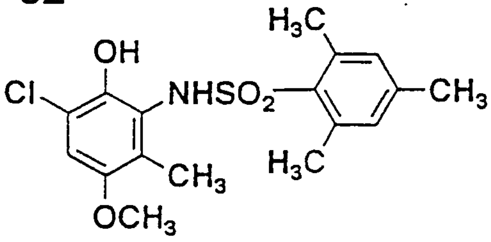

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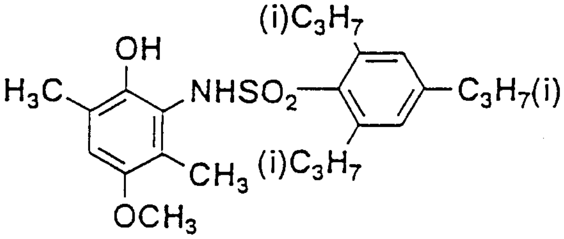

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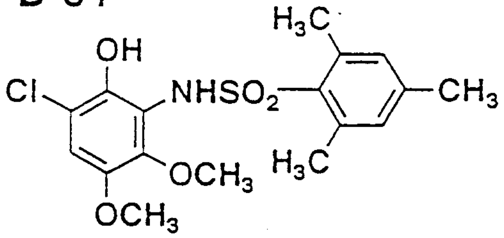

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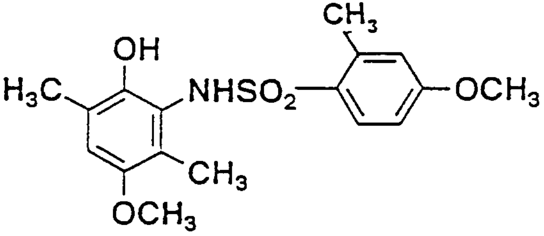

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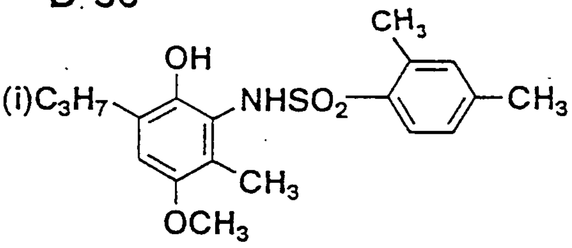

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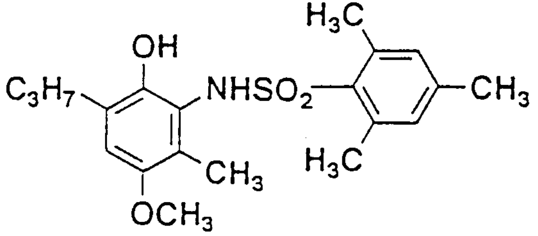

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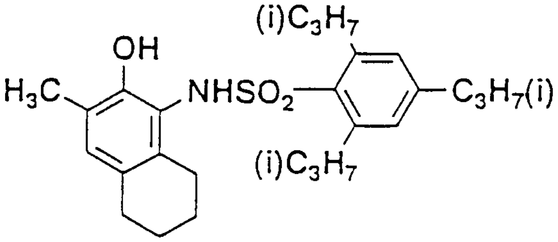

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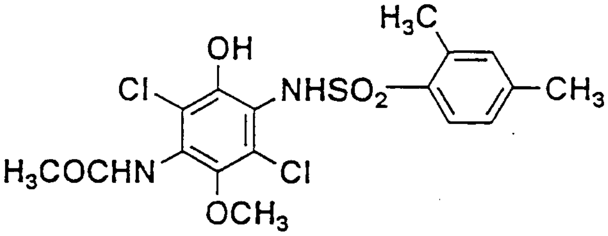

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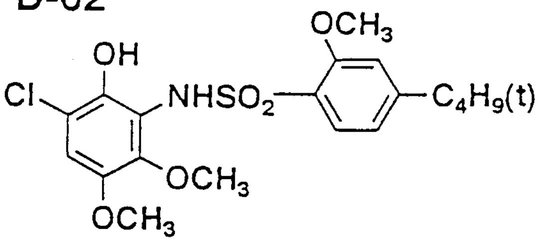

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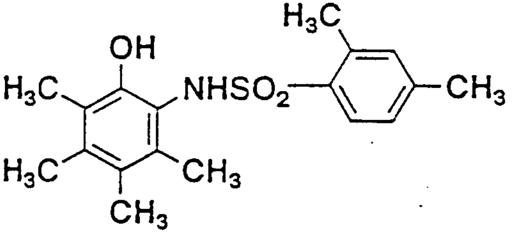

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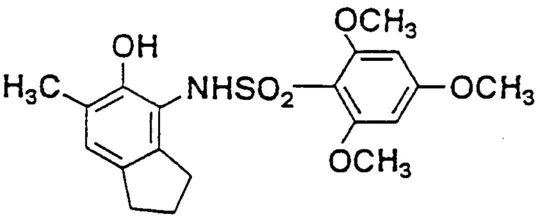

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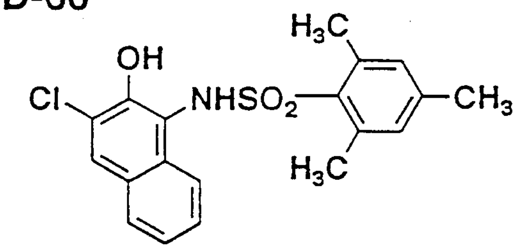

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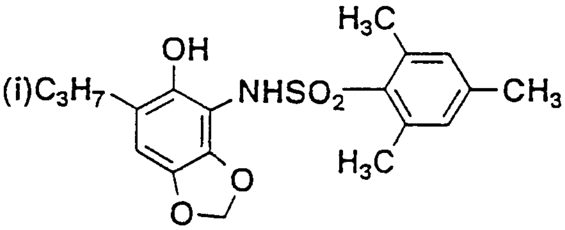


[0027] When the compounds represented by formula (1) or (2) are used in a silver halide photographic light-sensitive material, since these compounds allow rapid silver development as intended by the present invention, the image due to the reduced silver produced by the reduction reaction of these compounds alone can be used. Also an image can be formed by a cross-oxidizing reaction between a different kind of reducing agent and the oxidized product of the compound represented by formula (1) or (2). The reducing agent that is used in combination with the compound represented by formula (1) or (2) to carry out a cross-oxidizing reaction to form an image is described below.

1) Color-developing agents that can be used in combination with a coupler to form a dye image
Examples of these compounds include sulfonamidophenols, sulfonylhydrazines, sulfonylhydrazones, carbamoylhydrazines, and carbamoylhydrazones described, for example, in JP-A-8-110608, JP-A-9-34081, and JP-A-8-267839, and aminoantipyrine derivatives described in JP-A-9-120132.
2) DDR couplers capable of releasing a diffusible dye by coupling
Examples of these DDR couplers include compounds described, for example, in US-A-3 443 940, US-A-4 474 867, and US-A-4 483 914.
3) Dye-providing compounds (DRR compounds) that, when oxidized, release a diffusible dye
Examples of these compounds include compounds described, for example, in JP-A-59-65839, JP-A-59-69839, and JP-A-53-3819.
4) Reducing agents that are used in combination with dye-providing compounds [ROSET compounds (Nihon Shashin Gakkai-shi, Vol. 55, No. 3, page 185, 1992), BEND compounds, or the like (US-A-4 139 379)] that, when reduced, release a diffusible dye

[0028] In this image-forming method, a positive image can be formed by the reducing agent that has remained unoxidized by silver development. Examples of the dye-providing compounds include compounds described, for example, in JP-A-1-26842, JP-A-63-201653, and JP-A-201654.

[0029] When the compounds represented by formula (1) or (2) are used in a light-sensitive material, the coating amount thereof can be selected in a wide range. In particular, the coating amount is different when these compounds are used singly from the amount when they are used in combination with other reducing agents as described above. When the compounds represented by formula (1) or (2) are used singly, preferably the coating amount is 0.001 to 1,000 mmol/m^2, and more preferably 0.05 to 50 mmol/m^2. When the compounds represented by formula (1) or (2) are used in combination with other reducing agents, the coating amount of the reducing agent used for forming an image is preferably 0.001 to 1,000 mmol/m^2, and more preferably 0.05 to 50 mmol/m^2, although it varies depending on the molar extinction coefficient of the dye to be formed. On the other hand, when the compounds represented by formula (1) or (2) are used as an auxiliary developing agent, they are added appropriately in an amount of generally 0.001 to 1,000 times, preferably 0.01 to 100 times, and more preferably 0.05 to 10 times, the molar amount of the above reducing agent.

[0030] The method for adding the compound represented by formula (1) or (2) can be carried out by mixing, first, the compound, oil-soluble compounds to be used with, such as a coupler, and a high-boiling organic solvent (e.g. an alkyl phosphate and an alkyl phthalate), dissolving the resultant mixture in a low-boiling organic solvent (e.g. ethyl acetate and methyl ethyl ketone), dispersing the resulting solution in water using an emulsifying and dispersing method known in the art, and adding the emulsified dispersion. The solid dispersion method described in JP-A-63-271339 can also be used for the addition.

[0031] The compound for use in the present invention can be used in monochromatic silver halide photographic light-sensitive materials, and it can also be used in color photographic light-sensitive materials. In the following examples, color photographing materials wherein the compound (1) or (2) for use in the present invention is used are described.

[0032] In order to obtain colors ranging widely on the chromaticity diagram by using three primary colors: yellow, magenta, and cyan, use is made of a combination of at least three silver halide emulsion layers photosensitive to respectively different spectral regions. For example, a combination of three layers of a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, and a combination of a green-sensitive layer, a red-sensitive layer, and an infrared-sensitive layer, can be mentioned. The photosensitive layers can be arranged in various orders known generally for color photographic materials. Further, each of these photosensitive layers can be divided into two or more layers if necessary.

[0033] Further, after the formation of a color-formed image by heat development, the remaining silver halide and/or developed silver may or may not be removed. As a means for outputting to a different material based on its image information, the generally used projection exposure may be used, or the image information may be read photoelectrically by measuring the density of the transmitted light, and its signals may be outputted. The material to which the output is made may not be light-sensitive materials and may, for example, be sublimation-type thermographic (heat sensitive recording) materials, ink jet materials, electrophotographic materials, and full-color direct thermographic materials. An example of a preferable mode in the present invention is one in which, after the formation of a color-formed image by heat development, without carrying out additional processing for removing the remaining silver halide and the developed silver, the image information is read photoelectrically by measuring the transmitted density, using a CCD image sensor and diffused light, and the information is transformed into digital signals that in turn are subjected to image processing and are outputted to a heat development color printer, such as "PICTOGRAPHY" 3000" (trade name), manufactured by Fuji Photo Film Co., Ltd. In this case, a good print can be obtained quickly without using any of the processing solutions used in conventional color photography. Further, in this case, since the above digital signals can be processed and edited arbitrarily, the photographed image can be corrected (retouched), modified, and processed freely, to be outputted.

[0034] It is suitable that the light-sensitive material of the present invention is provided with at least one photosensitive layer on a support, and anti-halation layer under the photosensitive layer. The photosensitive layer may be a photosensitive layer that comprises a plurality of silver halide emulsion layers whose color sensitivities are substantially identical but whose sensitivities are different, and it is preferable that the photosensitive layer being a unit photosensitive layer having color sensitivity to any of blue light, green light, and red light, and in a multilayer silver halide color photographic light-sensitive material, the arrangement of the unit photosensitive layers is generally such that a red-sensitive layer, a green-sensitive layer, and a blue-sensitive layer in the order stated from the support side are placed. However, the above order may be reversed according to the purpose and such an order is possible that layers having the same color sensitivity have a layer different in color sensitivity therefrom between them. Nonphotosensitive layers such as various intermediate layers may be placed between, on top of, or under the above-mentioned silver halide photosensitive layers. The intermediate layer may contain, for example, the above-described couplers, developing agents, DIR compounds, color-mixing inhibitor, and dyes. Each of the silver halide emulsion layers constituting unit photosensitive layers respectively can preferably take a two-layer constitution comprising a high-sensitive emulsion layer and a low-sensitive emulsion layer, as described in DE 1 121 470 or GB-923 045. Generally, they are preferably arranged such that the sensitivities are decreased toward the support. As described, for example, in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, a low-sensitive emulsion layer may be placed away from the support and a high-sensitive emulsion layer may be placed nearer to the support.

[0035] The silver halide may be any of silver iodobromide, silver chloroiodobromide, silver bromide, silver chlorobromide, silver iodochloride, and silver chloride. The composition thereof is selected depending on the properties to be given to the light-sensitive silver halide. For example, when high sensitivity is required, as in the case of photographing materials, a silver iodobromide emulsion is mainly used. Further, in printing materials, in which rapid/easy development processing is regarded as important, silver chloride is used, in many cases. However, recently it has attempted, according to reports, to use silver chloride to make the processing of photographing materials rapid.

[0036] The size of the silver halide grains constituting the light-sensitive emulsion is preferably 0.1 to 2 μm, and particularly 0.2 to 1.5 μm, in terms of the diameter of a sphere having the same volume. The shape of the silver halide grains may be any shape, such as the shape of regular crystals, including cubic crystals, octahedral crystals, or tetradecahedral crystals; an irregular shape, including spherical shapes; and a tabular shape, including hexagons and rectangles. In the case of photographing materials, in order to provide high sensitivity, so-called high-aspect ratio tabular grains having a large diameter of the projected area to the thickness of the grains, are preferable. Herein the term "aspect ratio" means the value obtained by dividing the diameter of a circle equivalent to the projected area of the grain, by the thickness of the grain. The silver halide emulsion used in photographing materials comprises tabular grains preferably having an aspect ratio of 2 or more, more preferably 5 or more, further more preferably 8 or more, and most preferably 20 or more, that amount to generally 50% or more, preferably 80% or more, and more preferably 90% or more, of the projected area of all grains in the emulsion. In the case of grains having a smaller grain size (about 0.5 μm or less in terms of the diameter of a sphere equivalent to the volume of the grain), grains having a tabular degree of 25 or more are preferable, the tabular degree being obtained by dividing the aspect ratio by the thickness of the grain.

[0037] By increasing the aspect ratio, since a large projected area can be obtained with the volume being kept the same, the spectral sensitization rate can be increased. When the photographic sensitivity is proportional to the projected area of the grain, the amount of a silver halide required to obtain the same sensitivity can be reduced. On the other hand, when grains are prepared with the projected area of the grain being kept constant, by increasing the aspect ratio, the number of grains can be increased even using the same amount of a silver halide, and therefore the graininess (granularity) can be improved. Further, when high-aspect ratio grains are used, since the scattered light component large in scattering angle to the incident optical path is decreased, the sharpness can be increased.

[0038] The application techniques and properties of these high-aspect ratio tabular grains are disclosed, for example, in US-A-4 433 048, US-A-4 434 226, and US-A-4 439 520. Techniques for ultra-high-aspect ratio tabular grains having a thickness of less than 0.07 μm are disclosed, for example, in US-A-5 494 789, US-A-5 503 970, US-A-5 503 971, US-A-5 536 632, EP-A-0 699 945, EP-A-0 699 950, EP-A-0 699 948, EP-A-0 699 944, EP-A-0 701 165, and EP-A-0 699 946. The high-aspect ratio tabular grains described in these specifications are mainly made from silver bromide or silver iodobromide, and many of them are hexagonal tabular grains whose major planes are (111) planes. The grains having such a shape have generally two parallel twining planes within the (111) plane. To prepare high-aspect ratio thin tabular grains, it is a technical point that the distance between the two twining planes is made small. For that, it is important to control, for example, the binder concentration, the temperature, the pH, the excess halide ion species, the excess halide ion concentration, and the feed rate of the reaction liquid at the time of the formation of nuclei. To form high-aspect ratio tabular grains, it is a point that the formed tabular nuclei are allowed to grow not in the direction of the thickness of the tabular nuclei but in the direction toward the periphery, selectively. To this end, it is also important to control the feed rate of the reaction liquid for the growth of grains, and to choose a binder that is optimal for from the formation of the grains through the process of the growth. In the above specifications, there are descriptions to the effect that a gelatin low in methionine content is advantageous for making the aspect ratio high.

[0039] On the other hand, techniques for forming tabular grains by means of silver chloride high in silver chloride content are also disclosed. For instance, techniques for high-silver-chloride tabular grains whose major planes are (111) planes are disclosed, for example, in US-A-4 400 463, US-A-4 713 323, US-A-5 217 858, EP-A-0 423 840, and EP-A-0 647 877.

[0040] On the other hand, techniques for high-silver-chloride tabular grains whose major planes are (100) planes are disclosed, for example, in US-A-5 264 337, US-A-5 292 632, US-A-5 310 635, US-A-5 275 932, EU-A-0 534 395, EU-A-0 617 320, and International Publication No. WO 94/22054. These techniques are useful for preparing highly sensitive emulsions in which silver chloride is used and that are excellent in development rate and optical properties.

[0041] In addition to the above contrivances regarding shape, the silver halide grains are prepared to have a variety of structures in the grains. A generally used method is one in which grains are formed to have layers different in silver halide composition. In the case of silver iodobromide grains used for photographing materials, it is preferable to provide layers different in iodine content. There are known so-called inside-high-iodine-type core/shell grains, wherein the nuclei in the form of layers high in iodine content are covered with shells low in iodine content, for the purpose of controlling developability. Reversely thereto, there are known outside-high-iodine-type core/shell grains, wherein nuclei are covered with shells high in iodine content, which are effective in increasing the stability of the shape when the thickness of tabular grains is decreased. There is also known a technique for providing a high sensitivity, wherein nuclei low in iodine content are covered with first shells high in iodine content, and then second shells low in iodine content are deposited thereon. In this type of silver halide grains, the shells (corresponding to the fringes of the outer edges in the case of tabular grains) deposited on high-iodine layers are formed with dislocation lines due to crystal disorder, which contributes to the securement of a high sensitivity.

[0042] Further a technique for epitaxially growing, at the localized sites of formed host grains, crystals different therefrom in halogen composition, is preferably used for obtaining high sensitivity. For example, there is known a technique wherein crystals high in iodine content are epitaxially grown on parts (apexes or edges of the grain, or on planes of the grain) of surfaces of host grains rich in silver bromide. Reversely, there is known a technique wherein, on host grains of silver bromide or silver iodobromide, are grown epitaxially crystals having a solubility higher than the host grains (e.g. crystals increased in silver chloride content). The latter is preferably used in providing tabular grains particularly decreased in thickness with high sensitivity.

[0043] In high-silver-chloride tabular grains high in silver chloride content, it is preferable to carry out forming of localized phases high in silver bromide content or silver iodide content inside the grains or on the surfaces of the grains. Particularly, these localized phases are preferably grown epitaxially on the apexes or edges on the surfaces of the grains. These sites of the epitaxially grown crystals serve as sites where effective light-sensitive nuclei are formed, giving high sensitivity.

[0044] To improve the photographic properties of the light-sensitive silver halide emulsion, preferably doping of a salt or a complex salt of a metal into the grains is carried out. These compounds act as transitional or permanent traps of electrons or positive holes in the silver halide crystals, and they are useful for obtaining high sensitivity or high contrast, for improving the illuminance dependency or the environment (temperature or humidity) dependency at the time of exposure, or for suppressing a change in performance when pressure is applied before or after the exposure. As for these dopants, the method for doping can be chosen to suit the purpose; for example, the silver halide grains may be uniformly doped, specific sites in the grains may be locally doped, the subsurfaces or surfaces may be locally doped, or the above epitaxial parts may be locally doped.

[0045] Preferable metals include the first to third transitional metal elements, such as iron, ruthenium, rhodium, palladium, cadmium, rhenium, osmium, iridium, and platinum, and the amphoteric metal elements, such as thallium and lead. The ions of these metals are doped in a suitable form of a salt or a complex salt. Among the salts and complex salts, six-coordinate halogeno complexes or cyano complexes, wherein ligands are halide ions or cyanide ions, are preferably used. Further, complexes having organic ligands can also be used, such as a nitrosyl ligand, a carbonyl ligand, a thiocarbonyl ligand, a dinitrogen ligand, a bipyridyl ligand, a cyclopentadienyl ligand, and a 1,2-dithiolenyl ligand. Techniques concerning these are described, for example, in JP-A-2-236542, JP-A-1-116637, and JP-A-4-126629.

[0046] Further, doping with divalent anions of so-called chalcogen elements, such as sulfur, selenium, and tellurium, is also preferably carried out. These dopants are also effective in securing high sensitivity and in improving exposure condition dependency.

[0047] As a method employed to prepare silver halide grains, known method described, for example, by P. Glafkides in "Chemie et Phisique Photographique," Paul Montel, 1967; by G. F. Duffin in "Photographic Emulsion Chemistry," Focal Press, 1966; or by V. L. Zelikman et al. in "Making and Coating Photographic Emulsion," Focal Press, 1964, can be referred to. That is, any of pH regions among the acid process, the neutral process, the ammonia process, and the like can be used to prepare silver halide grains. Further, to supply a soluble silver salt solution and a soluble halogen salt solution that are reaction solutions, any of the single-jet method, the double-jet method, a combination thereof, and the like can be used. The controlled double-jet method, can also be used preferably, wherein the addition of reaction solutions are controlled, to keep the pAg in the reaction constant. A method in which the pH of the reaction liquid during the reaction is kept constant can also be used. In the step for forming grains of the light-sensitive silver halide emulsion for use in the present invention, a method in which the solubility of the silver halide is controlled by changing the temperature, pH, or pAg of the system can be used, and a thioether, a thiourea, and a rhodanate, can be used as a silver halide solvent, examples of these are described in JP-B-47-11386 ("JP-B" means examined Japanese patent publication), and JP-A-53-144319.

[0048] Generally, the preparation of the silver halide grains is carried out by feeding a solution of a water-soluble silver salt, such as silver nitrate, and a solution of a water-soluble halogen salt, such as an alkali halide, into a solution containing a water-soluble binder dissolved therein, such as gelatin, under controlled conditions. After the formation of the silver halide grains, the excess water-soluble salts are preferably removed. This step is called "desalting" or "washing", and various means can be used in the step. For example, the noodle water-washing method, in which a gelatin solution containing silver halide grains are made into a gel and the gel is cut into a string-shape, then the water-soluble salts are washed away using a cold water, and the sedimentation method, in which inorganic salts comprising polyvalent anions (e.g. sodium sulfate), an anionic surfactant, an anionic polymer (e.g. polystyrenesulfonic acid sodium salt), or a gelatin derivative (e.g. an aliphatic-acylated gelatin, an aromatic-acylated gelatin, and an aromatic-carbamoylated gelatin) is added, to allow the gelatin to aggregate, thereby removing the excess salts, can be used. In particular, the sedimentation method is preferably used because removal of the excess salts can be carried out rapidly.

[0049] In the present invention, generally it is preferable to use a chemically sensitized silver halide emulsion. The chemical sensitization contributes to giving high sensitivity to the prepared silver halide grains, and to giving exposure condition stability and storage stability. In the chemical sensitization, generally known sensitization methods may be used singly or in combination.

[0050] Preferably use is made of, as the chemical sensitization method, the chalcogen sensitization method, wherein a sulfur, selenium, or tellurium compound is used. As the sensitizer used therein, a compound is used that, when added to the silver halide emulsion, releases the above chalcogen element, to form a silver chalcogenide. The use of such sensitizers in combination is preferable to obtain high sensitivity and to keep fogging low.

[0051] The noble metal sensitization method, wherein gold, platinum, iridium, or the like is used, is also preferable. Particularly the gold sensitization method, wherein chloroauric acid is used alone or in combination with thiocyanate ions or the like that act as ligands of gold, can give high sensitivity. The use of a combination of gold sensitization with chalcogen sensitization can give higher sensitivity.

[0052] The so-called reduction sensitization method is also preferably used, wherein a compound having a suitable reducing ability is used during the grain formation to introduce reducing silver nuclei, to obtain high sensitivity. The reduction sensitization method, wherein an alkynylamine compound having an aromatic ring is added at the time of chemical sensitization, is also preferred. In carrying out the chemical sensitization, it is

[0053] also preferable to use various compounds adsorbable to silver halide grains, to control reactivity. Particularly the method wherein sensitizing dyes, such as cyanines and melocyanines, mercapto compounds, or nitrogen-containing heterocyclic compounds, are added prior to chalcogen sensitization or gold sensitization, is particularly preferable.

[0054] The reaction conditions under which the chemical sensitization is conducted vary in accordance with the purpose: The temperature is generally 30 to 95 °C, and preferably 40 to 75 °C; the pH is generally 5.0 to 11.0, and preferably 5.5 to 8.5; and the pAg is generally 6.0 to 10.5, and preferably 6.5 to 9.8.

[0055] Chemical sensitization techniques are described, for example, in JP-A-3-110555, JP-A-4-75798, JP-A-62-253159, JP-A-5-45833, and JP-A-62-40446.

[0056] In the present invention, preferably the so-called spectral sensitization, for sensitizing the light-sensitive silver halide emulsion to a desired light wavelength range, is carried out. Particularly, in a color photographic light sensitive material, for color reproduction faithful to the original, light-sensitive layers having light sensitivities to blue, green, and red are incorporated. These sensitivities are provided by spectrally sensitizing the silver halide. In the spectral sensitization, use is made of a so-called spectrally sensitizing dye that is adsorbed to the silver halide grains, to cause them to have sensitivity in the range of its own absorption wavelength.

[0057] Examples of such dyes include cyanine dyes, merocyanine dyes, composite cyanin dyes, composite merocyanine dyes, halopolar dyes, hemicyanine dyes, styryl dyes, and hemioxonol dyes. These examples are described, for example, in US-A-4,617,257, JP-A-59-180550, JP-A-64-13546, JP-A-5-45828, and JP-A-5-45834.

[0058] These spectral sensitizing dyes can be used singly or in combination, and a single use or a combination use of these sensitizing dyes is selected for the purpose of adjusting the wavelength distribution of the spectral sensitivity, and for the purpose of supersensitization. When using a combination of the dyes having supersensitizing effect, it is possible to attain sensitivity much larger than the sum of sensitivities which can be attained by each single dye.

[0059] Further, together with the sensitizing dye, it is also preferable to use a dye having no spectral sensitizing action itself, or a compound that does not substantially absorb visible light and that exhibits supersensitization. As an example of the supersensitizer, a diaminostilbene compound and the like can be mentioned. These examples are described, for example, in US-A-3 615 641 and JP-A-63-23145.

[0060] The addition of these spectrally sensitizing dyes and supersensitizers to the silver halide emulsion may be carried out at any time during the preparation of the emulsion. Different methods, such as addition when a coating solution is prepared from the chemically sensitized emulsion, addition after the completion of the chemical sensitization, addition during the chemical sensitization, addition prior to the chemical sensitization, addition after the formation of the grains and before the desalting, addition during the formation of the grains, and addition prior to the formation of the grains, can be used alone or in combination. The addition is preferably carried out in a step before the chemical sensitization, to obtain high sensitivity.

[0061] The amount of the spectrally sensitizing dye or the supersensitizer to be added may vary depending on the shape of the grains, the size of the grains, and the desired photographic properties, and it is generally in the range of 10^{-8} to 10^{-1} mol, and preferably 10^{-5} to 10^{-2} mol, per mol of the silver halide. These compounds can be added with them dissolved in an organic solvent, such as methanol and a fluoroalcohol, or with them dispersed together with a surfactant or gelatin in water.

[0062] In the silver halide emulsion used in the present invention, various stabilizers can be incorporated for the purpose of preventing fogging, or for the purpose of improving stability at storage. As a preferable stabilizer, nitrogen-containing heterocyclic compounds, such as azaindenes, triazoles, tetrazoles, and purines; mercapto compounds, such as mercaptotetrazoles, mercaptotriazoles, mercaptoimidazoles, and mercaptothiadiazoles, can be mentioned. Details of these compounds are described, for example, by T. H. James in "The Theory of the Photographic Process," Macmillan, 1997, pages 396 to 399, and references cited therein.

[0063] The timing when the antifoggant or the stabilizer is added to the silver halide emulsion may be at any stage in the preparation of the emulsion. The addition to the emulsion can be carried out at any time, singly or in combination, of after the completion of the chemical sensitization and during the preparation of a coating solution, at the time of the completion of the chemical sensitization, during the chemical sensitization, prior to the chemical sensitization, after the completion of the grain formation and before desalting, during the grain formation, or prior to the grain formation.

[0064] The amount of these antifogging agents or stabilizers to be added varies in accordance with the halogen composition of the silver halide emulsion and the purpose, and it is generally in the range of 10^{-6} to 10^{-1} mol, and preferably 10^{-5} to 10^{-2} mol, per mol of the silver halide.

[0065] The amount of the light-sensitive silver halide used in the light-sensitive material is suitably generally 0.05 to 20 g/m^2, and preferably 0.1 to 10 g/m^2, in terms of silver.

[0066] Organic metal salts, binders, high-boiling organic solvents, surfactants, hardeners, antifoggants, photographic stabilizers and their precursors, coating aids, antistatic agents, development accelerators, organic fluorocompounds, slip agents, polymer latexes, matting agents, bases (supports), film magazines (cartridges), and the like that can be used in the present invention are described, for example, also in EP-A-0 762 201 (A1) supra. In addition, the following compounds can be used effectively.

Dispersion mediums of oil-soluble organic compounds: P-3, 5, 16, 19, 25, 30, 42, 49, 54, 55, 66, 81, 85, 86, and 93 (pages 140 to 144) of JP-A-62-215272;
Latexes for impregnation of oil-soluble organic compounds: latexes described in US-A-4 199 363;
Scavengers for the oxidized product of a developing agent: compounds represented by formula (I) in column 2, lines 54 to 62 of US-A-4 978 606 (particularly I-, (1), (2), (6), and (12) (columns 4 to 5), compounds represented by formulae in column 2, lines 5 to 10 of US-A-4 923 787 (particularly compound 1 (column 3);
Antistaining agents: compounds represented by any of formulae (I) to (III) on page 4, lines 30 to 33 of EP-A-298,321 (particularly I-47, 72, III-1, and 27 (pages 24 to 48);
Antifading agents: compounds A-6, 7, 20, 21, 23, 24, 25, 26, 30, 37, 40, 42, 48, 63, 90, 92, 94, and 164 (pages 69 to 118) of EP-A-298,321, compounds II-1 to III-23 in columns 25 to 38 of US-A-5 122 444 (particularly III-10), compounds I-1 to III-4 on pages 8 to 12 of EP-A-471,347 (particularly II-2), and compounds A-1 to 48 in columns 32 to 40 of US-A-5 139 931 (particularly A-39 and 42);
Materials for reducing the amount to be used of color-formation enhancing agents or color-mixing inhibitors: compounds I-1 to II-15 on pages 5 to 24 of EP-A-411,324 (particularly I-46);
Formalin scavengers: compounds SCV-1 to 28 on pages 24 to 29 of EP-A-477,932 (particularly SCV-8);
Hardeners: compounds H-1, 4, 6, 8, and 14 on page 17 of JP-A-1-214845, compounds (H-1 to 54) represented by any of formulae (VII) to (XII) in columns 13 to 23 of US-A-4 618 573, compounds (H-1 to 76) represented by formula (6) shown in the lower right part on page 8 of JP-A-2-214852 (particularly H-14) and compounds recited in claim 1 of US-A-3 325 287;
Development-inhibitor precursors: compounds P-24, 37, and 39 (pages 6 to 7) of JP-A-62-168139 and compounds recited in claim 1 of US-A-5 019 492 (particularly 28 and 29 in column 7);
Antiseptics and mildewproofing agents: compounds I-1 to III-43 in columns 3 to 15 of US-A-4 923 790 (particularly

II-1, 9, 10, and 18 and III-25);

Stabilizers and antifogging agents: compounds I-1 to (14) in columns 6 to 16 of US-A-4 923 793 (particularly I-1, 60, (2), and (13)) and compounds 1 to 65 in columns 25 to 32 of US-A-4 952 483 (particularly 36);

Chemical sensitizers: triphenylphosphine selenides, and compound 50 of JP-A-5-40324;

Dyes: compounds A-1 to B-20 on pages 15 to 18 of JP-A-3-156450 (particularly A-1, 12, 18, 27, 35, 36, and B-5) and compounds V-1 to 23 on page 27 to 29 of JP-A-3-156450 (particularly V-1), compounds F-I-1 to F-II-43 on pages 33 to 55 of EP-A-445,627 (particularly F-I-11 and F-II-8), compounds III-1 to 36 on pages 17 to 28 of EP-A-457,153 (particularly III-1 and 3), fine crystal dispersions of Dye-1 to 124 of 8 to 26 of WO 88/04794, compounds 1 to 22 on pages 6 to 11 of EP-A-319,999 (particularly compound 1), compounds D-1 to 87 represented by any of formulas (1) to (3) (pages 3 to 28) of EP-A-519,306, compounds 1 to 22 represented by formula (I) (columns 3 to 10) of US-A-4 268 622, and compounds (1) to (31) represented by formula (I) (columns 2 to 9) of US-A-4 923 788;

UV absorbers: compounds (18B) to (18R) and 101 to 427 represented by formula (1) (pages 6 to 9) of JP-A-46-3335, compounds (3) to (66) represented by formula (I) (pages 10 to 44) and compounds HBT-1 to 10 represented by formula (III) (page 14) of EP-A-520,938, and compounds (1) to (31) represented by formula (1) (columns 2 to 9) of EP-A-521,823.

[0067] The silver halide photographic light-sensitive material of the present invention can be processed with a developer containing a developing agent, or with such a processing solution as an activator solution comprising an aqueous alkali solution, or it can be subjected to heat development processing. Also as is shown in JP-A-9-127670, a method can be utilized wherein, after the silver halide photographic light-sensitive material of the present invention is exposed imagewise, it is brought in close contact with the processing layer of a processing member and is heated, to form an image in the silver halide photographic light-sensitive material.

[0068] The processing layer of the processing member used preferably in the present invention contains at least a base and/or a base precursor.

[0069] As the base, an inorganic or organic base can be used. Examples of the inorganic base include the hydroxide, the phosphate, the carbonate, the borate, and an organic acid salt of an alkali metal or an alkali earth metal described in JP-A-62-209448, and the acetylide of an alkali metal or an alkali earth metal described, for example, in JP-A-63-25208.

[0070] Examples of the organic base include ammonia, aliphatic or aromatic amines (e.g. primary amines, secondary amines, tertiary amines, polyamines, hydroxyamines, and heterocyclic amines), amidines; bis-, tris-, or tetra-amidines; guanidines; water-soluble mono-, bis-, tris-, or tetra-guanidines; and quaternary ammonium hydroxides.

[0071] Examples of the base precursors that can be used include those of the decarboxylation type, the decomposition type, the reaction type, and the complex salt formation type.

[0072] In the present invention, as is described in EP-A-210,660 and US-A-4 740 445, a method is effectively employed wherein a base is produced by means of a combination of a basic metal compound that is hardly soluble in water, as a base precursor, with a compound (referred to as a complex-forming compound) capable of a complex-forming reaction with the metal ion constituting that basic metal compound, using water as a medium. In this case, although it is desirable to add the basic metal compound that is hardly soluble in water to the light-sensitive material, and to add the complex-forming compound to the processing member, the procedure may be reversed.

[0073] The amount to be added of the base or the base precursor is generally 0.1 to 20 g/m^2, and preferably 1 to 20 g/m^2. As the binder in the processing layer, a hydrophilic polymer can be used in the same manner as the light-sensitive member. Further, materials and other constitutions that can be used for the processing member are described in EP-0 762 201 (A1).

[0074] In a preferable example of the present invention, a method for subjecting to development a light-sensitive material that has been used for photographing by means of a camera is used, wherein the light-sensitive member and the processing member are put together with the light-sensitive layer and the processing layer facing each other, in the presence of water in an amount of 0.1 to 1 times the amount required for the maximum swelling of all the coating films of the light-sensitive member and the processing member, except the backing layers, and they are heated at a temperature of 60 to 100 °C for 5 to 60 sec.

[0075] Herein water may be any water generally used. Specifically, distilled water, deionized water, tap water, well water, mineral water, and the like can be used. These waters may be used preferably by adding a small amount of an antiseptic agent, to prevent scale formation, decay, or the like, or by filtering them through an activated-carbon filter, an ion-exchange resin filter, or the like, to be circulated.

[0076] The light-sensitive member and/or the processing member is stuck and heated with them swollen with water. The state of the swollen films is unstable, and therefore it is important to restrict the amount of water in the above range, in order to prevent color formation from becoming locally uneven.

[0077] The amount of water required for the maximum swelling can be found by immersing the light-sensitive member or the processing member, having a coating film to be measured, in the water that will be used, to allow it to swell enough, then measuring the thickness, and subtracting the weight of the coating film from the calculated weight of the maximum swell. Further, an example of the method for measuring the swell is also described in Photographic Science Engineering, Vol. 16 page 449 (1972).

[0078] According to the present invention, a silver halide photographic light-sensitive material excellent in the discrimination of an image and raw stock storability can be provided.

[0079] The present invention will now be described in more detail with reference to the following examples, but of course the present invention is not limited to them.

EXAMPLES

Example 1

〈Preparation Method of Light-Sensitive Silver Halide Emulsion-1〉

[0080] To a well-stirred aqueous gelatin solution (containing 30 g of inert gelatin and 2 g of potassium bromide in 1,000 ml of water), were added ammonia-ammonium nitrate as a solvent for silver halide, the temperature was kept at 75 °C, and then 1000 ml of an aqueous solution containing 1 mol of silver nitrate, and 1,000 ml of an aqueous solution containing 1 mol of potassium bromide and 0.03 mol of potassium iodide, were simultaneously added thereto, over 78 min. After washing with water and desalting, inert gelatin was added, for redispersion, thereby preparing a silver iodobromide emulsion having a diameter of the grain volume, which is assumed to be a sphere, of 0.76 μm, and an iodine content of 3 mol%. The diameter of the grain volume, which is assumed to be a sphere, was measured by Model TA-3, manufactured by Coulter Counter Co.

[0081] To the above emulsion were added potassium thiocyanate, chloroauric acid, and sodium thiosulfate, at 56 °C, to achieve optimal chemical sensitization. To this emulsion, each sensitizing dye corresponding to each of the spectral sensitivities was added at the time of preparation of the coating solution, to provide color sensitivities.

〈Preparation Method of Zinc Hydroxide Dispersion〉

[0082] 31 g of zinc hydroxide powder, whose primary particles had a grain size of 0.2 μm, 1.6 g of carboxylmethyl cellulose and 0.4 g of sodium polyacrylate, as a dispersant, 8.5 g of lime-processed ossein gelatin, and 158.5 ml of water were mixed together, and the mixture was dispersed by a mill containing glass beads for 1 hour. After the dispersion, the glass beads were filtered off, to obtain 188 g of a dispersion of zinc hydroxide.

〈Preparation Method of Emulsified Dispersion of Coupler〉

[0083] The oil-phase components and the aqueous-phase components of each composition shown in Table 1 were dissolved, respectively, to obtain uniform solutions at 60 °C. The oil-phase components and the aqueous-phase components were combined together and were dispersed in a 1-liter stainless steel vessel, by a dissolver equipped with a disperser having a diameter of 5 cm, at 10,000 rpm for 20 min. Warm water (as an additional water) was added thereto in the amount shown in Table 1, followed by stirring at 2,000 rpm for 10 min. Thus, emulsified dispersions of a coupler were prepared, respectively.

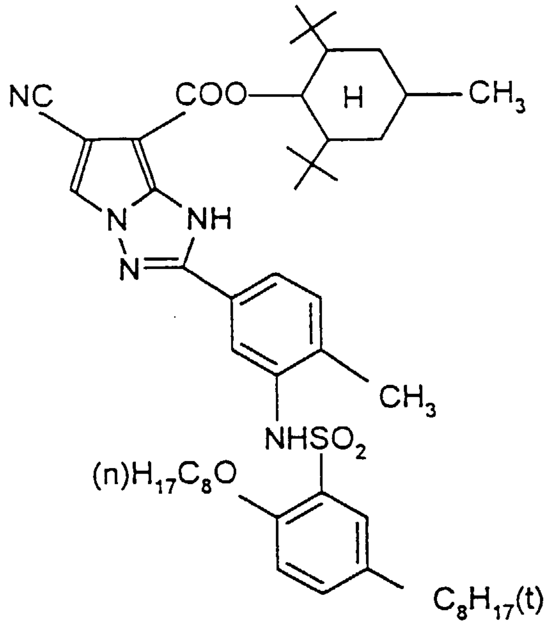
Table 1

		Cyan	Magenta	Yellow
Oil phase	Cyan coupler (1)	8.70 g	--	--
	Magenta coupler (2)	--	6.36 g	--
	Yellow coupler (3)	--	--	5.77 g
	Developing agent(4)	5.46 g	5.46 g	5.46 g
	Antifoggant (5)	3.0 mg	1.0 mg	10.0 mg
	High-boiling solvent (6)	7.08 g	5.91 g	5.62 g
	Ethyl acetate	24.0 ml	24.0 ml	24.0 ml

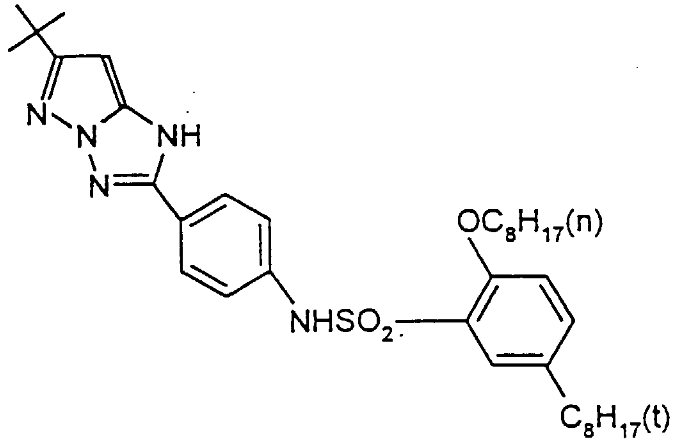
Table 1 (continued)

		Cyan	Magenta	Yellow
Aqueous phase	Lime-processed gelatin	12.0 g	12.0 g	12.0 g
	Surface-active agent (7)	0.60 g	0.60 g	0.60 g
	Water	138.0 ml	138.0 ml	138.0 ml
	Additional water	180.0 ml	180.0 ml	180.0 ml

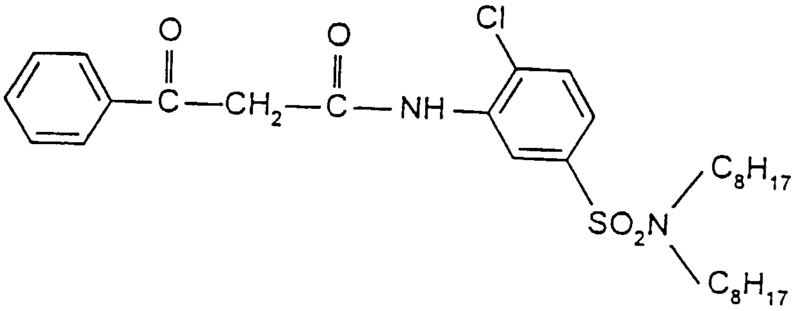
Cyan coupler (1)



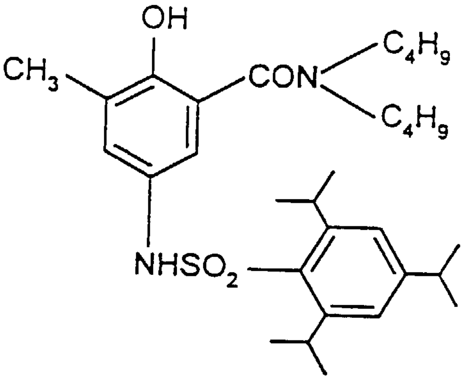
Magenta coupler (2)



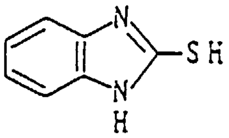
Yellow coupler (3)



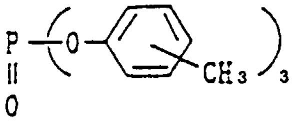
Developing agent (4)



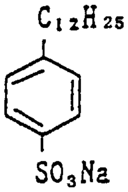
Antifoggant (5)



High-boiling solvent (6)



Surface-active agent (7)



By using the thus obtained materials, a heat-development light-sensitive material 101, having the multi-layer configuration shown in Table 2, was prepared.

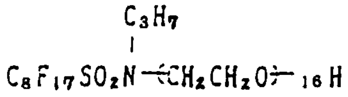
Table 2 Constitution of light-sensitive material 101

Layer Configuration	Additive	Added amount (mg/m^2)
Seventh layer Protective layer	Lime-processed gelatin	1000
	Matting agent (silica)	50
	Surface-active agent (8)	100
	Surface-active agent (9)	300
	Water-soluble polymer (10)	15
Sixth layer Interlayer	Lime-processed gelatin	375
	Surface-active agent (9)	15
	Zinc hydroxide	1130
	Water-soluble polymer (10)	15
Fifth layer Yellow color-forming layer	Lime-processed gelatin	1450
	Light-sensitive silver halide emulsion	692 (in terms of silver)
	Sensitizing dye (12)	3.65
	Yellow coupler (3)	462
	Developing agent (4)	437
	Antifoggant (5)	0.8
	High-boiling solvent (6)	450
	Surface-active agent (7)	48
	Water-soluble polymer (10)	20
Forth layer Interlayer	Lime-processed gelatin	1000
	Surface-active agent (9)	8
	Water-soluble polymer (10)	5
	Hardener (11)	65
Third layer Magenta color-forming layer	Lime-processed gelatin	993
	Light-sensitive silver halide emulsion	475 (in terms of silver)
	Sensitizing dye (13)	0.07
	Sensitizing dye (14)	0.71
	Sensitizing dye (15)	0.19
	Magenta coupler (2)	350
	Developing agent (4)	300
	Antifoggant (5)	0.06
	High-boiling solvent (6)	325
	Surface-active agent (7)	33
	Water-soluble polymer (10)	14

Table 2 (continued)

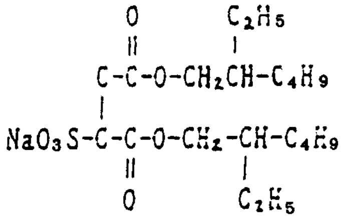
Layer Configuration	Additive	Added amount (mg/m^2)
Second layer Interlayer	Lime-processed gelatin	1000
	Surface-active agent (9)	8
	Zinc hydroxide	1130
	Water-soluble polymer (10)	5
First layer Cyan color-forming layer	Lime-processed gelatin	720
	Light-sensitive silver halide emulsion	346 (in terms of silver)
	Sensitizing dye (16)	1.52
	Sensitizing dye (17)	1.03
	Sensitizing dye (18)	0.05
	Cyan coupler (1)	348
	Developing agent (4)	218
	Antifoggant (5)	0.12
	High-boiling solvent (6)	283
	Surface-active agent (7)	24
	Water-soluble polymer (10)	10
	Transparent PET base (102 μm)	

Surface-active agent (8)

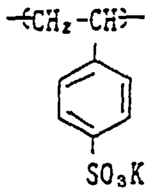


$$C_8F_{17}SO_2\underset{}{\overset{C_3H_7}{\overset{|}{N}}}\!-\!(CH_2CH_2O)_{16}H$$

Surface-active agent (9)

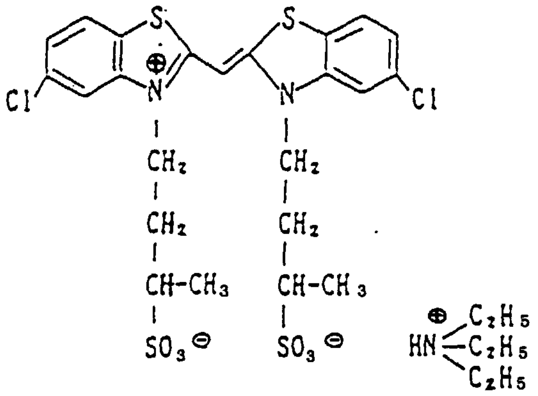


Water-soluble polymer (10)

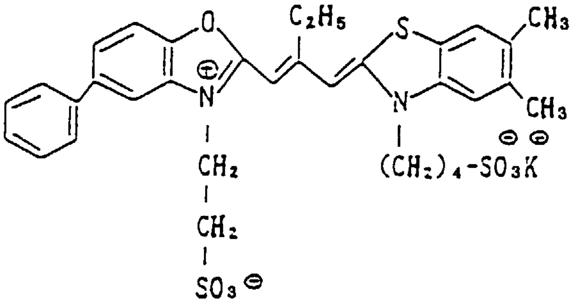


Hardener (11) $CH_2=CH-SO_2-CH_2-SO_2-CH=CH_2$

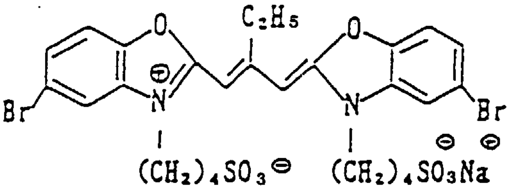
Sensitizing dye (12)



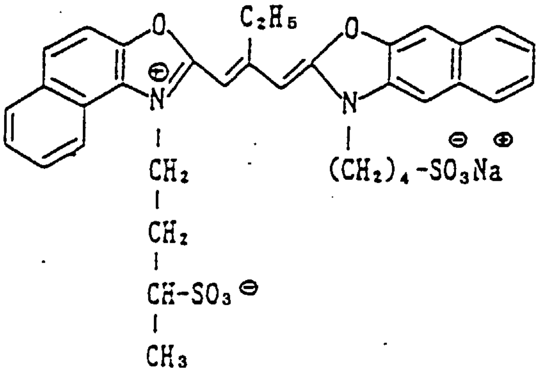
Sensitizing dye (13)



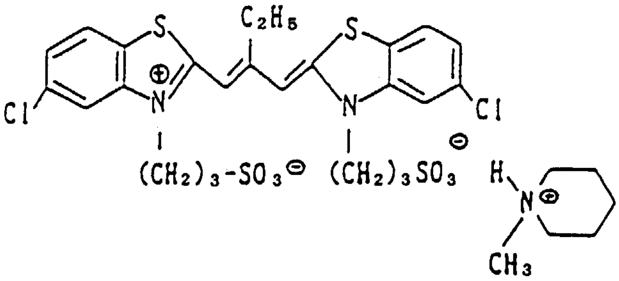
Sensitizing dye (14)



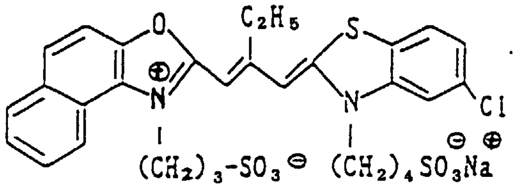
Sensitizing dye (15)



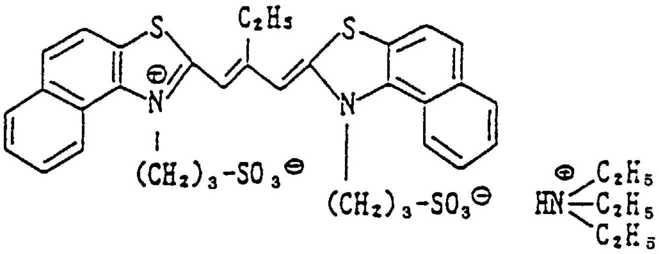
Sensitizing dye (16)



Sensitizing dye (17)



Sensitizing dye (18)

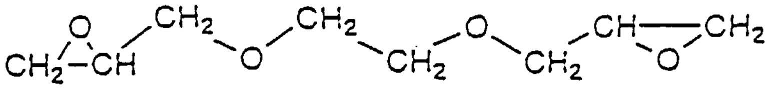


[0084] Further, Processing Material R-1, having the contents shown in Tables 3 was prepared.

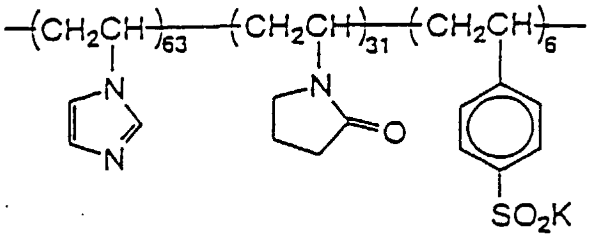
Table 3

Processing Material R-1		
Layer Configuration	Main added material	Added amount (g/m^2)
Fourth layer	Gelatin	0.22
	κ-carrageenan	0.06
	Silicone oil	0.02
	Matting agent (PMMA)	0.4
Third layer	Gelatin	0.24
	Hardener (H-2)	0.18
Second layer	Gelatin	2.41
	Dextran	1.31
	Mordant (P-1)	2.44
	Guanidine picolinic acid	5.82
	Potassium quinolinic acid	0.45
	Sodium quinolinic acid	0.36
First layer	Gelatin	0.19
	Hardener (H-2)	0.18
Undercoat layer		
PET base (63 μm)		

H-2



P-1



[0085] Further, Light-sensitive materials 102 to 115 were prepared in the same manner as in Light-sensitive material 101, except that the developing agent and the reducing agent in the third layer (magenta color-forming layer) were changed as shown in Table 4. The thus prepared Light-sensitive materials 101 to 115 were exposed to light at 2,500 lux for 0.01 sec through a B, G, R, or gray filter, whose density was respectively changed continuously. Warm water at 40 °C was applied to the surface of the thus exposed light-sensitive materials, in an amount of 15 ml/m^2, and then after each processing material and each film surface were brought together, they were subjected to heat development at 83 °C for 30 sec using a heat dram. After the processing, when the processing material was removed (pealed off), an image was obtained clearly on the side of the light-sensitive material corresponding to the filter used for the exposure. Immediately after the processing, for each Samples, the maximum density (Dmax) parts of exposed part and minimum density (Dmin) of white background, in terms of an transmittion density, were measured by an X-rite density-measuring apparatus. The results are shown in Table 5. Further, samples which were left to stand under the conditions of 45 °C and 80% relative humidity for 7 days, were processed in the same manner as above. The results are shown in Table 6.

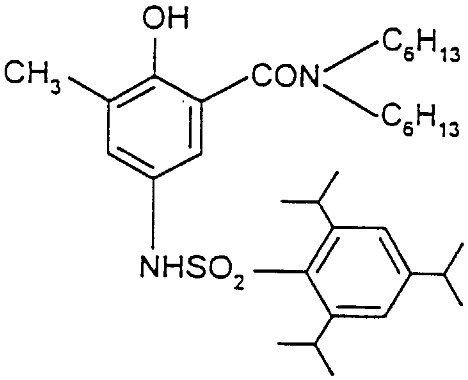
Table 4

Light-sensitive material No.	Developing agent/Added amount (mmol/m^2)	Reducing agent/Added amount (mmol/m^2)
101 (comparative example)	Developing agent (4) / 0.55	none
102 (comparative example)	Developing agent (a) / 0.55	none
103 (comparative example)	Developing agent (b) / 0.55	none
104 (comparative example)	Developing agent (c) / 0.55	none
105 (comparative example)	Developing agent (4) / 0.55	Reducing agent (x) / 0.2
106 (comparative example)	Developing agent (a) / 0.55	Reducing agent (x) / 0.2
107 (comparative example)	Developing agent (a) / 0.55	Reducing agent (y) / 0.2
108 (comparative example)	Developing agent (a) / 0.55	Reducing agent (z) / 0.2
109 (comparative example)	Developing agent (b) / 0.55	Reducing agent (z) / 0.2
110 (This invention)	Developing agent (4) / 0.55	Exemplified compound D-5 / 0.2
111 (This invention)	Developing agent (a) / 0.55	Exemplified compound D-5 / 0.2
112 (This invention)	Developing agent (a) / 0.55	Exemplified compound D-6 / 0.2
113 (This invention)	Developing agent (b) / 0.55	Exemplified compound D-5 / 0.2
114 (This invention)	Developing agent (b) / 0.55	Exemplified compound D-6 / 0.2

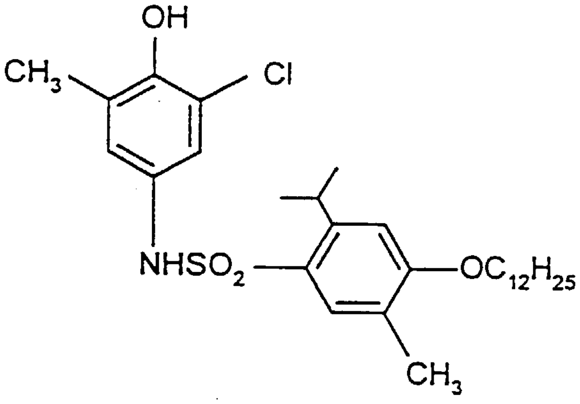
Table 4 (continued)

Light-sensitive material No.	Developing agent/Added amount (mmol/m^2)	Reducing agent/Added amount (mmol/m^2)
115 (This invention)	Developing agent (c) / 0.55	Exemplified compound D-5 / 0.2

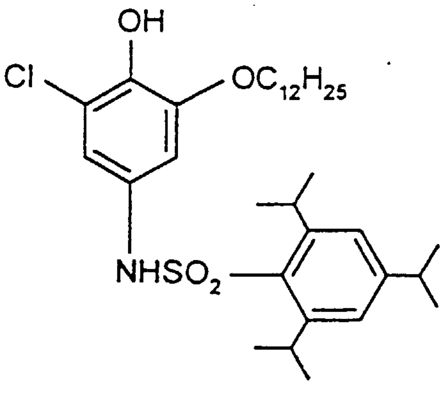
Developing agent (a)



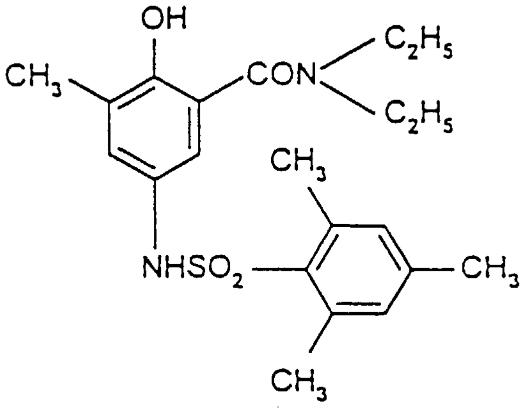
Developing agent (b)



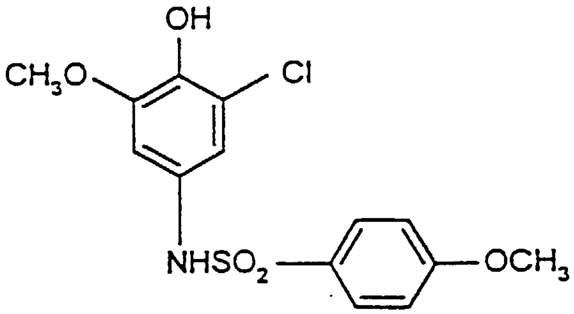
Developing agent (c)



Reducing agent (x)



Reducing agent (y)



Reducing agent (z)

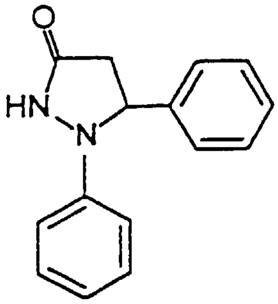


Table 5

Light-sensitive material No.	Dmax (G)	Dmin (G)	Dmax(IR)
101 (comparative example)	1.85	0.22	0.35

Table 5 (continued)

Light-sensitive material No.	Dmax (G)	Dmin (G)	Dmax(IR)
102 (comparative example)	1.02	0.21	0.31
103 (comparative example)	0.95	0.20	0.3
104 (comparative example)	0.88	0.20	0.29
105 (comparative example)	2.25	0.28	0.62
106 (comparative example)	2.33	0.27	0.62
107 (comparative example)	2.32	0.28	0.62
108 (comparative example)	2.13	0.28	0.38
109 (comparative example)	2.09	0.28	0.38
110 (This invention)	2.35	0.28	0.38
111 (This invention)	2.36	0.28	0.37
112 (This invention)	2.31	0.28	0.37
113 (This invention)	2.32	0.28	0.37
114 (This invention)	2.33	0.28	0.37
115 (This invention)	2.32	0.28	0.38

Table 6

Light-sensitive material No.	Dmax (G)	Dmin (G)	Dmax (IR)
101 (comparative example)	1.86	0.22	0.35
102 (comparative example)	1.03	0.21	0.31
103 (comparative example)	0.94	0.21	0.3
104 (comparative example)	0.89	0.20	0.29
105 (comparative example)	2.26	0.28	0.64
106 (comparative example)	2.31	0.27	0.62
107 (comparative example)	2.32	0.28	0.63
108 (comparative example)	1.90	0.28	0.34
109 (comparative example)	1.33	0.28	0.30
110 (This invention)	2.35	0.27	0.38
111 (This invention)	2.37	0.28	0.37
112 (This invention)	2.33	0.28	0.38
113 (This invention)	2.32	0.27	0.37
114 (This invention)	2.31	0.28	0.38
115 (This invention)	2.33	0.28	0.38

*(Note): Dmax(IR) represents a silver-image density.

[0086] Summerizing the results shown in Tables 5 and 6, in Comparative example Samples 101 to 104, although the developing agent was changed, it is recognized that the photographic properties were not improved so much. In Comparative example Samples 105 to 107, the effect of the combination use of the developing agent having a small molecular weight was recognized, but the density of the silver image in each color was increased that was unpreferable.

Further, in Comparative example Samples 108 and 109, wherein a 1-phenyl-3-pyrazolidinone derivative was used as a reducing agent, the effect of the addition disappeared completely after storage. In contrast, in Light-Sensitive Materials 110 to 115 of the present invention, it is understood that, while the increase in density of the silver image was quite small, a great increase in the dye image density was confirmed, and that effect was kept after storage.

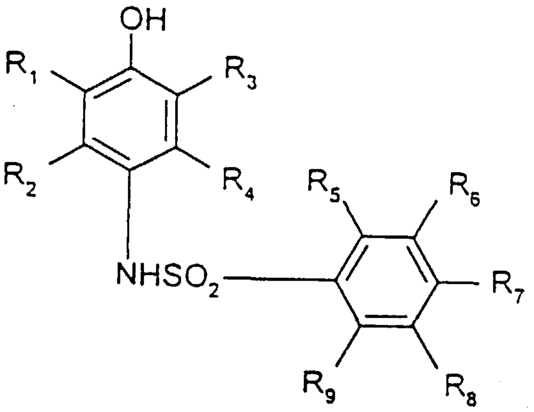
[0087] Then, these light-sensitive materials were set in cameras, and after shooting, they were processed in the same manner as above. The images obtained on the light-sensitive materials were outputted through a digital image reading/reproducing apparatus, Frontier SP-1000 (trade name, manufactured by Fuji Photo Film Co., Ltd.). In comparison with Light-Sensitive Materials 110 to 115, in Light-Sensitive Materials 101 to 104, wherein satisfactory color formation could not be obtained, Light-Sensitive Materials 105 to 107, wherein the silver image density was high, and Light-Sensitive Materials 108 and 109, that were stored under conditions of high temperature and high humidity, the image quality was poor because, for example, the granularity was unpreferably conspicuous.

[0088] Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

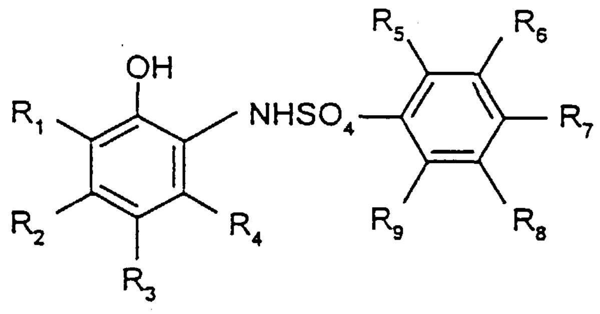
Claims

1. A silver halide photographic light-sensitive material which comprises at least a compound represented by the following formula (1) or (2):

formula (1)



formula (2)



wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, and R_9 each represent a hydrogen atom, a halogen atom, or a substituent having 4 or less carbon atoms or an I/O value of 1 or more; but in formula (1), R_2 and/or R_4, and R_5 and/or R_9, each represent a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom; and in formula (2), R_4, and R_5 and/or R_9 each represent a substituent (a halogen atom or a substituent having 4 or less carbon atoms or an I/O value of 1 or more), except a hydrogen atom; and when R_1 and R_2, R_3 and R_4, R_5 and R_6, R_6 and R_7, R_7 and R_8, and R_8 and R_9 each represent a substituent, except a hydrogen atom, the two of each of the combinations may independently bond together to form a ring.

2. The silver halide photographic light-sensitive material as claimed in claim 1, wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, and R_9 each represent a substituent having an I/O value of 1 or more, but 12 or less.

3. The silver halide photographic light-sensitive material as claimed in claim 1, wherein the compound represented by formula (1) or (2) is contained in an amount of 0.001 to 1,000 mmol/m^2.

4. The silver halide photographic light-sensitive material as claimed in claim 1 which further comprises a reducing agent capable of carrying out a cross-oxidizing reaction with the compound represented by formula (1) or (2), to form an image.

5. The silver halide photographic light-sensitive material as claimed in claim 4, wherein the reducing agent is a color-developing agent.

6. The silver halide photographic light-sensitive material as claimed in claim 4, wherein the reducing agent is contained in an amount of 0.001 to 1,000 mmol/m^2 and the compound represented by formula (1) or (2) is contained in an amount of 0.001 to 1,000 times, the molar amount of the reducing agent.

7. The silver halide photographic light-sensitive material as claimed in claim 1 which is a silver halide photographic heat-development light-sensitive material.

8. The silver halide photographic light-sensitive material as claimed in claim 1, which is, after exposed to light image-wise, brought into close contact with a processing layer of a processing member and heated, to form an image.

9. The silver halide photographic light-sensitive material as claimed in claim 8, wherein the processing layer of the processing member contains at least a base and/or a base precursor.

10. The silver halide photographic light-sensitive material as claimed in claim 1, wherein the substituent having 4 or less carbon atoms or an I/O value of 1 or more is selected from an alkyl group, an aryl group, an alkylcarbonamido group, an arylcarbonamido group, an alkylsulfonamide group, an arylsulfonamide group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an alkylcarbamoyl group, an arylcarbamoyl group, a carbamoyl group, an alkylsulfamoyl group, an arylsulfamoyl group, a sulfamoyl group, a cyano group, an alkylsulfonyl group, an arylsulfonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylcarbonyl group, an arylcarbonyl group, and an acyloxy group.

11. The silver halide photographic light-sensitive material as claimed in claim 1, wherein the halogen atom, or the substituent having 4 or less carbon atoms or an I/O value of 1 or more is a chlorine atom or a bromine atom, or a methyl group, an ethyl group, an isopropyl group, a n-butyl group, a t-butyl group, a 3-methanesulfonylamynophenyl group, an acetylamino group, a propionylamino group, a butyroylamino group, a benzoylamino group, a methanesulfonylamino group, an ethanesulfonylamino group, a benzenesulfonylamino group, a toluenesulfonylamino group, a methoxy group, an ethoxy group, a 4-methanesulfonylaminophenoxy group, a methylthio group, an ethylthio group, a butylthio group, a 4-methanesulfonylaminophenylthio group, a methylcarbamoyl group, a dimethylcarbamoyl group, an ethylcarbamoyl group, a diethylcarbamoyl group, a dibutylcarbamoyl group, a piperidinocarbamoyl group, a morpholinocarbamoyl group, a phenylcarbamoyl group, a methylphenylcarbamoyl group, an ethylphenylcarbamoyl group, a benzylphenylcarbamoyl group, a carbamoyl group, a methylsulfamoyl group, a dimethylsulfamoyl group, an ethylsulfamoyl group, a diethylsulfamoyl group, a dibutylsulfamoyl group, a piperidinosulfamoyl group, a morpholinosulfamoyl group, a phenylsulfamoyl group, a methylphenylsulfamoyl group, an ethylphenylsulfamoyl group, a benzylphenylsulfamoyl group, a sulfamoyl group, a cyano group, a methanesulfonyl group, an ethanesulfonyl group, a phenylsulfonyl group, a 4-chlorophenylsulfonyl group, a p-toluenesulfonyl group, a methoxycarbonyl group, an ethoxycarbonyl group, a butoxycarbonyl group, a phenoxycarbonyl group, an acetyl group, a propionyl group, a butyloyl group, a benzoyl group, an alkylbenzoyl group, an acetyloxy group, a propionyloxy group, or a butyloyloxy group.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 10 0327

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	EP 0 853 255 A (FUJI PHOTO FILM CO LTD) 15 July 1998 * page 3, line 3 - page 4, line 48 * * page 26, exemplary compound D-13 * * page 28, exemplary compound D-18 * * page 58, exemplary compounds II-59, II-63, II-66 and II-67 * * page 104, line 48 - page 105, line 23; claim 1 *	1-4,6-11	G03C1/498 G03C8/40 G03C7/30 G03C7/413 //C07C311/21
D,A	EP 0 764 876 A (FUJI PHOTO FILM CO LTD) 26 March 1997 * page 3, line 29 - line 50 * * page 9, line 36 - line 45 * * page 16, line 26 - page 36, line 6 * * page 49, line 39 - line 48 *	1-3,7-11	
D,A	DATABASE WPI Section Ch, Week 8533 Derwent Publications Ltd., London, GB; Class E14, AN 85-201389 XP002062573 & JP 60 128438 A (KONISHIROKU PHOTO IND CO LTD), 9 July 1985 * abstract *	1	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** G03C B41M
A	JP 62 203158 A (FUJI PHOTO FILM CO LTD) 7 September 1987 * page 8, exemplary compounds (33) and (34) *	1-4,6-11	
A	US 4 782 004 A (TAKEUCHI MASASHI ET AL) 1 November 1988 * column 2, line 56 - column 17, line 3 * * column 32, line 29 - column 42, line 11 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	25 March 1999	Lindner, T

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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25-03-1999

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