

51X⁸⁸

Castillo Grau & As **liados**
ABOGADOS

SUPERINDUSTRIA Y COMERCIO

Radicación : 0001701 00000002
Fecha (M/D): 2000-09-15 10:21:13

Folios: 8

Trámite : 002 PATENTES D 1 REGISTRO/ 444 RESPUESTA
Dependencia: 0000 DIVISION DE NUEVAS CREACIONES

Señores

DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Santafé de Bogotá, D.C.

Re.: Expediente No. 00 - 47.404

Solicitud de Patente

En relación con la última providencia recaída en este expediente, me permito manifestarle lo siguiente:

1.- La copia oficial de la solicitud de patente básica estadounidense No. 60/140.965, debidamente traducida, ya fue presentada con mi escrito del 26 de Julio del 2000.

2.- Acompaño el arte final por triplicado.

3.- Modifico el título de la invención en la siguiente forma

**"COMPUESTOS SULFONAMIDOBENZANILIDA UTILES COMO ANTAGONIS-
TAS DE RECEPTORES BASUREROS DE MACROFAGOS"**

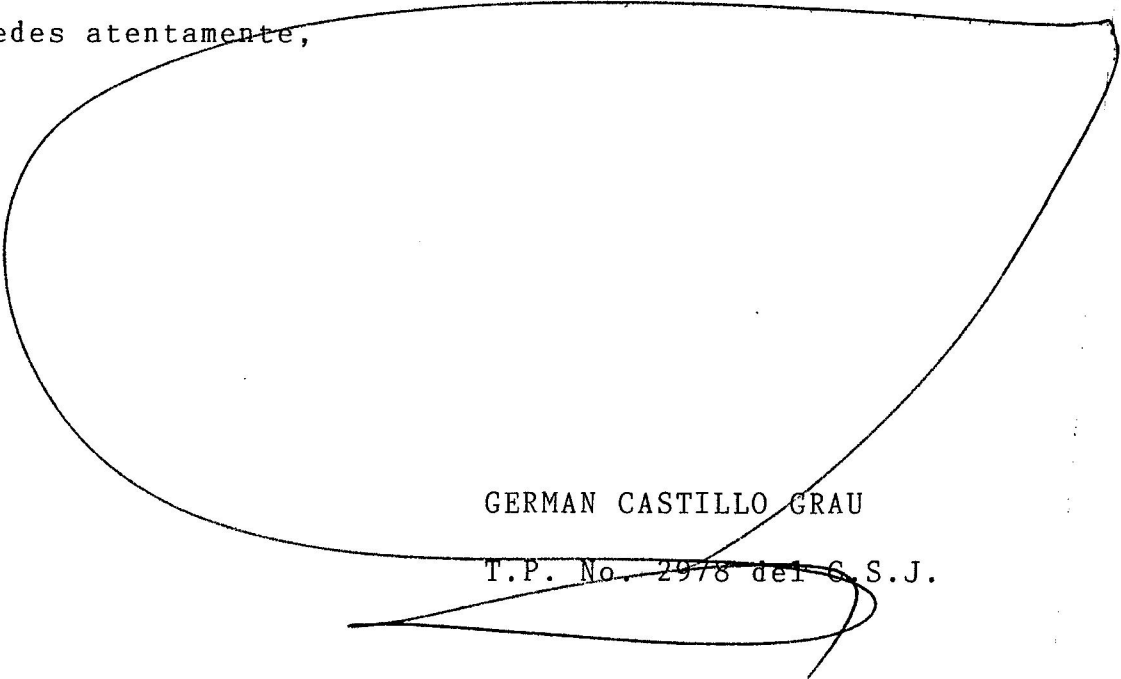
4.- Por motivo de lo anterior, acompaño nueva carátula, extracto, tarjeta de archivo temático y tarjeta de propietario.

La solicito darle curso a esta petición.

Página No. 2

Expediente No. 00 - 47.404

De Ustedes atentamente,



GERMAN CASTILLO GRAU

T.P. No. 2978 del G.S.J.

Folio 68

416
2002/08/29

2020
Bogotá, D.C.

Doctor(a)
GERMÁN CASTILLO GRAU
Apoderado(a)

REFERENCIA:	Radicación No.	00-47404
	Trámite	002
	Evento	001
	Actuación	416
	Oficio No.	860
	Folios	001

Teniendo en cuenta que la solicitud de privilegio de patente que se tramita bajo el expediente indicado en la referencia, reúne los requisitos de forma establecidos en los artículos 26 y 27 de la Decisión 486 de la Comisión de la comunidad andina, y en las demás disposiciones vigentes sobre la materia, se envía el extracto de la solicitud a la Oficina de comunicaciones para efecto de su publicación en la Gaceta de Propiedad Industrial, conforme lo establece el artículo 40 de la misma Decisión.

Cúmplase

Dado en Bogotá, D.C., a los

ALIX CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

Bogotá, D.C., 04-05-05 El extracto de esta solicitud fue publicado en el número 519 de la Gaceta de Propiedad Industrial, de fecha 29-08-02. El término hábil señalado por la ley expiró el 26-11-02 y SI ☐ NO ☒ se presentaron oposiciones por parte de terceros.

202040

69

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 00-47404

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION** FUE
PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 519, DE FECHA 29 DE
AGOSTO DE 2002, EL TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL 26 DE
NOVIEMBRE DE 2002.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación
en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad
so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo
44 de la Decisión
486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO _____

63

Castillo Grau & Asociados

ABOGADOS

SUPERINDUSTRIA Y COMERCIO

Radicación : 00047404 00000003

Folios:

Fecha (AMD): 2003-01-20 10:17:53

Trámite : 002 PATENTES D 1 REGISTRO/ 538 PETICION

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Señora Jefe
DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Bogotá, D.C.

Expediente No. 00 47.404
Solicitud de Patente a nombre
de "SMITHKLINE BEECHAM
CORPORATION"
Código : 02-01-538

En relación con la solicitud contenida en el Expediente de la referencia y, en particular, con la publicación del extracto de la misma en la Gaceta de la Propiedad Industrial No. 519 de 29 de Agosto de 2002, por medio del presente escrito muy respetuosamente me permito solicitarle se sirva proceder a efectuar el **EXAMEN DE PATENTABILIDAD** de la solicitud aquí contenida.

Como consecuencia de esta solicitud, acompaño el comprobante de pago por concepto de la tasa respectiva, Recibo No. 3.608.

De Usted Atentamente,

GERMAN CASTILLO GRAU
C.C. 17.017.671 de Bogotá
TP 2.908 del C.S.J.

6572
375
2005/05/19

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, DC, 05 de mayo de 2005

Apoderado: Germán Castillo Grau

Oficio: 15709

ASUNTO

Radicación: 00-47404

Trámite 002

Evento 001

Actuación 430

Folios

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

Documentos estudiados:

a

- ◆ capítulo descriptivo, folios 04 a 19;
- ◆ capítulo reivindicatorio modificado, folios 20 a 23;
- ◆ 1° examen de forma, folios 33 y 34;
- ◆ respuesta al 1° examen de forma, folio 36;
- ◆ solicitud de la cual se reivindica prioridad y la traducción exigida, folios 37 a 58;
- ◆ 2° examen de forma, folio 67;
- ◆ solicitud del examen de patentabilidad, folios 70 y 71.

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Objeto de la invención:

El título de la invención "COMPUESTOS SULFONAMIDOBENZANILIDA UTILES COMO ANTAGONISTAS DE RECEPTORES BASUREROS DE MACROFAGOS". Tienen como objeto compuestos derivados de sulfonamido-benzanilida y las formulaciones que los comprenden.

El campo de la invención, según la Clasificación Internacional de Patentes: A61K 31/70

-Excepciones de Patentabilidad:

El artículo 20 de la Decisión 486 de la Comisión de la Comunidad Andina establece

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en su inciso d) que no serán patentables: *“los métodos terapéuticos o quirúrgicos para el tratamiento humano o animal, así como los métodos de diagnóstico aplicados a los seres humanos o a animales”*.

Las reivindicaciones 4 a 8, reclaman un método para tratamiento del cuerpo humano o animal, el cual incluye la administración de un compuesto de la presente solicitud en una cantidad eficaz, por lo tanto están inmersas bajo el alcance del artículo 20 de la Decisión 486.

Determinación del estado de la técnica:

El artículo 16 de la Decisión 486 de la Comisión establece: *“El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.*

Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40.”

Se realizo la búsqueda del estado de la técnica con fecha anterior a la fecha de presentación de la primera solictud, de la cual se reivindica prioridad, 12 de enero1999. Consultada la fuente de información con que cuenta este despacho se encontró los siguientes documentos:

No.	Documento No.	Título	Fecha de Publicación
D1	US4334011	Color photographic light sensitive materials	08-junio-1982
D2	US4454225	Color photographic light-sensitive materials	12 – junio-1984

Evaluación de los requisitos de patentabilidad:

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:
"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial."

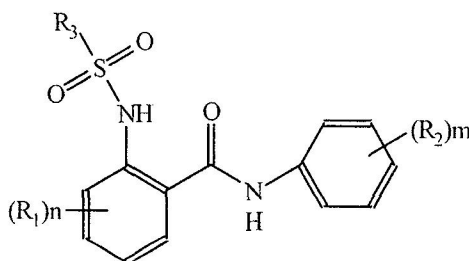
En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

Evaluación de la Novedad:

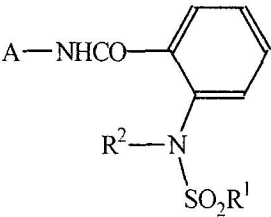
El art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece: *"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica."* *"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."*

Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

La solicitud en estudio reclama compuestos sulfonamido-benzanilida sustituidos que caen dentro de la formula:

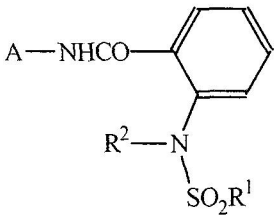


-La anterioridad D1 enseña los compuestos de fórmula:



Igual que en la solicitud en estudio son derivados sulfonamido-benzanilida, que cuando se hacen los reemplazos de los significados para cada se llega a los compuestos reclamados en la solicitud en estudio, tal como se muestra en los compuestos específicos descritos en la anterioridad, y a lo largo de toda la descripción, por lo tanto los compuestos de la solicitud en estudio no tienen novedad.

-D2 describe compuestos derivados de sulfonamido-benzanilida formula:



Igual que en la solicitud en estudio son derivados sulfonamido-benzanilida, que cuando se hacen los reemplazos de los significados para cada se llega a los compuestos reclamados en la solicitud, demostrando que los compuestos reclamados en la solicitud en estudio, no son nuevos, carecen de novedad.

Cuando una solicitud esta afectada su novedad, obviamente no posee nivel inventivo.

En conclusión los requisitos de Patentabilidad de la presente solicitud **están** afectadas así:

No.	Documento	Reivindicaciones	Requisito que afecta
D1.	US4.334.011	1 a 2	Novedad
D2	US4.454.225	1 a 2	Novedad

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

69-76

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la circular única No. 10 de 2001.



DORIS ELENA POLO CORDOBA

Jefe de División de Nuevas Creaciones(E)

El anterior requerimiento fue notificado por fijación en lista, de fecha

19 MAYO 2005

CONCEPTO TÉCNICO No. 654	EXAMINADOR TÉCNICO Código No. 202012
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2077

United States Patent [19]

Aoki et al.

[11] 4,334,011

[45] Jun. 8, 1982

[54] COLOR PHOTOGRAPHIC LIGHT SENSITIVE MATERIALS

[75] Inventors: Kozo Aoki; Yoshio Seoka; Yukio Yokota, all of Minami-ashigara, Japan

[73] Assignee: Fuji Photo Film Co., Ltd., Kanagawa, Japan

[21] Appl. No.: 213,513

[22] Filed: Dec. 5, 1980

[30] Foreign Application Priority Data

Dec. 5, 1979 [JP] Japan 54-157729

[51] Int. Cl.³ G03C 1/40

[52] U.S. Cl. 430/552; 430/553

[58] Field of Search 430/384, 385, 472, 473, 430/552, 553

[56] References Cited

U.S. PATENT DOCUMENTS

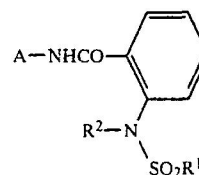
2,367,531	1/1945	Salminen et al.	430/552
2,369,929	2/1946	Vittum et al.	430/552
2,536,010	12/1950	Schmidt et al.	430/473
4,124,396	11/1978	Osborn	430/553
4,254,212	3/1981	Yagihara et al.	430/553
4,264,722	4/1981	Yagihara et al.	430/553

Primary Examiner—J. Travis Brown

Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak and Seas

[57] ABSTRACT

Color photographic light sensitive materials are disclosed, comprising a cyan dye forming coupler represented by formula (I)



wherein A represents a cyan coupler residue, but the —NHCO group does not bond to A in the active position of A, R¹ represents a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, R² represents hydrogen or a substituted or unsubstituted alkyl group, and the various positions of the phenyl group of the formula (I) may be substituted with from 1 to 3 substituents selected from the group consisting of hydrogen, a halogen atom, an alkyl group or an alkoxy group.

11 Claims, No Drawings

D 1

COLOR PHOTOGRAPHIC LIGHT SENSITIVE MATERIALS

BACKGROUND OF THE INVENTION

The present invention relates to color photographic light sensitive materials containing a novel cyan dye forming coupler.

When color development is carried out after a silver halide photographic light sensitive material is exposed to light, an oxidized aromatic primary amine developing agent reacts with dye forming couplers to form color images. In this process generally, color reproduction by a subtractive process is utilized, by which dye images of cyan, magenta and yellow, which are complement colors of red, green and blue, respectively, are formed for reproduction of red, green and blue. For example, as cyan dye forming couplers, various phenols and naphthols have been known.

Generally, in positive type light sensitive materials to be observed directly (e.g., color paper, color positive, or color slide, etc.), phenols are often used from the view-point of color reproduction. It has been desired to improve these phenols, because those giving good color reproduction are often inferior in the fastness of color images. On the other hand, phenols which form dye images having good fastness often do not have absorption characteristics suitable for color reproduction. In order to improve these drawbacks, it is necessary in the latter case that the phenols are modified so as to show adsorption characteristics suitable for color reproduction without damaging the fastness of color images.

For the purpose of satisfying the above described requirements, it has been known to introduce a chlorine atom into the 6-position of 2-acylaminophenol cyan couplers, as described in U.S. Pat. No. 2,367,531, but fastness with respect to heat of such color images shows remarkable deterioration. Furthermore, it has been known to introduce a fluorinated carbonamido group into the 2-position of 2,5-diacylaminophenol cyan couplers as described in U.S. Pat. No. 2,895,826, but fastness with respect to light of such color images shows remarkable deterioration.

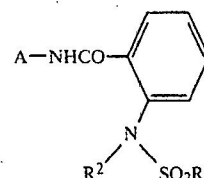
SUMMARY OF THE INVENTION

An object of the present invention is to provide couplers which are excellent in fastness and in color reproduction, by which the above described drawbacks are overcome.

It has been found that the above described object can be attained if an o-sulfonamidobenzoylamino group is introduced into a nucleus of certain cyan couplers, by which the couplers of the present invention are formed, having excellent characteristics in that they form a suitable color hue for color reproduction while also providing high fastness of color images.

Furthermore, the couplers of the present invention are also advantageous in that the lowering of the density is small in case of processing with a bleaching solution having a weak oxidation ability or a fatigued bleaching solution.

More particularly, the object of the present invention has been attained by using couplers represented by formula (I).



(I)

In the formula, A represents a cyan coupler residue, but the —NHCO group does not bond to A in the active coupling position of A, R¹ represents a substituted or unsubstituted alkyl group or aryl group, R² represents hydrogen or a substituted or unsubstituted alkyl group, and the various positions of the phenyl group of the formula (I) may be substituted with from 1 to 3 substituents selected from the group consisting of hydrogen, a halogen atom, an alkyl group, or an alkoxy group.

DETAILED DESCRIPTION OF THE INVENTION

A represents a phenol cyan coupler residue and a naphthol cyan coupler residue. R¹ preferably represents a substituted or unsubstituted alkyl group having from 1 to 22 carbon atoms or a substituted or unsubstituted aryl group having 6 to 22 carbon atoms, R² preferably represents hydrogen or a substituted or unsubstituted alkyl group having from 1 to 22 carbon atoms, and the various positions of the phenyl group of the formula (I) may be substituted with from 1 to 3 substituents selected from the group consisting of hydrogen, a halogen atom (for example, a fluorine atom, a chlorine atom or a bromine atom), an alkyl group having 1 to 22 carbon atom (for example, a methyl group, a butyl group or a pentadecyl group, etc.) or an alkoxy group (for example, a methoxy group, an ethoxy group or a 2-ethylhexyloxy group, etc.).

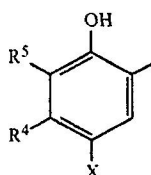
The substituents of the alkyl groups and aryl groups represented by R¹ and R² are selected from a halogen atom, a nitro group, a cyano group, an aryl group (for example, a phenyl group, a naphthyl group, etc.), an alkoxy group (for example, a methoxy group, an ethoxy group, etc.), an aryloxy group (for example, a phenyloxy group, a naphthyloxy group, etc.), a carboxy group, an alkylcarbonyl group (for example, an acetyl group, a tetradecanoyl group, etc.), an arylcarbonyl group (for example, a benzoyl group, etc.), an alkoxy-carbonyl group (for example, a methoxycarbonyl group, a benzyloxycarbonyl group, etc.), an aryloxycarbonyl group (for example, a phenyloxycarbonyl group, a p-tolyloxycarbonyl group, etc.), an acyloxy group (for example, an acetyloxy group, a tetradecanoyloxy group, etc.), a sulfamoyl group (for example, an N-ethylsulfamoyl group, an N-octadecylsulfamoyl group, etc.), a carbamoyl group (for example, an N-ethylcarbamoyl group, an N-methyl-N-dodecylcarbamoyl group, etc.), an acylamino group (for example, an acetylaminogroup, a benzamido group, etc.), a diacylamino group (for example, a succinimido group, a hydantoinyl group, etc.), a ureido group (for example, a methyl ureido group, a phenylureido group, etc.), an arylamino group (for example, a (4-methoxyphenyl)amino group, etc.), an N-alkylaminogroup (for example, an N-methylanilino group, an N-butylanilino group, etc.), an N-acylanilino group (for example, an N-acetylanilino group, an N-trichloroacetylanilino

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group, etc.), a hydroxy group, and a mercapto group, etc. Multiple substituents may be present.

Examples of R^1 include a methyl group, a butyl group, a methoxyethyl group, a dodecyl group, a phenoxypropyl group, a p-chlorophenoxybutyl group, a p-tolyl group, a p-dodecylphenyl group, a p-chlorophenyl group, and a naphthyl group. Examples of R^2 include a methyl group, a butyl group, an octyl group, a hexadecyl group, a 2-chloroethyl group, and a 2-methoxyethyl group.

Among the cyan coupler residues represented by A, preferred residues are phenol cyan coupler residues represented by formula (II).



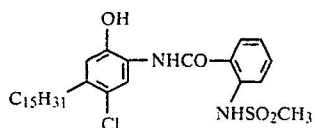
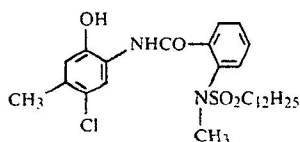
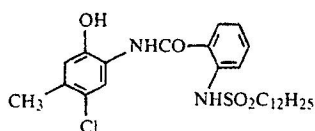
In the formula (II), R^4 represents a substituted or unsubstituted alkyl group, alkylacylamino group, or arylacylamino group, wherein the substituents are the same as those of the alkyl group represented by R^1 as described above. Examples of the alkyl group include a methyl group, an ethyl group, a butyl group, a pentadecyl group, a phenylthiomethyl group and a chloromethyl group. Examples of the alkylacylamino group include a butyrylamino group, a pivaloylamino group and a 2-(2',4'-di-tert-amylphenoxy)butanamido group. An example of the arylacylamino group includes a benzoylamino group.

R^5 represents hydrogen or a halogen atom (a fluorine atom, chlorine atom or bromine atom). X represents a group capable of being released by an oxidation coupling reaction with a developing agent (for example, hydrogen, a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, an imido group, a sulfonamido group or a thiocyanato group, etc.).

As a particularly preferred R^4 , there is a substituted or unsubstituted alkylacylamino group.

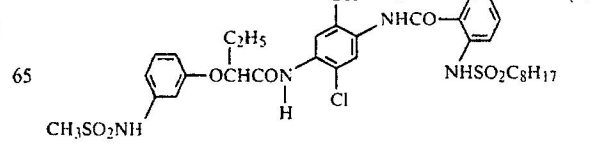
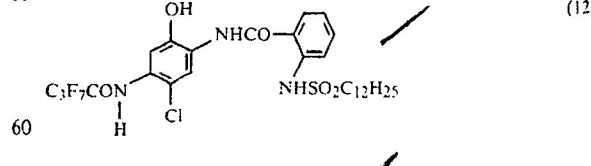
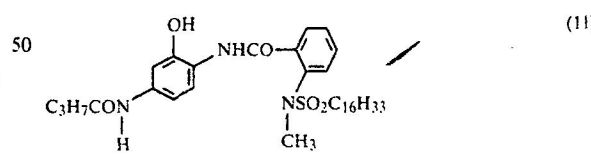
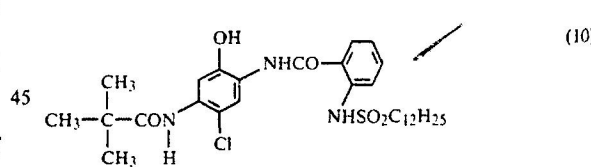
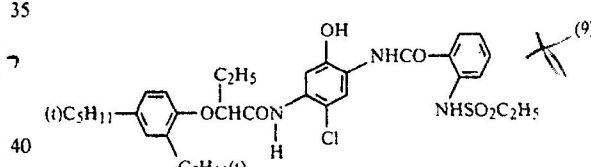
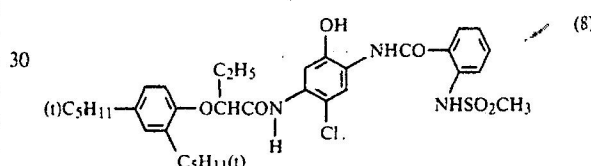
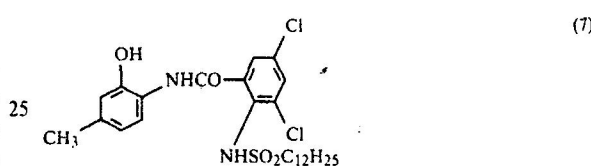
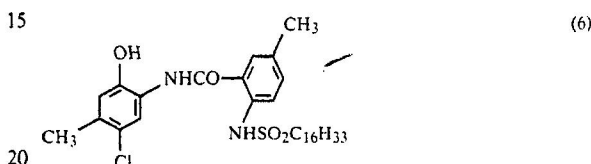
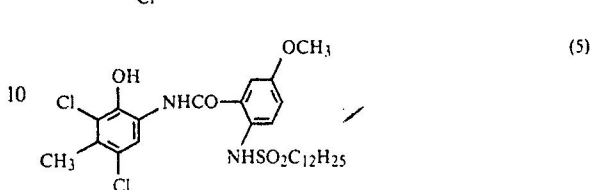
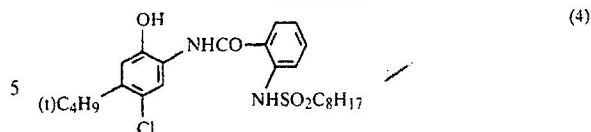
Hydrogen is particularly preferred as R^5 .

Examples of such couplers included in the scope of the present invention are described below, but the couplers are not limited thereto.



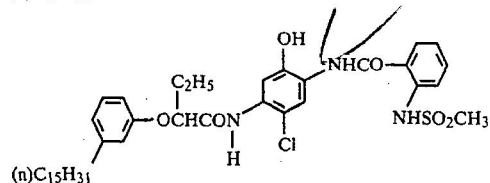
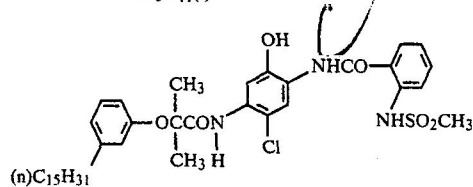
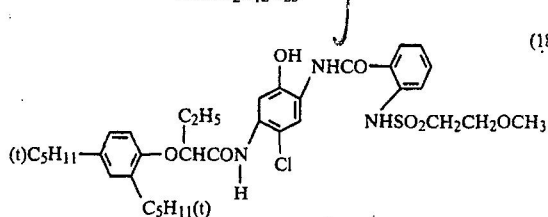
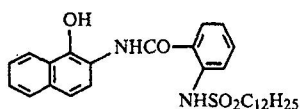
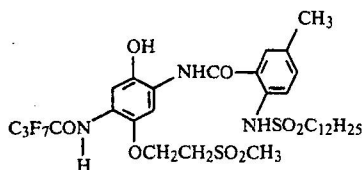
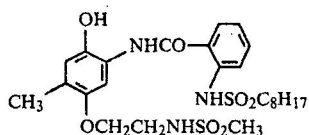
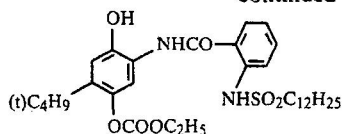
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-continued



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-continued



Compounds according to the present invention can be synthesized by processes as described below.

Anthranilic acid ester is condensed with corresponding sulfonic acid chloride, using pyridine or triethylamine as a deacidifying agent, to produce o-sulfonylaminobenzoic acid ester. If necessary, it is possible to carry out N-alkylation thereof, using an alkylhalide and a strong base such as sodium hydride. The resulting ester is hydrolyzed in the presence of alkali hydroxide to produce a benzoic acid derivative, which is then processed with thionyl chloride and phosphorus oxychloride to produce acid chloride. The resulting acid chloride and the corresponding 2-aminophenol derivative are refluxed in acetonitrile, by which o-sulfonylaminobenzoylaminophenol can be synthesized.

In the case of synthesizing 2,5-diacylaminophenol derivatives, a 5-nitro derivative is first synthesized. After the nitro group is reduced to form an amino group, the product is reacted with another acid chloride to produce a coupler.

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Examples of synthesis of typical couplers according to the present invention are described below.

Synthesis of

5 4-chloro-2-(2-dodecan-sulfonamidobenzoylamino)-5-methylphenol: Coupler (1)

1. Synthesis of 2-dodecansulfonamidobenzoyl chloride:

16.5 g of ethyl anthranilate and 22 g of dodecansulfonyl chloride were dissolved in 100 ml of tetrahydrofuran. To the mixture, 17 ml of triethylamine was added dropwise at 50° C. After stirring for 8 hours, 200 ml of ethyl acetate was added, and the mixture was washed with diluted hydrochloric acid and then with water. An oily product obtained by distilling off the solvent in vacuum was dissolved in 100 ml of ethanol, and a solution obtained by dissolving 12 g of sodium hydroxide in 100 ml of water was added thereto. The mixture was stirred at 50° C. for 4 hours. Crystals separated by acidifying with hydrochloric acid after cooling were gathered and washed with water. When dried, 26 g of crystals were obtained. 100 ml of benzene was added to the crystals and 14 ml of thionyl chloride was added dropwise thereto. After heated for 3 hours with refluxing, the solvent and excess thionyl chloride were distilled off in vacuum to produce the desired acid chloride.

2. Synthesis of Coupler (1):

9.4 g of 2-amino-4-chloro-5-methylphenol was dissolved in 120 ml of acetonitrile, and the acid chloride obtained in the first step described above was added dropwise thereto with refluxing. After added dropwise, the mixture was stirred for 3 hours with refluxing. After cooling, ethyl acetate was added and water wash was repeated three times. A residue obtained by distilling off the solvent in vacuum was recrystallized with ethyl acetate-hexane to obtain 24 g of crystals having a melting point of 124°-125° C.

Elementary analysis:

Calculated: C 61.34, H 7.33, N 5.50; Found: C 61.00, H 7.46, N 5.50.

Synthesis of

45 4-chloro-5-[2-(2,4-di-tert-amylphenoxy)-butanamido]-2-(2-methanesulfonamidobenzoylamino)phenol: Coupler (8).

1. Synthesis of 2-methanesulfonamidobenzoyl chloride:

30.2 g of methyl anthranilate was dissolved in a mixture of 50 ml of acetonitrile and 25 ml of pyridine, and 20 ml of methanesulfonyl chloride was added dropwise thereto. After stirring at a room temperature for 2 hours, the mixture was poured into an aqueous mixture of excess hydrochloric acid and ice to form crystals. The resulting crystals were washed with water and dissolved in 100 ml of ethanol. After adding a solution obtained by dissolving 20 g of sodium hydroxide in 100 ml of water, the mixture was stirred at 60° C. for 4 hours. Crystals separated by acidifying with hydrochloric acid were gathered and washed with water. After drying, 39 g of crystals were obtained. To the crystals, 16 ml of benzene was added and 26 ml of thionyl chloride was then added dropwise. After heating for 6 hours under refluxing, the solvent and excess thionyl chloride were removed in vacuum to obtain the desired acid chloride.

2. Synthesis of Coupler (8):

28 g of 2-amino-4-chloro-5-nitrophenol was dissolved in 100 ml of acetonitrile and the acid chloride obtained in the above was added dropwise thereto with refluxing. After adding dropwise, the mixture was stirred for 4 hours with refluxing. After cooling, the separated crystals were gathered to obtain 32 g of the crystals. These crystals were dissolved in 250 ml of isopropanol, and subjected to hydrogenation in an autoclave using a vanadium-carbon catalyst (at 50° C., and an initial hydrogen pressure of 50 kg/cm²). After removed the catalyst by filtration, the solvent with distilled off in vacuum. The residue obtained was dissolved in 200 ml of acetonitrile. 28 g of 2-(2,4-di-tert-amylphenoxy)butan-
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Elementary analysis:

Calculated: C 62.04, H 6.74, N 6.39; Found: C 62.10, H 6.78, N 6.24.

Photographic emulsion layer or multilayer in the photographic light sensitive materials produced utilizing the coupler(s) of the present invention may contain color image forming couplers other than the couplers of the present invention. It is preferred that these other couplers be nondiffusible ones having a hydrophobic ballast group in the molecule. Also, the other couplers may be 4-equivalent and/or 2-equivalent couplers. Furthermore, the layers may contain colored couplers having a color correction effect or couplers releasing a development inhibitor (a so-called DIR coupler). The other couplers may also be those which form a colorless product by a coupling reaction.

As yellow forming couplers, known ketomethylene type couplers can be used. Among them, benzoylacetyl type and pivaloylacetyl type compounds are advantageously used. Examples of the yellow forming couplers capable of being used include those described in U.S. Pat. Nos. 2,875,057, 3,265,506, 3,408,194, 3,551,155, 3,582,322, 3,725,072 and 3,891,445, German Pat. No. 1,547,868, German patent application (OLS) Nos. 2,219,917, 2,261,361 and 2,414,006, British Pat. No. 1,425,020, Japanese patent publication No. 10783/76 and Japanese patent application (OPI) Nos. 26133/72, 73147/73, 102636/76, 6341/75, 123342/75, 130442/75, 21827/76, 87650/75, 82424/77 and 115219/77.

As magenta forming couplers, pyrazolone type compounds, inidazolone type compounds and cyanoacetyl type compounds can be used, and pyrazolone type compounds are particularly advantageous to use. Examples of the magenta forming couplers include those described in U.S. Pat. Nos. 2,600,788, 2,983,608, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,834,908 and 3,891,445, German Pat. No. 1,810,464, German patent application (OLS) Nos. 2,408,665, 2,417,945, 2,418,959 and 2,424,467, Japanese patent publication No. 6031/65 and Japanese patent application (OPI) Nos. 20826/76, 58922/77, 129538/74, 74027/74, 159336/75, 42121/77, 74028/74, 60233/75, 26541/76 and 55122/78.

As cyan forming couplers, phenol type compounds and naphthol type compounds can be used in addition to

the cyan forming couplers of this invention. Examples of them include those described in U.S. Pat. Nos. 2,369,929, 2,434,272, 2,474,293, 2,512,908, 2,895,826, 3,034,892, 3,311,476, 3,458,315, 3,476,563, 3,583,971, 3,591,383, 3,767,411 and 4,004,929, German patent application (OLS) Nos. 2,414,830 and 2,454,329 and Japanese patent application (OPI) Nos. 59838/73, 26034/76, 5055/73, 146828/76, 69624/77 and 90932/77.

As colored couplers, it is possible to use those described, for example, in U.S. Pat. Nos. 3,476,560, 2,521,908 and 3,034,892, Japanese patent publication Nos. 2016/69, 22335/63, 11304/67 and 32461/69, Japanese patent application (OPI) Nos. 26034/76 and 42121/77 and German patent application (OLS) No. 2,418,959.

As DIR couplers, it is possible to use those described, for example, in U.S. Pat. Nos. 3,227,554, 3,617,291, 3,701,783, 3,790,384 and 3,632,345, German patent application (OLS) Nos. 2,414,006, 2,454,301 and 2,454,329, British Pat. No. 953,454, Japanese patent application (OPI) Nos. 69624/77 and 122335/74 and Japanese patent publication No. 16141/76.

The light sensitive materials may contain compounds releasing a development inhibitor other than the DIR couplers. For example, it is possible to use those described in U.S. Pat. Nos. 3,297,445 and 3,379,529, German patent application (OLS) No. 2,417,914 and Japanese patent application (OPI) Nos. 15271/77 and 9116/78.

Two or more of both the couplers of the present invention and the known couplers may be contained in the same layer. The same compound may be contained in two or more layers.

Both the couplers of the present invention and the known couplers are typically added in an amount of from 2×10^{-3} mol to 5×10^{-1} mol, and preferably from 1×10^{-2} mol to 5×10^{-1} mol, per mol of silver in the emulsion layer in which the coupler is contained.

Both the couplers of the present invention and the known couplers are incorporated in the silver halide emulsion layers by known methods, for example, by a method as described in U.S. Pat. No. 2,322,027. For example, they can be dispersed in a hydrophilic colloid after being dissolved in phthalic acid alkyl esters (dibutyl phthalate or dioctyl phthalate, etc.), phosphoric acid esters (diphenyl phosphate, triphenyl phosphate, tricresyl phosphate or dioctylbutyl phosphate), citric acid esters (for example, tributyl acetylcitrate), benzoic acid esters (for example, octyl benzoate), alkylamides (for example, diethyl laurylamide) or aliphatic acid esters (for example, dibutoxyethyl succinate or dioctyl azelate), etc. or organic solvents having a boiling point of from about 30° C. to 150° C. Examples include a lower alkyl acetate such as ethyl acetate or butyl acetate, ethyl propionate, secondary butyl alcohol, methyl isobutyl ketone, β -ethoxyethyl acetate or methyl cellosolve acetate, etc. The above described high boiling point organic solvents and low boiling point organic solvents may be used as a mixture thereof.

Furthermore, it is possible to use a method of dispersing with using polymers, as described in Japanese patent publication No. 39853/76 and Japanese patent application (OPI) No. 59943/76.

If the couplers have acid groups such as a carboxylic acid group or a sulfonic acid group, they are incorporated in the hydrophilic colloid in the form of an alkaline aqueous solution.

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In the light sensitive materials produced by the present invention, the hydrophilic colloid layers may contain an ultraviolet ray absorbing agent. For example, it is possible to use benzotriazole compounds substituted by aryl groups (for example, those described in U.S. Pat. No. 3,533,794), 4-thiazolidone compounds (for example, those described in U.S. Pat. Nos. 3,314,794 and 3,352,681), benzophenone compounds (for example, those described in Japanese patent application (OPI) No. 2784/71), cinnamic acid ester compounds (for example, those described in U.S. Pat. Nos. 3,705,805 and 3,707,375), butadiene compounds (for example, those described in U.S. Pat. No. 4,045,229) and benzoxazole compounds (for example, those described in U.S. Pat. No. 3,700,455). Further, it is possible to use those described in U.S. Pat. No. 3,499,762 and Japanese patent application (OPI) No. 48535/79. Ultraviolet ray absorbing couplers (for example, α -naphthol type cyan dye forming couplers) or ultraviolet ray absorbing polymers may be used, too. These ultraviolet ray absorbing agents may be mordanted in a specified layer.

The photographic emulsions used in the present invention can be prepared by processes as described in *Chimie et Physique Photographique*, by P. Glaftides (published by Paul Montol C., 1967); *Photographic Emulsion Chemistry*, by G. F. Duffin (published by The Focal Press Co., 1966); and *Making and Coating Photographic Emulsion*, by V. L. Zwlikman et al (published by The Focal Press Co., 1964). Namely, any of an acid process, a neutral process and an ammonia process may be used. Further, as a type of reaction of a soluble silver salt with a soluble halogen salt, any of a one-way mixing process, a simultaneous mixing process, or a combination thereof may be used.

It is also possible to use a process of forming particles in a presence of excess silver ions (a so-called reverse mixing process). As one type of the simultaneous mixing process, it is possible to use a process which comprises maintaining a constant pAg of a liquid phase while forming silver halide (the so-called controlled double jet process).

According to this process, silver halide emulsions wherein the crystal form is regular and the particle size is nearly uniform are obtained.

Two or more silver halide emulsions prepared separately may be used as a mixture thereof, if desired.

Cadmium salts, zinc salts, lead salts, thallium salts, iridium salts or complex salts thereof, rhodium salts or complex salts thereof and iron salts or complex salts thereof, etc., may be incorporated in the step of forming silver halide particles or of physical aging.

As a binder or a protective colloid in the photographic emulsions, gelatin is advantageously used, but hydrophilic colloids other than gelatin can also be used. For example, it is possible to use proteins such as gelatin derivatives, graft polymers of gelatin with another high molecular substance, albumin or casein, etc.; saccharides such as cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose or cellulose sulfate, etc., sodium alginate or starch derivatives, etc.; and various synthetic hydrophilic high molecular materials such as homopolymers or copolymers including polyvinyl alcohol, polyvinyl alcohol semiacetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinylpyrazole, etc.

As the gelatin, not only lime-processed gelatin, but also acid-processed gelatin and enzyme-processed gela-

tin, as described in *Bull. Soc. Sci. Phot. Japan*, No. 16, page 30 (1966) may be used. Further, hydrolysis products and enzymatic decomposition products of gelatin can be used, too. As gelatin derivatives, it is possible to use those which are obtained by reacting gelatin with various compounds, for example, acid halides, acid anhydrides, isocyanates, bromoacetic acid, alkane sulfones, vinyl sulfonamides, maleimide compounds, polyalkylene oxides and epoxy compounds, etc. Examples of them have been described in U.S. Pat. Nos. 2,614,928, 3,132,945, 3,186,846 and 3,312,553, British Pat. Nos. 861,414, 1,033,189 and 1,005,784 and Japanese patent publication No. 26845/67, etc.

As the graft polymers of gelatin, it is possible to use those obtained by grafting gelatin with homo- or copolymers of vinyl monomers such as acrylic acid, methacrylic acid and derivatives thereof such as esters or amides, etc., acrylonitrile or styrene, etc. Particularly, it is preferred to use graft polymers of gelatin with polymers having a some degree of compatibility with gelatin, for example, polymers of acrylic acid, methacrylic acid, acrylamide, methacrylamide or hydroxyalkyl methacrylate, etc. Examples thereof have been described in U.S. Pat. Nos. 2,763,625, 2,831,767 and 2,956,884.

Typical examples of the synthetic high molecular materials are those described in German patent application (OLS) No. 2,312,708, U.S. Pat. Nos. 3,620,751 and 3,879,205 and Japanese patent publication No. 7561/68.

For the purpose of preventing fogging in the step of producing light sensitive materials, during preservation or during photographic processing or to stabilize photographic properties, it is possible to add various compounds to the photographic emulsions used in the present invention. Namely, it is possible to add many compounds known as antifogging agents or stabilizing agents such as azoles, for example, benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazole and mercaptotetrazoles (particularly, 1-phenyl-5-mercaptopotetrazole), etc.; mercaptopyrimidines; mercaptotriazines; thioketo compounds such as oxazoline thione; azaindenes, for example, triazaindenes, tetrazaindenes (particularly, 4-hydroxy substituted-(1,3,3a,7)-tetrazaindenes) and pentazaindenes, etc.; benzenethiosulfonic acids, benzenesulfonic acids and benzenesulfonic acid amides, etc. For example, it is possible to use compounds as described in U.S. Pat. Nos. 3,954,474 and 3,982,947 and Japanese patent publication No. 28660/77.

For the purpose of increasing sensitivity, increasing contrast, or accelerating development, the photographic emulsion layers of the photographic light sensitive materials of the present invention may contain, for example, polyalkylene oxide or derivatives thereof such as ethers, esters or amines, etc., thio ether compounds, thiomorpholinic acid, quaternary ammonium salts, urethane derivatives, urea derivatives, imidazole derivatives and 3-pyrazolidones, etc. For example, it is possible to use compounds as described in U.S. Pat. Nos. 2,400,532, 2,423,549, 2,716,062, 3,617,280, 3,772,021 and 3,808,003 and British Patent 1,488,991, etc., for these purpose also.

The photographic emulsions used in the present invention may be spectrally sensitized with methine dyes or others. The dyes used include cyanine dyes, merocya-

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anine dyes, compound cyanine dyes, compound merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly suitable dyes are dyes belonging to cyanine dyes, merocyanine dyes and compound merocyanine dyes. These dyes may have as a basic heterocyclic nucleus any of nuclei utilized generally for cyanine dyes. Namely, it is possible to utilize a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus and a pyridine nucleus, etc.; nuclei wherein an alicyclic hydrocarbon ring is condensed with the above described nuclei; and nuclei wherein an aromatic hydrocarbon ring is condensed with the above described nuclei, that is, an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus, etc. These nuclei may have substituents on the carbon atoms.

In the merocyanine dyes and the compound merocyanine dyes, it is possible to utilize as a nucleus having ketomethylene structure, a 5- or 6-membered heterocyclic nucleus such as a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanin nucleus or a thiobarbituric acid nucleus, etc.

Examples of useful sensitizing dyes are those described in German Pat. No. 929,080, U.S. Pat. Nos. 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,959, 3,672,897, 3,694,217, 4,025,349 and 4,046,572, British Patent 1,242,588 and Japanese patent publication Nos. 14030/69 and 24844/77.

These sensitizing dyes can be used alone, or they may be used as a combination thereof. The combinations of the sensitizing dyes are often used for, particularly, the purpose of supersensitization. Typical examples of them have been described in U.S. Pat. Nos. 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862 and 4,026,707, British Pat. Nos. 1,344,281 and 1,507,803, Japanese patent publication Nos. 4936/68 and 12375/78 and Japanese patent application (OPI) Nos. 110618/77 and 109925/77.

The emulsions may contain dyes which do not have a spectral sensitization function themselves or substances which do not substantially absorb visible rays, but show a supersensitization function, together with the sensitizing dyes. For example, they may contain aminostilbene compounds substituted with a nitrogen containing heterocyclic group (for example, U.S. Pat. Nos. 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensates (for example, U.S. Pat. No. 3,743,510), cadmium salts or azaindene compounds, etc. Combinations described in U.S. Pat. Nos. 3,615,613, 3,615,641, 3,617,295 and 3,635,721 are particularly preferred.

In the light sensitive materials produced with utilizing the present invention, the hydrophilic colloid layers may contain water soluble dyes as filter dyes or for the purpose of preventing irradiation or others. Such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Particularly, oxonol dyes, hemioxonol dyes and merocyanine dyes are preferred. Examples of such dyes capable of being used include those described in British Pat. Nos. 584,609 and 1,177,429, Japanese patent application (OPI) Nos. 85130/73, 99620/74, 114420/74 and

108115/77 and U.S. Pat. Nos. 2,274,782, 2,533,472, 2,956,879, 3,148,187, 3,177,078, 3,247,127, 3,540,887, 3,575,704, 3,653,905, 3,718,472, 4,071,312 and 4,070,352.

In the light sensitive materials produced with utilizing the present invention, photographic emulsion layers and other hydrophilic colloid layers may contain whitening agents such as stilbene, triazine, oxazole or coumarin type whitening agents. These whitening agents may be soluble in water. In the case of water insoluble whitening agents, they may be used as a dispersion. Examples of fluorescent whitening agents have been described in U.S. Pat. Nos. 2,632,701, 3,269,840 and 3,359,102 and British Pat. Nos. 852,075 and 1,319,763, etc.

When the present invention is carried out, known antifading agents may be used therewith. Furthermore, the color image stabilizers may be used in the light sensitive materials according to the present invention, alone or as a mixture of two or more of them. The antifading agents include, for example, hydroquinone derivatives as described in U.S. Pat. Nos. 2,360,290, 2,418,613, 2,675,314, 2,701,197, 2,704,713, 2,728,569, 2,732,300, 2,735,765, 2,710,801 and 2,816,028 and British Pat. No. 1,363,921, etc., gallic acid derivatives as described in U.S. Pat. Nos. 3,457,079 and 3,069,262, etc., p-alkoxyphenols as described in U.S. Pat. Nos. 2,735,765 and 3,698,909 and Japanese patent publication Nos. 20977/74 and 6623/77, p-oxyphenol derivatives as described in U.S. Pat. Nos. 3,432,300, 3,573,050, 3,574,627 and 3,764,337 and Japanese patent application (OPI) Nos. 35633/77, 147434/77 and 152225/77, and bisphenols as described in U.S. Pat. No. 3,700,455.

The light sensitive materials according to the present invention may contain hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives or ascorbic acid derivatives as anti-color-fogging agents. Examples thereof are described in U.S. Pat. Nos. 2,360,290, 2,336,327, 2,403,721, 2,418,613, 2,675,314, 2,701,197, 2,704,713, 2,728,659, 2,732,300 and 2,735,765, Japanese patent application (OPI) Nos. 92988/75, 92989/75, 93928/75, 110337/75 and 146235/77 and Japanese patent publication No. 23813/75, etc.

The present invention can be applied to multilayer multicolor photographic materials comprising layers of at least two different spectral sensitivities on a base. The multilayer technicolor photographic materials generally have at least a red-sensitive emulsion layer, a green-sensitive emulsion layer, and a blue-sensitive emulsion layer on a base. The order of these layers can be suitably selected as occasion demands. Generally, the red-sensitive emulsion layer contains a cyan forming coupler, the green-sensitive emulsion layer contains a magenta forming coupler, and the blue-sensitive emulsion layer contains a yellow forming coupler, but other combinations can be adopted if desired.

In the photographic light sensitive materials produced according to the present invention, the photographic emulsion layers and other layers are produced by applying to a flexible base, such as conventionally used plastic films, paper or cloth, etc. or rigid bases such as glass, porcelain or metal, etc. As useful elastic bases, there are films composed of semisynthetic or synthetic high molecular materials such as cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polystyrene, polyvinyl chloride, polyethylene terephthalate or polycarbonate, etc. and papers to which a baryta layer or α -olefin polymer (for example, polyethylene, polypropylene or ethylene-butene copolymer) is applied or

laminated. The bases may be colored with dyes or pigments. In order to intercept light, the bases may be blackened. The surface of these bases is generally subjected to an undercoating treatment in order to improve adhesion to the photographic emulsion layer, etc. The surface of the bases may be subjected to corona discharging, ultraviolet ray application or flame treatment etc. before or after the undercoating treatment. Further, the present invention can be used for color light sensitive materials comprising a layer having low oxygen permeability (for example, a layer composed of polyvinyl alcohol or homopolymer or copolymer of acrylonitrile, etc.) between the base and the photographic emulsion.

Photographic processing of the light sensitive materials of the present invention can be carried out by known processes. Known processing solutions can be used. The processing temperature is generally selected from the range from 18° C. to 50° C., but a temperature lower than 18° C. or a temperature higher than 50° C. may be used. Known development processes for forming silver images (black-white photographic processing) and development processing for forming dye images may be adopted as the color photographic processing, according to the particular purpose.

The color developing solution generally consists of an alkaline aqueous solution containing a color developing agent. As the color developing agent, it is possible to use known primary aromatic amine developing agents, for example, phenylenediamines (for example, 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline and 4-amino-3-methyl-N-ethyl-N-methoxyethylaniline, etc.).

In addition, compounds described in *Photographic Processing Chemistry*, pages 226 to 229, by L. F. A. Mason (published by Focal Press, 1966), U.S. Pat. Nos. 2,193,015 and 2,592,364 and Japanese patent application (OPI) No. 64933/73, etc. may be used, too.

The color developing solution is capable of containing pH buffers such as sulfites, carbonates, borates or phosphates of alkali metals, and development restrainers or antifogging agents such as bromides, iodides or organic antifogging agents. Furthermore, if desired, the solution may contain water softeners, preservatives such as hydroxylamine, organic solvents such as benzyl alcohol or diethylene glycol, development accelerators such as polyethylene glycol, quaternary ammonium salts or amines, dye forming couplers, competition couplers, fogging agents such as sodium borohydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, viscosity-imparting agents, polycarboxylic acid chelating agents as described in U.S. Pat. No. 4,083,723 and antioxidants as described in German patent application (OLS) No. 2,622,950, etc.

The photographic emulsion layers after color development are generally subjected to bleaching. The bleaching may be carried out simultaneously with fixing or may be carried out respectively. As bleaching agents, compounds of polyvalent metals such as iron (III), cobalt (IV), chromium (VI) or copper (II), etc., peracids, quinones and nitroso compounds are used. For example, it is possible to use ferricyanides, bichromates, organic complex salts of iron (III) or cobalt (III) and complex salts of aminopolycarboxylic acids such as ethylenediaminetetraacetic acid, nitrilotriacetic acid or 1,3-

diamino-2-propanol tetraacetic acid, etc. or organic acids such as citric acid, tartaric acid or malic acid, etc.; persulfates and permanganates; and nitrosophenol, etc. Among them, potassium ferricyanide, sodium (ethylenediaminetetraacetato) iron (III) complex and ammonium (ethylenediaminetetraacetato) iron (III) complex are particularly useful. (Ethylenediaminetetraacetato) iron (III) complex salts are useful for both a bleaching solution or a one-bath bleach-fixing solution.

To the bleaching solution or the bleach-fixing solution, it is possible to add various additives in addition to bleaching accelerators as described in U.S. Pat. Nos. 3,042,520 and 3,241,966 and Japanese patent publication Nos. 8506/70 and 8836/70, etc. and thiol compounds described in Japanese patent application (OPI) No. 65732/78.

In the following, the present invention is illustrated in detail by examples, but the invention is not limited thereto.

EXAMPLE 1

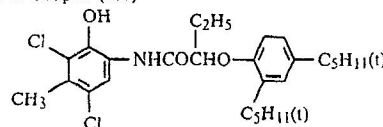
A solution obtained by heating 25 g of Coupler (1): 4-chloro-2-(2-dodecanesulfonamidobenzoylamino)-5-methylphenol, 25 g of trioctyl phosphate and 50 ml of ethyl acetate to 50° C. was added to 250 ml of an aqueous solution containing 25 g of gelatin and 1.0 g of sodium dodecylbenzenesulfonate. The mixture was stirred and allowed to pass 5 times through a colloid mill after heated previously, by which the mixture was finely dispersed to obtain an emulsion.

The whole of this emulsion was added to 1.0 kg of a photographic emulsion containing 54 g of silver iodobromide and 60 g of gelatin. After 80 ml of a 2% aqueous solution of 4,6-dichloro-4-hydroxytriazine as a hardening agent was added, a pH of the dispersion mixture was adjusted to 6.0 and the mixture was applied to a cellulose triacetate film base so as to obtain a dry film thickness of 7.0 microns. The resulting film was designated as Sample A.

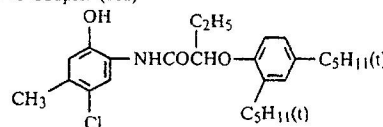
Films were prepared by the same procedure as described above, except using equimolar amounts of Couplers (4), (8), (10) and (12) instead of the above described Coupler (1). These films were designated as Samples B, C, D and E, respectively.

For purposes of comparison, films were prepared by the same procedure as described above, except using an equimolar amount of Couplers (101), (102), (103), (104) and (105) as described below instead of the above described Coupler (1). These films were designated as Samples F, G, H, I and J.

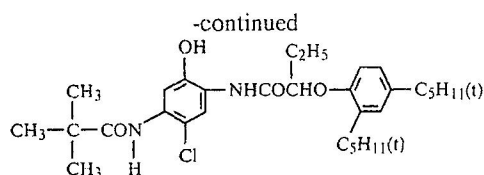
Comparative Coupler (101)



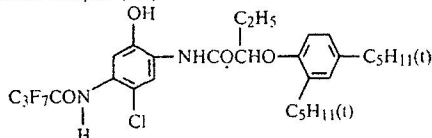
Comparative Coupler (102)



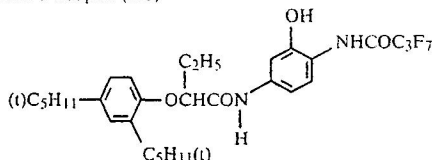
Comparative Coupler (103)



Comparative Coupler (104)



Comparative Coupler (105)



These films were subjected to a continuous exposure by means of a sensitometric wedge and processed thereafter as follows.

Color development step		
1. Color development	33° C.	3.5 minutes
2. Bleach-fixation	33° C.	1.5 minutes
3. Water wash	25 to 30° C.	2.5 minutes

The composition of each processing solution for the color development step was as follows

Color developing solution:

Benzyl alcohol	15 ml
Diethylene glycol	8 ml
Ethylenediaminetetraacetic acid	5 g
Sodium sulfite	2 g
Anhydrous potassium carbonate	30 g
Hydroxylamine sulfate	3 g
Potassium bromide	0.6 g
4-Amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate	5 g
Water	to make 1 liter
	pH 10.2

Bleach-fixing solution:

Ethylenediaminetetraacetic acid	2 g
(Ethylenediaminetetraacetato) iron (III) complex	40 g
Sodium sulfite	5 g
Ammonium thiosulfate	70 g
Water	to make 1 liter

When absorption spectra of the resulting samples after processing were measured, the results shown in Table 1 were obtained.

TABLE 1

Film sample	Coupler	Absorption maximum mμ	Half width of absorption mμ
A	(1) (this invention)	646	136
B	(4) (this invention)	650	138
C	(8) (this invention)	651	136
D	(10) (this invention)	646	134
E	(12) (this invention)	648	132
F	(101) (comparison)	649	138
G	(102) (comparison)	625	138
H	(103) (comparison)	626	136

TABLE 1-continued

Film sample	Coupler	Absorption maximum mμ	Half width of absorption mμ
I	(104) (comparison)	632	132
J	(105) (comparison)	658	137

As is seen from this Table, the couplers of this invention form dyes having absorption maximum in the range of 645 to 655 mμ which is suitable for color reproduction.

Then, the fastness to light and heat of each film after development was examined. Fastness to heat was determined by allowing the film to remain at 100° C. for 6 days in the dark, and by allowing the film to remain at 60° C. and 70% RH for 6 weeks in the dark, and fastness to light was determined by exposing the film to light for 6 days by means of a xenon tester (100,000 lux). The results are described in Table 2 as reduction ratios of the density based on an initial density of 1.0.

TABLE 2

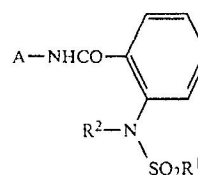
Film Sample	Coupler	100° C., for 6 days	60° C., 70% RH, for 6 weeks	Light (xenon), for 6 days
A	(1) (this invention)	22%	4%	12%
B	(4) (this invention)	18%	3%	12%
C	(8) (this invention)	2%	3%	15%
D	(10) (this invention)	2%	1%	7%
E	(12) (this invention)	11%	6%	13%
F	(101) (comparison)	79%	8%	18%
G	(102) (comparison)	38%	7%	28%
H	(103) (comparison)	10%	9%	29%
I	(104) (comparison)	13%	9%	50%
J	(105) (comparison)	16%	12%	38%

As is clear from Table 2, Comparative Coupler (101) which has the absorption maximum suitable for color reproduction (as shown in Table 1) is inferior in fastness to heat and Comparative Coupler (105) is inferior in fastness to light. On the other hand, Comparative Couplers (102), (103) and (104) which are relatively excellent in fastness of color images are not suitable for color reproduction because of having absorptions at shorter wavelengths. On the contrary, the couplers of the present invention not only have a suitable absorption maximum but also are excellent in fastness to both of light and heat.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A color photographic silver halide light sensitive material comprising a cyan dye forming coupler represented by formula (I)



wherein A represents a cyan coupler residue, but the —NHCO group does not bond to A in the active posi-

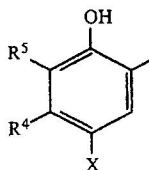
tion of A, R¹ represents a substituted or unsubstituted alkyl group or aryl group, R² represents hydrogen or a substituted or unsubstituted alkyl group, and the various positions of the phenyl group of the formula (I) may be substituted with from 1 to 3 substituents selected from the group consisting of hydrogen, a halogen atom, an alkyl group, or an alkoxy group.

2. A color photographic light sensitive material as in claim 1, wherein R¹ represents a substituted or unsubstituted alkyl group having from 1 to 22 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 22 carbon atoms; R² represents hydrogen or a substituted or unsubstituted alkyl group having from 1 to 22 carbon atoms; and the various positions of the phenyl group of the formula (I) may be substituted with from 1 to 3 substituents selected from the group consisting of hydrogen, a halogen atom, an alkyl group having from 1 to 22 carbon atom or an alkoxy group.

3. A color photographic light sensitive material as in claim 2, wherein R¹ is a methyl group, a butyl group, a methoxyethyl group, a dodecyl group, a phenoxypropyl group, a p-chlorophenoxybutyl group, a p-tolyl group, a p-dodecylphenyl group, a p-chlorophenyl group, or a naphthyl group; and R² is a methyl group, a butyl group, an octyl group, a hexadecyl group, a 2-chloroethyl group, or a 2-methoxyethyl group.

4. A color photographic light sensitive material as in claim 1, 2 or 3, wherein the substituents of the alkyl groups and aryl groups represented by R¹ and R² are selected from a halogen atom, a nitro group, a cyano group, an aryl group, an alkoxy group, an aryloxy group, a carboxy group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, an acyloxy group, a sulfamoyl group, a carbamoyl group, an acylamino group, a diacylamino group, a ureido group, an arylamino group, an N-alkylanilino group, an N-acylanilino group, a hydroxy group, and a mercapto group.

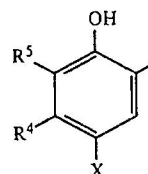
5. A color photographic light sensitive material as in claim 1, 2 or 3, wherein A represents a phenol cyan coupler residue represented by formula (II)



wherein R⁴ represents a substituted or unsubstituted alkyl group, alkylacylamino group, or arylacylamino group; R⁵ represents hydrogen or a halogen atom; and

X represents a group capable of being released by an oxidation coupling reaction with a developing agent.

6. A color photographic light sensitive material as in claim 4, wherein A represents a phenol cyan coupler residue represented by formula (II)



(II)

wherein R⁴ represents a substituted or unsubstituted alkyl group, alkylacylamino group, or arylacylamino group; R⁵ represents hydrogen or a halogen atom; and X represents a group capable of being released by an oxidation coupling reaction with a developing agent.

7. A color photographic light sensitive material as in claim 5, wherein R⁴ is a substituted or unsubstituted alkylacylamino group; and R⁵ is hydrogen.

8. A color photographic light sensitive material as in claim 5, wherein the substituents of R⁴ are selected from a halogen atom, a nitro group, a cyano group, aryl group, an alkoxy group, an aryloxy group, a carboxy group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxy carbonyl group, an aryloxy carbonyl group, an acyloxy group, a sulfamoyl group, a carbamoyl group, an acylamino group, a diacylamino group, a ureido group, an arylamino group, an N-alkylanilino group, an N-acylanilino group, a hydroxy group, and a mercapto group.

9. A color photographic light sensitive material as in claim 5, wherein X represents hydrogen, a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, an imido group, a sulfonamido group or a thiocycano group.

10. A color photographic light sensitive material as in claim 5, wherein R⁴ is an alkyl group selected from a methyl group, an ethyl group, a butyl group, a pentadecyl group, a phenylthiomethyl group, and a chloromethyl group, or an alkylacylamino group selected from a butylamino group, a pivaloylamino group and a 2-(2',4'-di-tert-amylphenoxy)butanamido group or the arylacylamino group of R⁴ represents a benzoylamino group.

11. A color photographic light sensitive material as in claim 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10, wherein the cyan dye forming coupler represented by formula (I) is present in a red-sensitive layer.

* * * * *

United States Patent [19]

Sakai et al.

[11] 4,454,225

[45] * Jun. 12, 1984

[54] COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

[75] Inventors: Nobuo Sakai; Yoshio Seoka; Kozo Aoki, all of Kanagawa, Japan

[73] Assignee: Fuji Photo Film Co., Ltd., Kanagawa, Japan

[*] Notice: The portion of the term of this patent subsequent to Jun. 8, 1999 has been disclaimed.

[21] Appl. No.: 384,119

[22] Filed: Jun. 1, 1982

[30] Foreign Application Priority Data

Jun. 1, 1981 [JP] Japan 56-84163

[51] Int. Cl.³ G03C 1/46

[52] U.S. Cl. 430/505; 430/552;
430/553; 430/554; 430/555; 430/558

[58] Field of Search 430/505, 551, 552, 553,
430/554, 555, 558

[56] References Cited

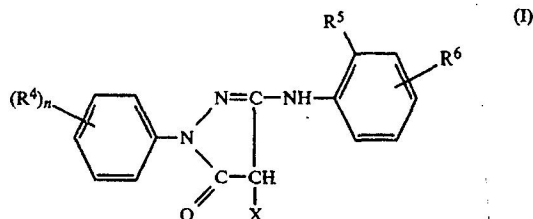
U.S. PATENT DOCUMENTS

3,127,269 3/1964 Greenhalgh et al. 430/386
3,703,375 11/1972 Groet et al. 430/505
4,334,011 6/1982 Aoki et al. 430/553

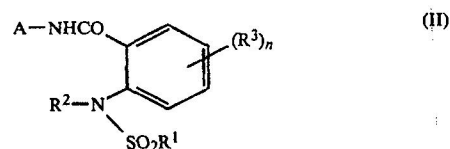
Primary Examiner—J. Travis Brown
Attorney, Agent, or Firm—Sughrue, Mion, Zinn,
Macpeak, and Seas

[57] ABSTRACT

A color photographic light-sensitive material comprising a support having thereon a green-sensitive silver halide emulsion layer containing a magenta dye forming coupler represented by the following general formula (I)



wherein R⁴ represents a halogen atom, a substituted or unsubstituted alkyl group or a substituted or unsubstituted alkoxy group; R⁵ represents a hydrogen atom, a halogen atom, a nitro group, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted acylamino group; R⁶ represents a hydrogen atom, a halogen atom or a mono-valent organic residue; X represents a hydrogen atom or a group capable of being released upon coupling and exhibiting a two-equivalent property; and n represents an integer from 1 to 5 and when n represents 2 or more, R⁴ may be the same or different, and a red-sensitive silver halide emulsion layer containing a cyan dye forming coupler represented by the following general formula (II)



wherein A represents a cyan coupler residue, but the -NHCO group does not bond to A in the active position of A; R¹ represents a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, R² represents hydrogen or a substituted or unsubstituted alkyl group; each R³ independently represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; and n represents an integer from 1 to 3 and when n represents 2 or more. The color photographic light-sensitive material provides a color image in which the yellow stain at the unexposed area upon irradiation of light is prevented.

19 Claims, No Drawings

DZ

COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a color photographic light-sensitive material containing a coupler, and more particularly to a color photographic light-sensitive material capable of providing a color image in which yellow discoloration at the unexposed areas due to irradiation of light is prevented.

BACKGROUND OF THE INVENTION

By the color development of a color photographic light-sensitive material, after exposure, an oxidized aromatic primary amine developing agent is reacted with a coupler to form a dye, thus, a color image is formed. In this system, a subtractive method is generally used for color reproduction. In accordance with such a system blue, green and red colors are reproduced by forming yellow, magenta and cyan color images which are in complimentary relation thereto, respectively. In general, acylacetamide or dibenzoylmethane type couplers are employed for forming yellow or color images, pyrazolone, cyanoacetyl or indazolone type couplers are used for forming magenta color images, and phenol type couplers, for example, phenols and naphthols, are utilized for forming cyan color images.

To produce color photographs, couplers which form dyes are incorporated into a developer or are present in light-sensitive photographic emulsion layer(s). A variety of 5-pyrazolone type couplers for forming magenta color images are known. Known substituents at the 3-position of the 5-pyrazolone ring include an alkyl group, an aryl group, the alkoxy groups as described in U.S. Pat. No. 2,439,098, the acylamino groups as described in U.S. Pat. Nos. 2,369,489 and 2,600,788, and the ureido groups as described in U.S. Pat. No. 3,558,319 and an anilino group. 3-Anilino-5-pyrazolone type couplers have often been described in the art since U.S. Pat. No. 2,311,081 (U.S. Pat. No. Re. 22,329) was issued and several improvements have been proposed. British Pat. No. 956,261 discloses that azomethine dyes obtained from derivatives in which the ortho position of the anilino group is substituted with an alkoxy group or a halogen atom have advantageous spectral absorption for color photography in that undesired absorption in the red light region is particularly low.

Specific examples of diffusion resistant couplers which belong to this type and are capable of being incorporated into photographic emulsions are described in U.S. Pat. Nos. 3,930,861, 3,907,571, 3,928,044 and 3,935,015, etc.

These couplers have the characteristics that the undesired absorption of magenta azomethine dyes obtained upon color formation using the same in the red light region is low, the cut off the main absorption is good at the longer wavelength side, and magenta color images having a high color density are obtained because the coloration speed is high. Furthermore, their solubility in organic solvents having a high boiling point is improved so that, after dissolving these couplers in organic solvents, the couplers are emulsion dispersed in an aqueous medium in the form of colloidal particles and then added to emulsions. However, these couplers have the disadvantages that the degree of yellow staining at the unexposed portion after color development processing is high and this degree of yellow staining is increased

upon irradiation with light. These disadvantages are particularly serious for color light-sensitive material such as color printing papers, etc. which are irradiated with actinic rays for a long period of time.

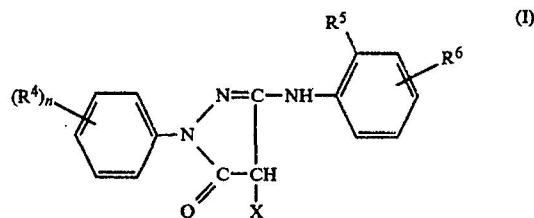
In order to eliminate these disadvantages, it has been proposed that the structure of the coupler per se is appropriately selected thereby improving the light fastness. On the other hand, many methods for improving the light fastness using various additives have also been proposed. For example, methods in which a compound such as an ultraviolet radiation absorbing agent, a hydroquinone derivative, a phenol derivative, or tocopherol, etc. is employed are known. Further, a compound in which the hydroxy group in the above described hydroquinone derivative, phenol derivative or chroman derivative such as tocopherol is substituted with an alkoxy group, an acyloxy group, etc. is recently proposed for the purpose. However, these methods using such additives have a limit. For example, a relatively large amount of the compound must be added to obtain sufficient light fastness which is frequently accompanied with various disadvantages, for examples, coloration, change in color hue, formation of fog, etc. due to the compound added.

SUMMARY OF THE INVENTION

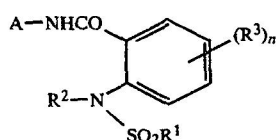
An object of the present invention is to provide a color photographic light-sensitive material capable of forming a color image in which yellow discoloration at the unexposed areas due to irradiation of light is prevented.

Other objects of the present invention will become more apparent from the detailed description of the invention and the examples hereinbelow.

After various investigation, it has been found that the above described objects of the present invention can be achieved by comprising a support having thereon a green-sensitive silver halide emulsion layer containing a magenta dye forming coupler represented by the following general formula (I)



wherein R^4 represents a halogen atom, a substituted or unsubstituted alkyl group or a substituted or unsubstituted alkoxy group; R^5 represents a hydrogen atom, a halogen atom, a nitro group, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group or a substituted or unsubstituted acylamino group; R^6 represents a hydrogen atom, a halogen atom or a mono-valent organic residue; X represents a hydrogen atom or a group capable of being released upon coupling and exhibiting a two-equivalent property; and n represents an integer from 1 to 5 and when n represents 2 or more, R^4 may be the same or different, and a red-sensitive silver halide emulsion layer containing a cyan dye forming coupler represented by the following general formula (II)

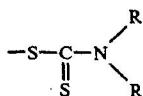


(II)

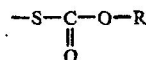
wherein A represents a cyan coupler residue, but the —NHCO group does not bond to A in the active position of A; R¹ represents a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group, R² represents hydrogen or a substituted or unsubstituted alkyl group; R³ represents a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group; and n represents an integer from 1 to 3 and when n represents 2 or more, R³ may be the same or different.

DETAILED DESCRIPTION OF THE INVENTION

In the above described general formula (I), R⁴ represents a hydrogen atom, a halogen atom (for example, a fluorine atom, a chlorine atom, a bromine atom, etc.), an alkyl group having 1 to 22 carbon atoms which may be substituted or an alkoxy group having 1 to 22, preferably 1 to 15, carbon atoms which may be substituted. n represents an integer from 1 to 5 and when n represents 2 or more, R⁴ may be the same or different. Preferably, R⁴ represents a halogen atom or an alkoxy group having 1 to 15 carbon atoms. R⁵ represents a hydrogen atom, a halogen atom, a nitro group, an alkyl group having 1 to 22 carbon atoms which may be substituted, an alkoxy group having 1 to 22 carbon atoms which may be substituted or an acylamino group which may be substituted. R⁶ represents a hydrogen atom, a halogen atom or a mono-valent organic residue, for example, a nitro group, a carbamoyl group having up to 22 carbon atoms which may be substituted, a sulfamoyl group having up to 22 carbon atoms which may be substituted, an alkyl succinimido group having up to 22 carbon atoms which may be substituted, an alkoxy-carboamido group having up to 22 carbon atoms which may be substituted, an alkoxy-carboalkylamino group having up to 22 carbon atoms which may be substituted, an alkylaminocarboalkylamino group having up to 22 carbon atoms which may be substituted, an aralkoxy-carboalkylamino group having up to 22 carbon atoms which may be substituted, an arylaminocarboalkylamino group having up to 22 carbon atoms which may be substituted or an aralkylaminocarboalkylamino group, etc. X represents a hydrogen atom or a group capable of being released upon coupling and exhibiting a two-equivalent property, for example, an alkylthio group which may be substituted, an arylthio group which may be substituted, an aralkylthio group which may be substituted, a group of the formula



wherein R represents a hydrogen atom, an alkyl group or an aryl group, a pyrazolyl group which may be substituted, an imidazolyl group which may be substituted, a triazolyl group which may be substituted, or a group of the formula



wherein R represents a hydrogen atom, an alkyl group or an aryl group, etc.

In the general formula (I), R⁴ is preferably a halogen atom, R⁵ is preferably a halogen atom and X is preferably an alkylthio group, an arylthio group or an aralkylthio group.

In the above described general formula (II), A represents a cyan coupler residue, but the —NHCO group does not bond to A in the active coupling position of A, R¹ represents a substituted or unsubstituted alkyl group having from 1 to 22 carbon atoms or a substituted or unsubstituted aryl group having 6 to 22 carbon atoms, with an alkyl group being preferred, R² represents hydrogen or a substituted or unsubstituted alkyl group having from 1 to 22 carbon atoms, with a hydrogen atom and an unsubstituted alkyl group being preferred, R³ represents a hydrogen atom, a halogen atom (for example, a fluorine atom, a chlorine atom, a bromine atom, etc.), an alkyl group having from 1 to 22 carbon atoms (for example, a methyl group, a butyl group, a pentadecyl group, etc.) or an alkoxy group having from 1 to 22 carbon atoms (for example, a methoxy group, an ethoxy group, a 2-ethyl hexyloxy group, etc.), n represents an integer from 1 to 3 and when n represents 2 or more, R³ may be the same or different.

The substituents of the alkyl groups and aryl groups represented by R¹ and R² are selected from a halogen atom, a nitro group, a cyano group, an aryl group (for example, a phenyl group, a naphthyl group, etc.), an alkoxy group (for example, a methoxy group, an ethoxy group, etc.), an aryloxy group (for example, a phenyloxy group, a naphthyloxy group, etc.), a carboxy group, an alkylcarbonyl group (for example, an acetyl group, a tetradecanoyl group, etc.), an arylcarbonyl group (for example, a benzoyl group, etc.), an alkoxy-carbonyl group (for example, a methoxycarbonyl group, a benzyloxycarbonyl group, etc.), an aryloxy-carbonyl group (for example, a phenyloxycarbonyl group, a p-tolyloxycarbonyl group, etc.), an acyloxy group (for example, an acetyloxy group, a tetradecanoyloxy group, etc.), a sulfamoyl group (for example, an N-ethylsulfamoyl group, an N-octadecylsulfamoyl group, etc.), a carbamoyl group (for example, an N-ethylcarbamoyl group, an N-methyl-N-dodecylcarbamoyl group, etc.), an acylamino group (for example, an acetilamino group, a benzamido group, etc.), a diacylamino group (for example, a succinimido group, a hydantoinyl group, etc.), a ureido group (for example, a methyl ureido group, a phenylureido group, etc.), an arylamino group (for example, a (4-methoxyphenyl)amino group, etc.), an N-alkylanilino group (for example, an N-methylanilino group, an N-butylanilino group, etc.), an N-acylanilino group (for example, an N-acetylanilino group, an N-trichloroacetylanilino group, etc.), a hydroxy group, and a mercapto group, etc. When an alkyl group is substituted with a fluorine atom, the group may be the so-called polyfluoroalkyl group.

Examples of R¹ include a methyl group, a butyl group, a methoxyethyl group, a dodecyl group, a phenoxypropyl group, a p-chlorophenoxybutyl group, a p-tolyl group, a p-dodecylphenyl group, a p-chlorophenyl group, and a naphthyl group. Examples of R² in-

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

RADICACIÓN: 0-47404

EDICTO No. 11611

LA SECRETARÍA GENERAL AD-HOC
HACE SABER:

Que esta Superintendencia profirió **Resolución No. 21523 de 30-AGO-2005**. Que el contenido de la parte resolutive es como sigue: El Superintendente de Industria y Comercio.

RESUELVE

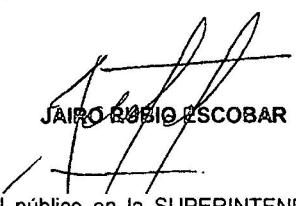
ARTICULO PRIMERO: Negar el privilegio de patente de invención para la solicitud correspondiente a "COMPUESTOS SULFONAMIDOBENZANILIDA UTILES COMO ANTAGONISTAS DE RECEPTORES BASUREROS DE MACROFAGOS".

ARTICULO SEGUNDO: Notificar personalmente el contenido de la presente resolución al doctor Germán Castillo Grau, o a quien haga sus veces, en su calidad de apoderado de Smithkline Beecham Corporation., entregándole copia de la misma, advirtiéndole que contra ella procede el recurso de reposición interpuesto ante el Superintendente de Industria y Comercio, al momento de la notificación o dentro de los 5 días hábiles siguientes a ella.

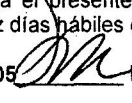
NOTIFÍQUESE Y CUMPLASE

Dada en Bogotá, D.C., a los 30 AGO. 2005

EL SUPERINTENDENTE DE INDUSTRIA Y COMERCIO,


JAIRO RUBIO ESCOBAR

Para notificar a los interesados, se fija el presente EDICTO en lugar visible al público en la SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO, por el término de (10) diez días hábiles contados a partir de las 8:30 a.m. de hoy.

Secretaría General Ad-Hoc 13-SEP-2005 

Secretaría General Ad-Hoc

EDICTO No. 11611

Este edicto se desfija hoy 26-SEP-2005 a las cinco (5:00 p.m.) 