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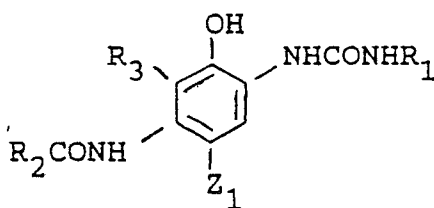
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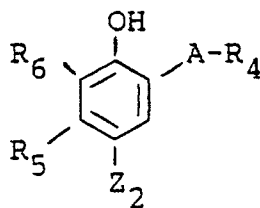
(54) Silver halide color photographic materials.

(57) Silver halide color photographic material comprising a support having coated thereon one or more silver halide emulsion layers, wherein at least one of said layers comprises in combination at least one of the cyan couplers having the following Formula (I) and at least one of the cyan couplers having the following Formula (II):



Formula (I)

wherein R₁ is an aryl group, R₂ is an alkyl group or an aryl group, R₃ is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group, and Z₁ is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent,



Formula (II)

wherein A is a -NHCO- group or a -CONH- group, R₄ is an alkyl group, R₅ is an alkyl group, R₆ is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group or R₅ and R₆ can combine to form a benzene ring, and Z₂ is a hydrogen atom, a halogen atom or a group which can be split off by the reaction

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of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.

Such combination of cyan couplers, when associated with the silver halide color photographic materials, gives high sensitivity and, upon coupling with the oxidized aromatic primary amine-type color developing agents, cyan indoaniline dyes very stable to light, heat, humidity and to bleaching solutions which have a weak oxidation power or are exhausted.

Silver Halide Color Photographic Materials

FIELD OF THE INVENTION

5 The present invention relates to silver halide color photographic materials and, more particularly, to silver halide color photographic materials which contain a specific combination of cyan couplers.

BACKGROUND OF THE ART

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It is known that the development of the light-sensitive silver halides of photographic materials can produce color photographic images. A silver image is produced by means of an aromatic primary amino-type developer compound in the presence of color couplers which react with the oxidized developing
15 substance to form a dye in the areas corresponding to the silver image.

In the subtractive three-color photographic process, light sensitive color photographic materials are used which include, coated on a support, one or more red-sensitive silver halide emulsion layers, one or more green-sensitive silver halide emulsion layers, and one or more blue-sensitive silver halide emulsion layers, each layer comprising color couplers, wherein upon color development cyan, magenta and yellow
20 dye images are respectively formed.

The couplers used to produce cyan image dyes generally derive from phenols and naphthols (as described, for example, in US patents 2,367,351, 2,423,730, 2,474,293, 2,772,161, 2,772,162, 2,895,826, 2,920,961, 3,002,836, 3,466,622, 3,476,563, 3,880,661, 3,996,253, 3,758,308, in FR patents 1,478,188 and 1,479,043, and in GB patent 2,070,000). These types of couplers can be used either in photographic layers
25 or in the processing baths. In the former case, when it is desired that they do not migrate from a layer into another, they can have ballasting substituents. They can bear also hydrophilic or hydrophobic substituents if they must be introduced into photographic layers, respectively, dissolved in water or in an organic solvent. Upon reaction with the oxidation products of the aromatic primary amino-type developing agents, such couplers give indoaniline dyes with consumption of four equivalents of silver ions per mole of dye and, preferably, two equivalents of silver ions per mole of dye when the reactive methine group (in the para
30 position to the phenolic hydroxylic group) is substituted with atoms or groups which are split off during the coupling reaction.

Heretofore, naphthol cyan couplers have been used in the red sensitive layers of silver halide photographic materials because they give a cyan dye, formed by the reaction with an oxidized product of a
35 color developing agent, having absorptions at longer wavelength region respect to dyes given by phenol type couplers, that being preferred in connection with color reproduction.

On the other hand, in recent years, color photographic materials tend to be shifted towards materials of high sensitivity and high image quality. Using naphthol cyan couplers, image quality is deteriorated due to color fading of the cyan dye by reduced ferrous ions produced in large amount in the step of bleaching
40 processing.

Recently, couplers having absorption spectra similar to naphthol couplers, which can improve color fading of dyes during bleaching processing, have been disclosed in US patents 4,333,999, 4,451,559, 4,465,766 and 4,554,244. Also, combinations of cyan couplers for use in silver halide color photographic materials are described or suggested in EP patents 112,514, 159,914, 159,912, 231,832, 254,151, 254,318,
45 255,292 and 256,537 and in GB patent 2,171,215.

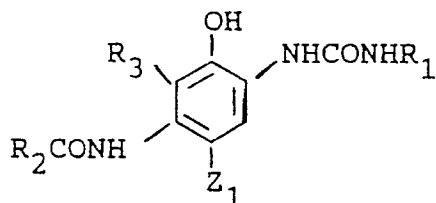
However, none of the these techniques known in the art can give silver halide color photographic materials which can satisfy both characteristics of sensitivity and image quality at the same time, nor do the above patents specifically describe in their examples the combination of cyan couplers of this invention.

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SUMMARY OF THE INVENTION

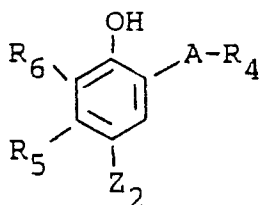
According to the present invention, there is provided a specific combination of cyan couplers for use in color photography, said combination comprising cyan couplers having the following Formula (I) and cyan

couplers having the following Formula (II):



Formula (I)

wherein R_1 is an aryl group, R_2 is an alkyl group or an aryl group, R_3 is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group, and Z_1 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent,



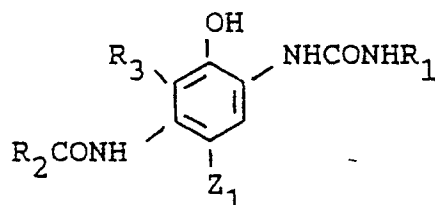
Formula (II)

wherein A is a -NHCO- group or a -CONH- group, R_4 is an alkyl group, R_5 is an alkyl group, R_6 is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group or R_5 and R_6 can combine to form a benzene ring, and Z_2 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.

Such a combination of cyan couplers, when associated with silver halide color photographic materials, gives high sensitivity and, upon coupling with the oxidized aromatic primary amine-type color developing agents, cyan indoaniline dyes very stable to light, heat and humidity. They are also stable to bleaching solutions which have a weak oxidation power or are exhausted.

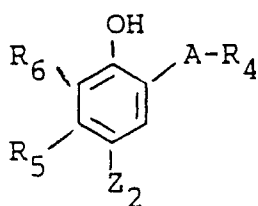
DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a silver halide color photographic material comprising a support having coated thereon one or more silver halide emulsion layers, wherein at least one of said layers comprises in combination at least one of the cyan couplers having the following Formula (I) and at least one of the cyan couplers having the following Formula (II):



Formula (I)

wherein R_1 is an aryl group, R_2 is an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.) or an aryl group of up to 20 carbon atoms, R_3 is a hydrogen atom, a halogen atom (such as fluorine, bromine, chlorine, etc.), an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.) or an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.), and Z_1 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent,



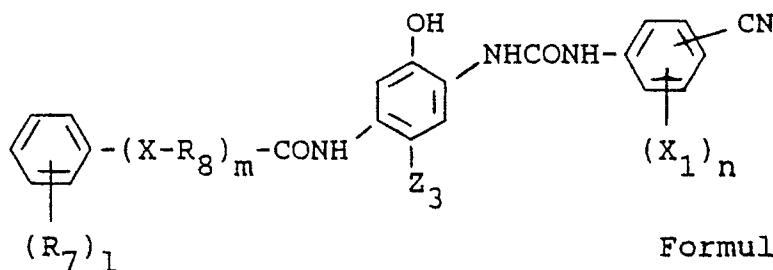
Formula (II)

wherein A is a -NHCO- group or a -CONH- group, R₄ is an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.), R₅ is an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.), R₆ is a hydrogen atom, a halogen atom, an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.) or an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.) or R₅ and R₆ can combine to form a benzene ring, and Z₂ is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.

The aryl group represented by R₁ of Formula (I) is, e.g., a phenyl group, a naphthyl group, or other aryl group of up to 30 carbon atoms, and preferably is a phenyl group. This group is allowed to have a single substituent or a plurality of substituents; for example, typical substituents introducible to the aryl group include halogen atoms (such as fluorine, chlorine, bromine, etc.), alkyl groups (such as methyl, ethyl, propyl, butyl, dodecyl, etc.), hydroxyl group, cyano group, nitro group, alkoxy groups (such as methoxy, ethoxy, etc.), alkylsulfonamido groups (such as methylsulfonamido, octylsulfonamido, etc.), arylsulfonamido groups (such as phenylsulfonamido, naphthylsulfonamido, etc.), alkylsulfamoyl groups (such as butylsulfamoyl), arylsulfamoyl (such as phenylsulfamoyl), alkyloxycarbonyl groups (such as methyloxycarbonyl), aryloxycarbonyl groups (such as phenyloxycarbonyl), aminosulfonamido groups, acylamino groups, carbamoyl groups, sulfonyl groups, sulfinyl groups, sulfoxy groups, sulfo groups, aryloxy groups, alkoxy groups, alkylcarbonyl groups, arylcarbonyl groups, aminocarbonyl groups, and the like. Two different members of these groups are allowed to be introduced to the aryl group. The preferred group represented by R₁ is a phenyl group, the more preferred is a phenyl group having one or more substituents including halogen atoms and cyano groups.

When the term "group" is used in the present invention to describe a chemical compound or substituent, the described chemical material includes the basic group and that group with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent, only an unsubstituted chemical material is intended to be included. For example, "alkyl group" includes not only alkyl moieties as methyl, ethyl, octyl, dodecyl, etc., but also such moieties bearing substituent groups such as halogen, cyano, hydroxyl, nitro, amine, carboxylate, etc. On the other hand, "alkyl moiety" includes only methyl, ethyl, octyl, dodecyl, etc.

In the present invention, the preferred cyan couplers having Formula (I) are the compounds having the following Formula (III):



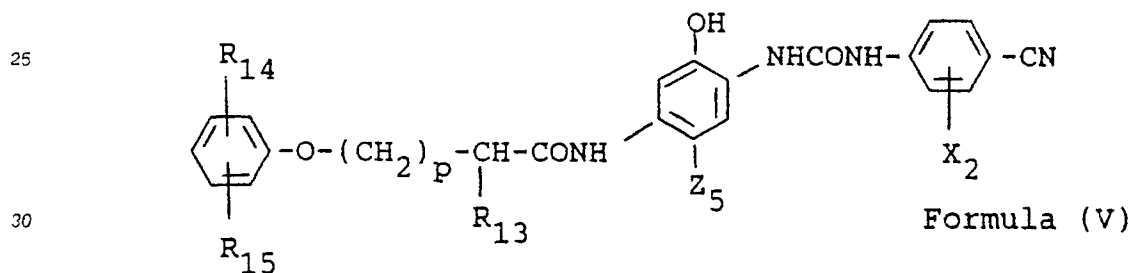
Formula (III)

wherein X₁ is a hydrogen atom, a halogen atom or a monovalent organic group, R₇ is a hydrogen atom or a substituent exemplified by a halogen atom (such as fluorine, bromine, chlorine, etc.), a hydroxyl group, a nitro group, an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, iso-propyl, tert.-butyl, n-octyl, n-dodecyl, etc.), an alkyloxycarbonyl group (such as methyloxycarbonyl), an aryloxycarbonyl group (such as phenyloxycarbonyl), an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.), an aryloxy group (such as phenoxy), an alkylcarbonyl group (such as methylcarbonyl, propylcarbonyl, octylcarbonyl, etc.), an arylcarbonyl (such as phenylcarbonyl), an acyloxy group (such as acetoxy, benzoyloxy, etc.), an

alkylsulfonyl group (such as methylsulfonyl, octylsulfonyl, etc.), an arylsulfonyl group (such as phenylsulfonyl), an acyl group (such as acetyl), an acylamino group, a sulfonamido group (such as methylsulfonamido, octylsulfonamido, phenylsulfonamido, etc.), a sulfamoyl group (such as butylsulfamoyl, phenylsulfamoyl, etc.), and the like, X is an oxygen atom or a sulfur atom, R_8 is a straight-chain or a branched-chain alkylene group, n is an integer of 0 to 3, m is an integer of 0 to 4 and 1 is an integer of 1 to 4, and Z_3 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.

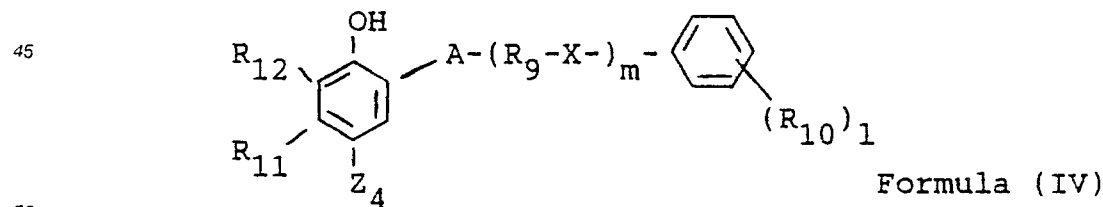
Examples of monovalent organic group represented by X_1 include a halogen atom (such as fluorine, chlorine, bromine, etc.), a nitro group, an amino group, a cyano group, a hydroxy group, a carboxy group, an alkyl group (such as methyl, ethyl, propyl, isopropyl, t-butyl, octyl, etc.), an aralkyl group (such as benzyl, phenethyl, etc.), an alkoxy group (such as methoxy, ethoxy, benzyloxy, etc.), an aryloxy group (such as phenoxy, p-nitrophenoxy, etc.), an acylamino group (such as acetylamino, propionylamino, benzoylamino, phenoxyacetylamino, etc.), a carbamoyl group (such as methylcarbamoyl, dimethylcarbamoyl, phenylcarbamoyl, diphenylcarbamoyl, etc.), a sulfonamido group (such as methanesulfonamido, butanesulfonamido, benzenesulfonamido, p-toluenesulfonamido, etc.), a sulfamoyl group (such as methylsulfamoyl, dimethylsulfamoyl, phenylsulfamoyl, etc.), an alkylcarbonyl group (such as methylcarbonyl, propylcarbonyl, octylcarbonyl, etc.), an arylcarbonyl group (such as phenylcarbonyl), an alkoxycarbonyl group (such as methyloxycarbonyl, ethyloxycarbonyl, butyloxycarbonyl, t-butyloxycarbonyl, etc.), an aryloxycarbonyl group (such as phenyloxycarbonyl), and the like.

In the present invention, the more preferred cyan couplers having Formula (I) are the compounds having the following formula (V):



wherein X_2 is a hydrogen atom or a halogen atom (such as fluorine, chlorine, bromine, etc.), R_{13} is a hydrogen atom or an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, propyl, butyl, octyl, dodecyl, etc.), R_{14} and R_{15} may be either the same or different and each is a hydrogen atom, an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, butyl, dodecyl, etc.) or an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.), provided that the sum of carbon atoms of R_{13} , R_{14} and R_{15} is from 8 to 20, p is an integer of 0 to 2, and Z_5 is a hydrogen atom or a chlorine atom.

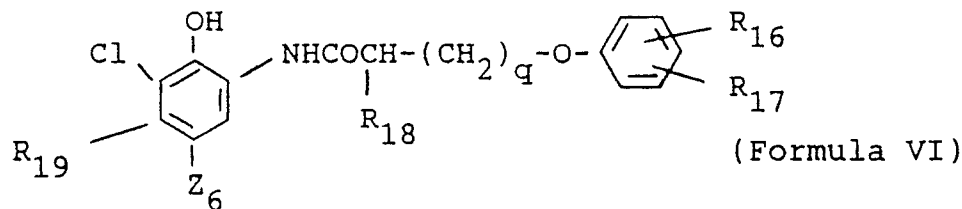
In the present invention, the preferred cyan couplers having Formula (II) are the compounds having the following Formula (IV):



wherein A is a $-NHCO-$ group or a $-CONH-$ group, R_9 is a branched-chain or a straight chain alkylene group, R_{10} is a hydrogen atom or a substituent of the type described for R_7 of Formula (III), X is an oxygen atom or a sulfur atom, R_{11} is an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, propyl, butyl, dodecyl, etc.), R_{12} is a hydrogen atom, a halogen atom (such as fluorine, chlorine, bromine, etc.) or an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, propyl, butyl, dodecyl, etc.) or R_{11} and R_{12} can combine to form a benzene ring, 1 is an integer of 1 to 4, m is an integer of 0 to 1, and Z_4 is a hydrogen atom, a halogen atom (such as fluorine, chlorine, bromine, etc.) or a group which can be split off by the

reaction of said coupler with oxidized product of an aromatic primary amine-type color developing agent.

The more preferred cyan couplers having Formula (II) in the present invention include those compounds having the following Formula (VI):



wherein R_{16} and R_{17} may be either the same or different and each is a hydrogen atom, an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, propyl, butyl, pentyl, dodecyl, etc.) or an alkoxy group of up to 20 carbon atoms (such as methoxy, ethoxy, etc.), R_{18} is a hydrogen atom or an alkyl group of up to 20 carbon atoms (such as methyl, ethyl, propyl, butyl, pentyl, dodecyl, etc.), provided that the sum of carbon atoms of R_{16} , R_{17} and R_{18} is from 8 to 20, R_{19} is an alkyl group of 1 to 2 carbon atoms (such as methyl or ethyl), q is an integer of 0 to 2, and Z_6 is a hydrogen atom or a chlorine atom.

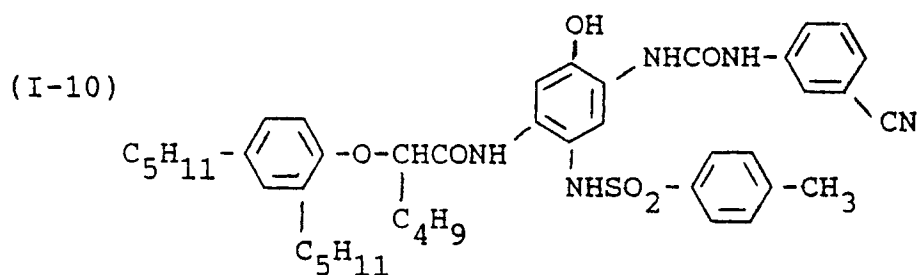
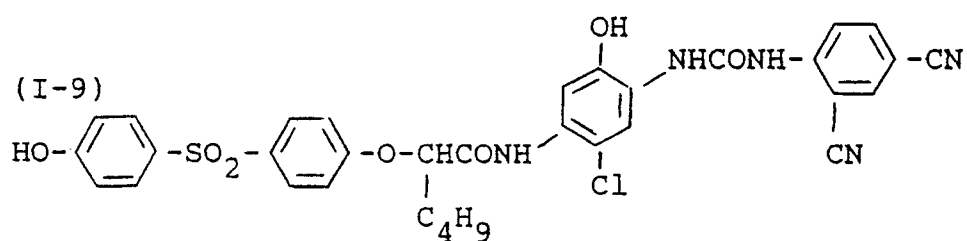
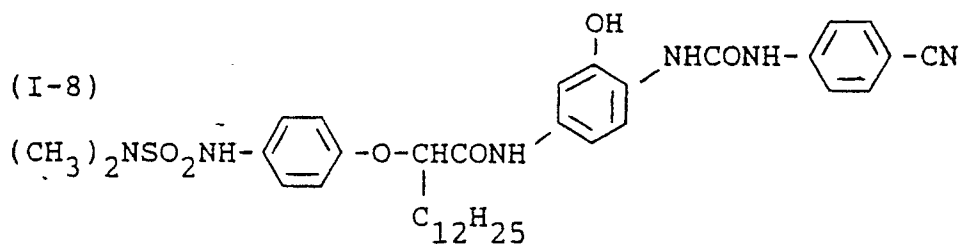
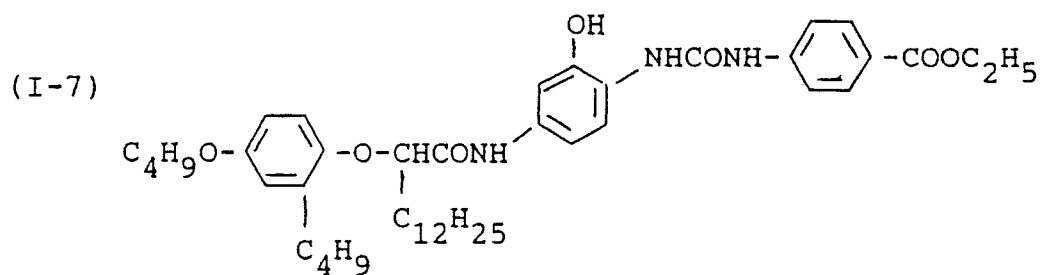
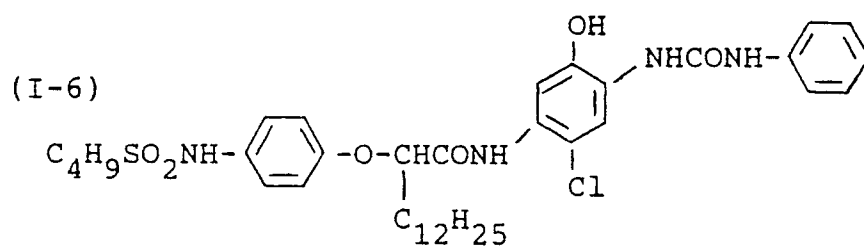
In formulas (I), (II), (III) and (IV), the groups that can be split off by the reaction of these couplers with the oxidized product of the aromatic primary amine-type color developing agents represented by Z_1 , Z_2 , Z_3 and Z_4 are all known to those skilled in the art. Any of these groups changes the reactivity of the coupler or is split from the coupler to fulfill its development-inhibiting, bleach-inhibiting and color-compensation inhibiting functions to thereby advantageously act in the coupler-containing layers or other layers of the silver halide color photographic material. Typical examples of such groups include, for example, alkoxy groups, aryloxy groups, arylazo groups, thiether, carbamoyloxy groups, acyloxy groups, imido groups, sulfonamido groups, thiocyanato group or heterocyclic groups (such as oxazolyl, diazolyl, triazolyl, tetrazolyl, etc.), and the like. The particularly preferred examples represented by Z are a hydrogen atom or a chlorine atom.

The cyan couplers used in combination according to the present invention are incorporated in a silver halide emulsion layer of the color photographic material. The skilled in the art knows that, if the cyan couplers are incorporated into the silver halide emulsion layer, they are, in most instances, required not to diffuse within the layers themselves. A group bearing a ballasting group such as a hydrophobic residue with 8 to 20 carbon atoms is introduced into the coupler molecules in order to avoid said diffusing process. Such substituent is called "ballasting group" and is linked, directly or through one or more of imino, ether, carbonamido, sulfonamido, ureido, ester, imido, carbamoyl, sulfamoyl, phenylene, etc. groups, to the coupler molecule. Such ballasting group is preferably comprised by the group R_2 of Formula (I) and R_4 of Formula (II). Some examples of ballasting groups are illustrated in US patent 4,009,038, in European patents 87,930, 84,100, 87,931, 73,146, 88,563, in German patents 3,300,412, 3,351,012, in Japanese patents J5 8033248, J5 8033250, J58031334, J5 8106539. Preferably, such ballasting groups comprise alkyl chains, the total carbon atoms of which are from 8 to 20.

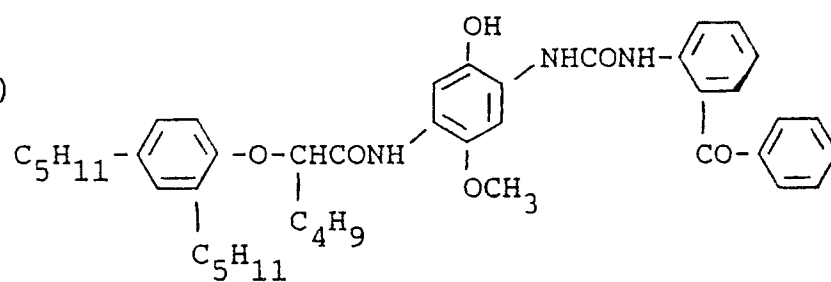
The cyan couplers of Formula (I) and (II) can readily be synthesized by use of methods well known in the art such as described, for example, in US Patents 3,758,308, 4,333,999 and 4,451,559 for couplers of Formula (I) and in US patents 2,369,929 and 3,772,002 for couplers of Formula (II).

Specific examples of cyan couplers represented by the Formulas (I) and (II) are illustrated below, but the present invention is not limited thereby.

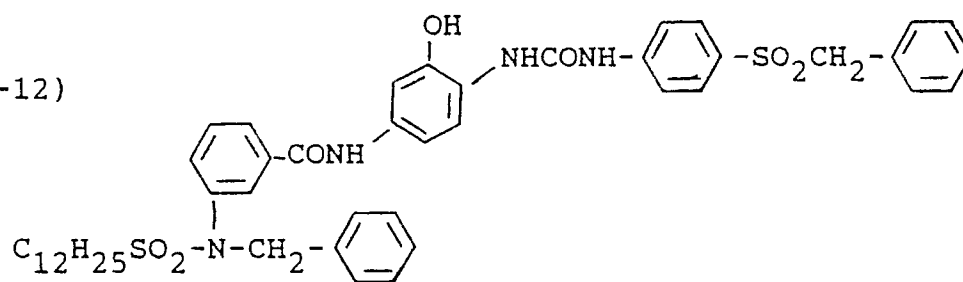




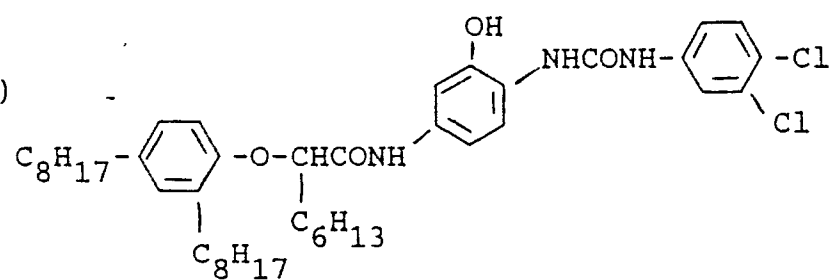
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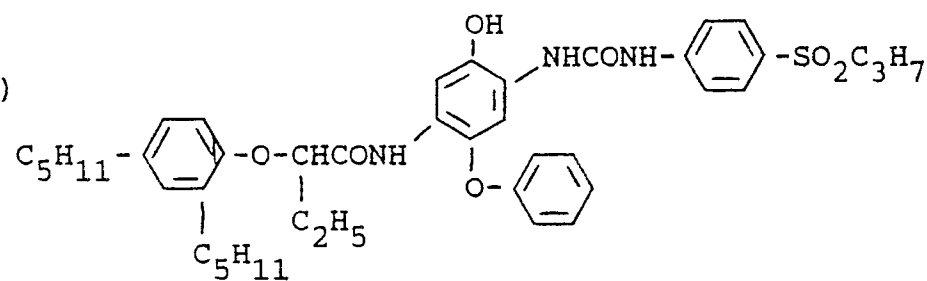
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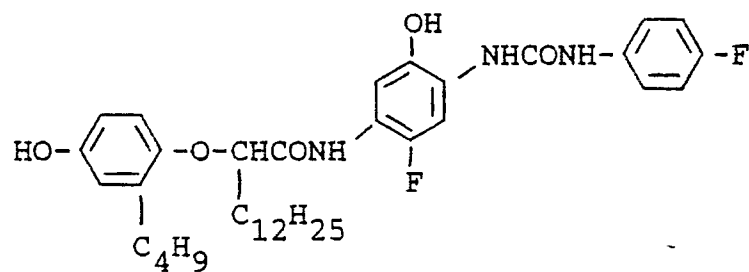
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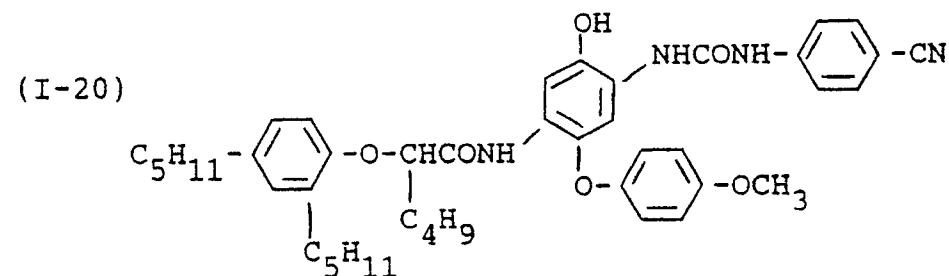
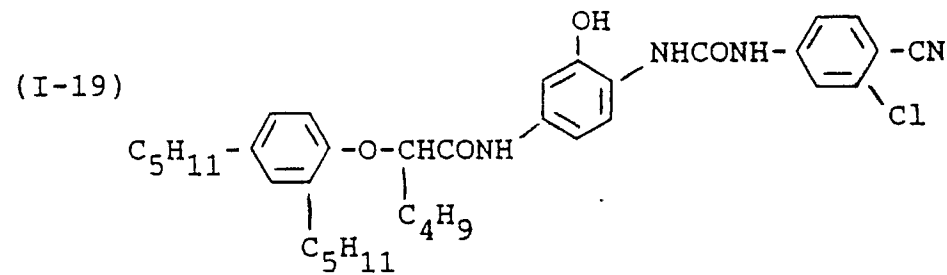
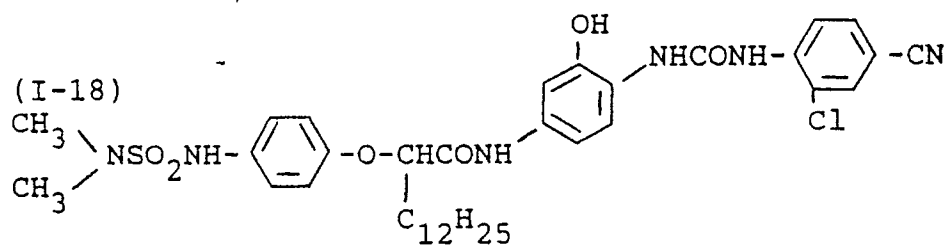
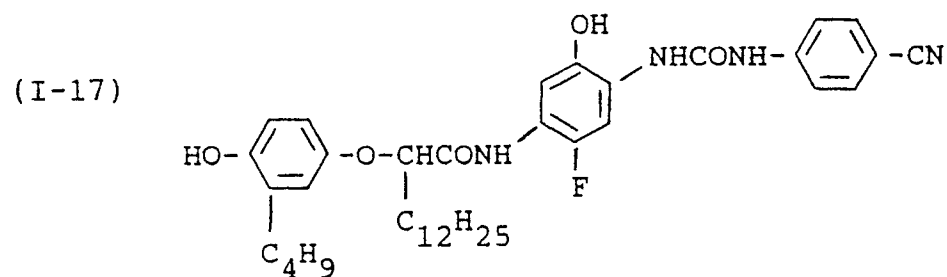
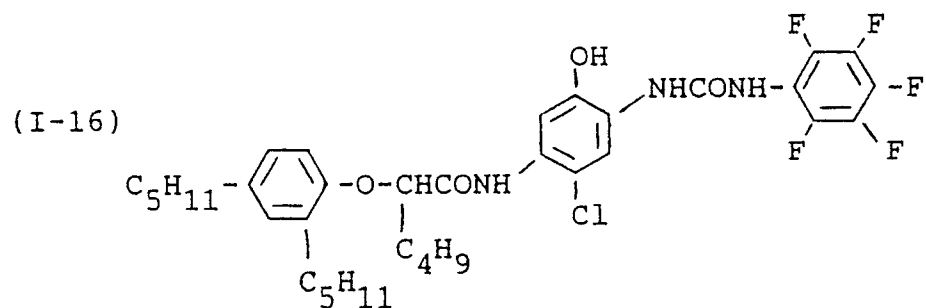


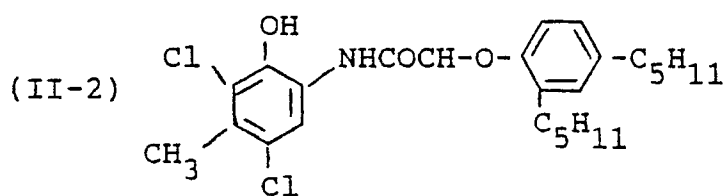
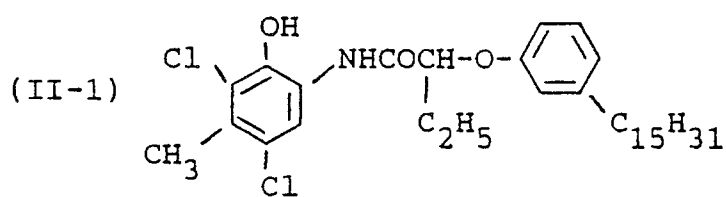
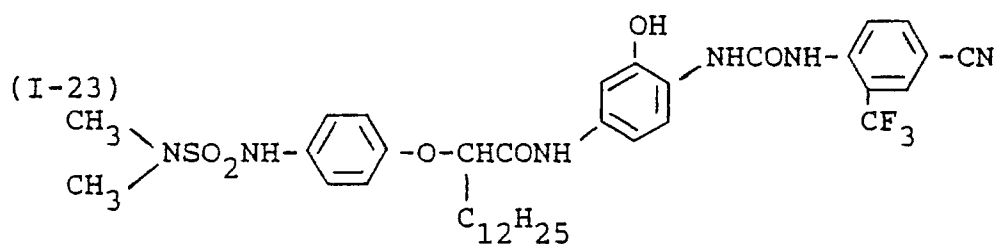
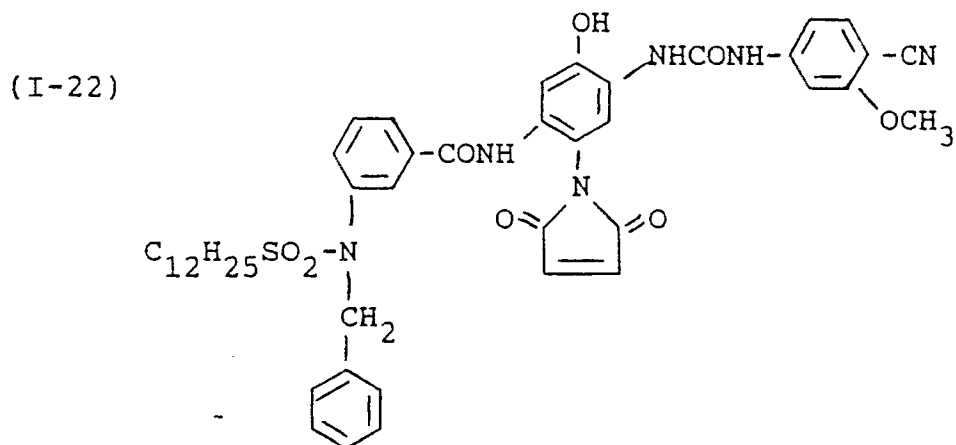
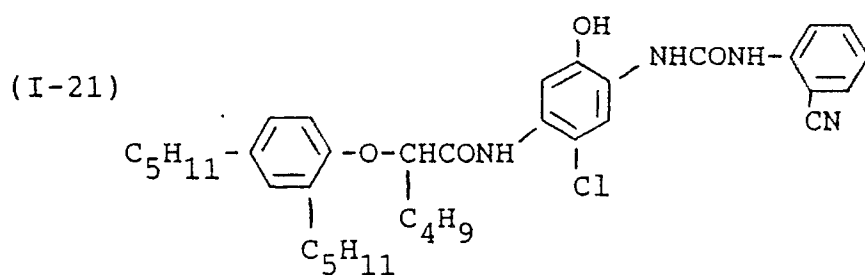
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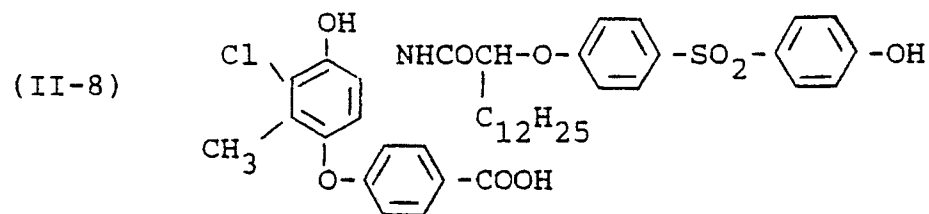
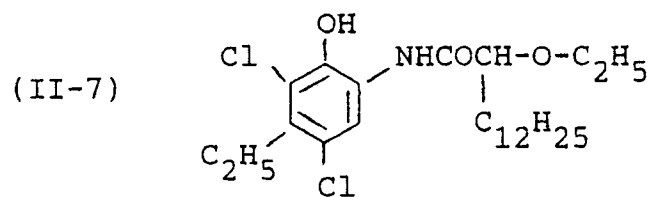
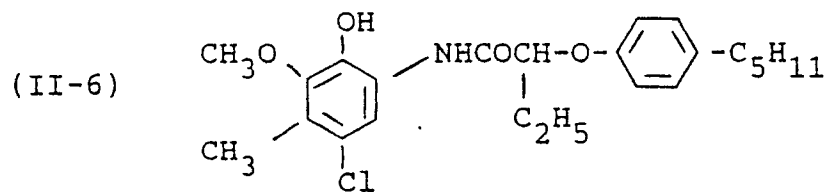
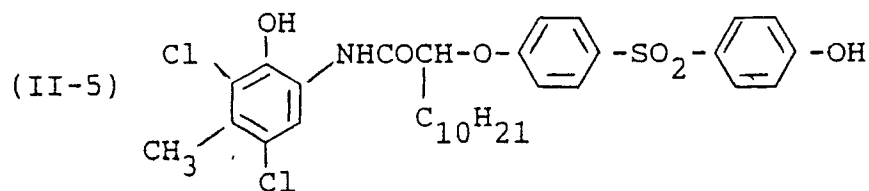
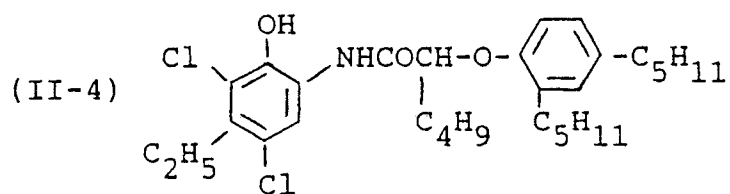
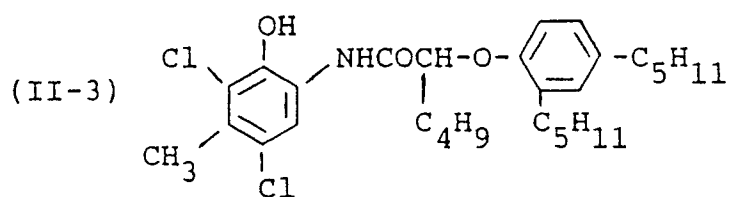


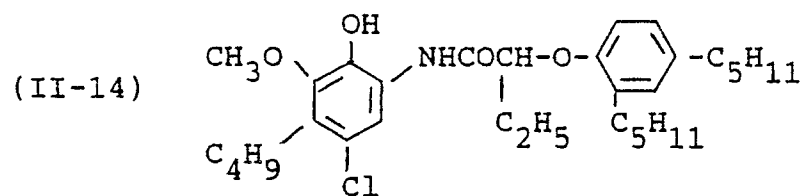
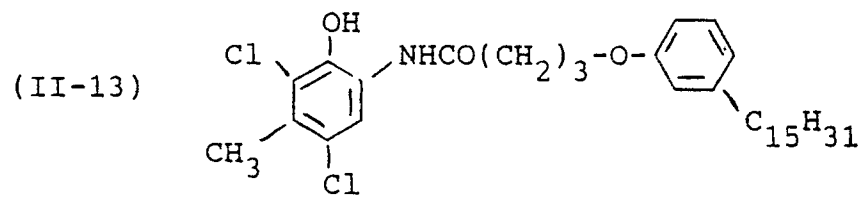
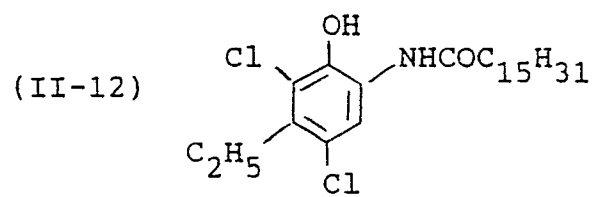
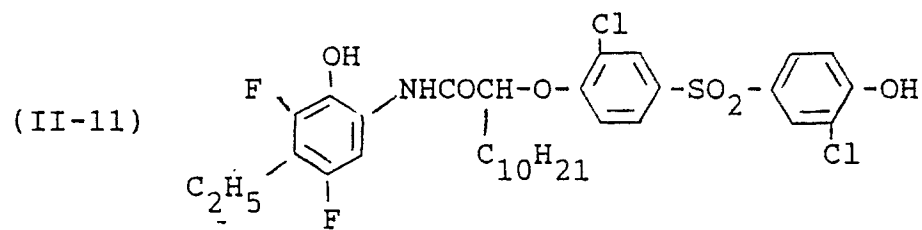
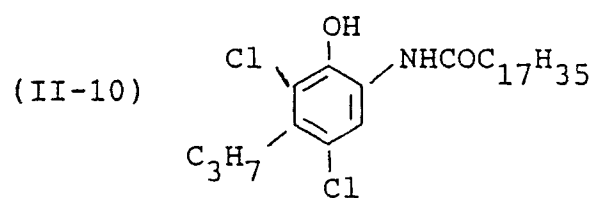
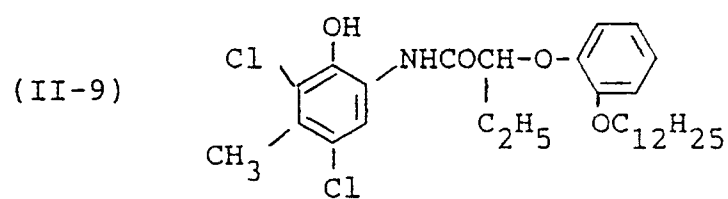
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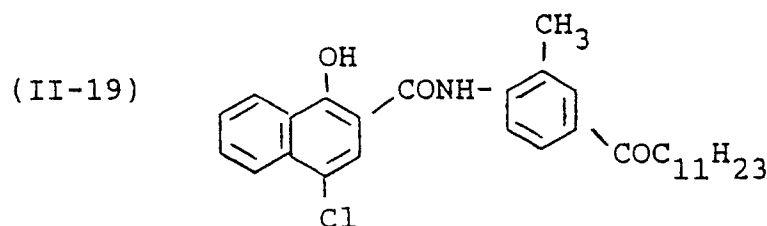
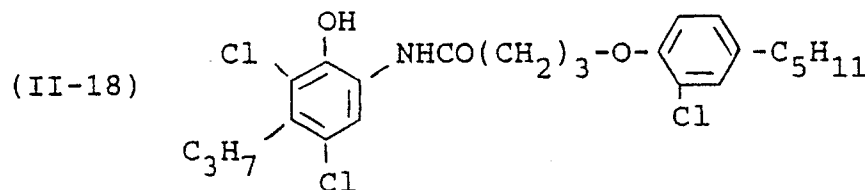
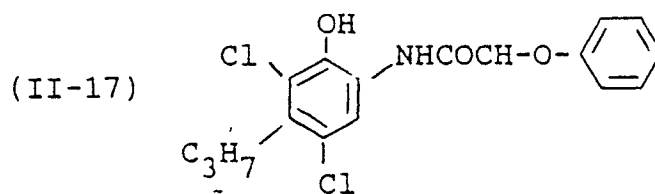
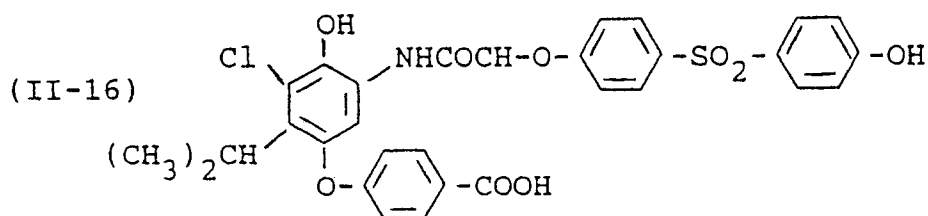
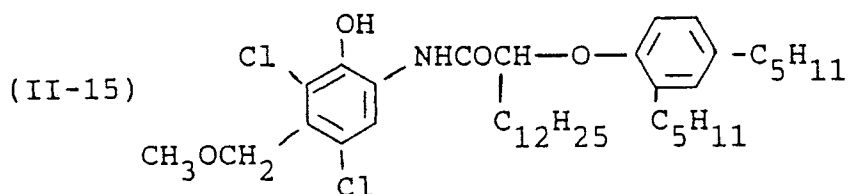












The silver halide color photographic materials of the present invention comprise at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one silver-halide red-sensitive silver halide emulsion layer, said layers being associated with yellow, magenta and cyan dye-forming couplers. As used herein, the word "associated" means that the cyan dye-forming couplers according to the present invention and the silver halide emulsions are positioned in such a way as to image-wise produce in the photographic layers upon coupling with the oxidized aromatic primary amine-type developing agents very stable cyan indoaniline dyes. Such cyan couplers may be incorporated in the silver halide emulsion layers, in an adjacent layer or in the processing solutions. In a preferred form, the cyan couplers are incorporated in the silver halide emulsion layer.

Preferably, the silver halide emulsion layer comprising the combination of cyan couplers of general Formula (I) and (II) described above is a red-sensitive silver halide emulsion layer. The couplers of Formula (I) and (II) can be used in an arbitrary proportion in the combination thereof, but it is desirable that the cyan coupler of Formula (I) is used in an amount of from 10 to 90 mol % based on the total amount of said couplers in the silver halide emulsion layer, and more preferably from 25 to 85 mol %. In the silver halide emulsion layer said cyan couplers of Formula (I) and (II) are present in a total amount of from about

6.5×10^{-3} to about 80×10^{-3} mol per mol of silver halide contained in said silver halide emulsion layer, and preferably from about 13.5×10^{-3} to about 53.5×10^{-3} mol per mol of silver halide.

In order to introduce the couplers of the present invention into the silver halide emulsion layer, some conventional methods known to the skilled in the art can be employed. According to US patents 2,322,027, 2,801,170, 2,801,171 and 2,991,177, the couplers can be incorporated into the silver halide emulsion layer by the dispersion technique, which consists of dissolving the coupler in a water-immiscible high-boiling organic solvent and then dispersing such a solution in a hydrophilic colloidal binder under the form of very small droplets. The preferred colloidal binder is gelatin, even if some other kinds of binders can be used.

Another type of introduction of the couplers into the silver halide emulsion layer consists of the so-called "loaded-latex technique". A detailed description of such technique can be found in BE patents 853,512 and 869,816, in US patents 4,214,047 and 4,199,363 and in EP patent 14,921. It consists of mixing a solution of the couplers in a water-miscible organic solvent with a polymeric latex consisting of water as a continuous phase and of polymeric particles having a mean diameter ranging from 0.02 to 0.2 micrometers as a dispersed phase.

Another useful method is further the Fisher process. According to such a process, couplers having a water-soluble group, such as a carboxyl group, a hydroxy group, a sulfonic group or a sulfonamido group, can be added to the photographic layer for example by dissolving them in an alkaline water solution.

The cyan couplers of the combination of the present invention are generally incorporated into a red-sensitive silver halide emulsion layer to form one of the differently sensitized silver halide emulsion layers of a multilayer color photographic material. Such material generally comprises a support base having coated thereon one or more red-sensitive silver halide emulsion layers, one or more green-sensitive silver halide emulsion layers, one or more blue-sensitive silver halide emulsion layers and additionally filter layers, interlayers, protective layers and sub-layers. The layer units can be coated in any conventional order, but in a preferred layer arrangement the red-sensitive layers are coated nearest the support and are overcoated by the green-sensitive layers, a yellow filter layer and the blue-sensitive layers.

More preferably, the red-sensitive silver halide emulsion layer, associated according to this invention with the combination of the cyan couplers of Formulae (I) and (II), is composed of two or more silver halide emulsion layers sensitized to the same spectral region of the visible spectrum, the uppermost silver halide emulsion layer of which having the highest sensitivity and the lowermost silver halide emulsion layer having the lowest sensitivity, as described in GB patent 923,045, in FR patent 2,043,433 and in US patent 4,582,780. Most preferably, the uppermost red-sensitive silver halide emulsion layer having the highest sensitivity comprises the combination of the cyan couplers of Formulae (I) and (II), the other red-sensitive silver halide emulsion layers comprising the cyan couplers of Formula (I).

The sensitive layers are each associated with at least one image dye forming compound. Incorporated dye forming couplers constitute exemplary preferred image-dye providing compounds. The blue, green and red-responsive layers preferably contain yellow, magenta and cyan image-dye providing couplers, respectively.

The most useful yellow-forming couplers are conventional open-chain ketomethylene type couplers. Particular examples of such couplers are benzoylacetanilide type and pivaloyl acetanilide type compounds. Yellow-forming couplers that can be used are specifically described in US patents 2,875,057, 3,265,506, 3,408,194, 3,551,151, 3,682,322, 3,725,072 and 3,891,445, in DE patents 2,219,917, 2,261,361 and 2,414,006, in GB patent 1,425,020, in JP patent 10,783/76 and in JP patent applications 26,133/72, 73,147/73, 102,636/76, 6,341/75, 123,342/75, 130,442/75, 1,827/76, 87,650/75, 82,424/77 and 115,219/77.

The most useful magenta-forming couplers are conventional pyrazolone type compounds, indazolone type compounds, cyanoacetyl compounds, pyrazoletriazole type compounds, etc, and particularly preferred couplers are pyrazolone type compounds. Magenta-forming couplers are described for example in US patents 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, in DE patent 1,810,464, in DE patent applications 2,408,665, 2,417,945, 2,418,959 and 2,424,467 and in JP patent applications 20,826/76, 58,922/77, 129,538/74, 74,027/74, 159,336/75, 42,121/77, 74,028/74, 60,233/75, 26,541/76 and 55,122/78.

Colored couplers can be used which include those described for example in US patents 3,476,560, 2,521,908 and 3,034,892, in JP patent publications 2,016/69, 22,335/63, 11,304/67 and 32,461/69, in JP patent applications 26,034/76 and 42,121/77 and in DE patent application 2,418,959.

DIR (Development Inhibitor Releasing) couplers can be used which include those described for example in US patents 3,227,554, 3,617,291, 3,701,783, 3,790,384 and 3,632,345, in DE patent applications 2,414,006, 2,454,301 and 2,454,329, in GB patent 953,454, in JP patent applications 69,624/77, 122,335/74 and 16,141/76.

In addition to DIR couplers, some other compounds which release development inhibitors upon

development can also be present in the light-sensitive material. Such kind of DIR compounds is described for example in US patents 3,297,445 and 3,379,529, in DE patent application 2,417,914, in JP patent applications 15,271/77 and 9,116/78.

Two or more kinds of the couplers described above can be incorporated in the same layer, or the same coupler can also be present in two or more layers.

Said couplers can be introduced into the silver halide emulsion layers of the photographic materials by using some of the methods described above. Moreover, said couplers are made non-diffusing by means of the above described ballasting groups.

The present invention is not limited to photographic materials with a particular type of emulsion or silver halides. It can therefore find an application with photographic materials containing different types of emulsions or silver halides, such as for example those described in Research Disclosure 17643, I, December 1978.

The emulsions which can be used in the present invention can be chemically and optically sensitized as described in Research Disclosure 17643, III and IV, December 1978. They can contain optical brighteners, antifogging agents and stabilizers, filtering and antihalo dyes, hardeners, coating aids, plasticizers and lubricants and other auxiliary substances as described for example in Research Disclosure 17643, V, VI, VIII, X, XI and XII, December 1978.

The layers of the photographic material can contain various colloids, alone or in combination, such as binding materials, as for example described in Research Disclosure 17643, IX, December 1978.

The photographic materials which can be used in the present invention can contain orthochromatic or panchromatic emulsions, as well as unsensitized emulsions. In particular and more preferably, they can be emulsions for color photography as described in Research Disclosure 17643, VII, December 1978. Such photographic materials, in particular, can be of the negative color print type or of the reversal type, of the color paper type or of the movie positive type. Of course, unconventional photographic materials of the transfer type, which make use of negative or direct positive emulsions, such as for example those described in US patents 3,277,550 and 3,227,551, can use the couplers of the present invention.

The above described emulsions can be coated onto several support bases (cellulose triacetate, paper, resin-coated paper, polyester, and the like) by adopting various methods, as described in Research Disclosure 17643, XV and XVI, December 1978.

For the production of color photographic images according to the present invention, the silver halide emulsion layers exposed to light radiation to form a latent image, are developed with a compound of the aromatic amine type in the presence of the color couplers. Suitable developing compounds are in particular the p-phenylenediamine derivatives, for example 2-amino-5-diethylamino-toluene chlorhydrate (called CD2), 2-amino-N-ethyl-N-(β -methanesulfonamido)-m-toluidine sesquisulfate monohydrate (called CD3), 4-amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)-aniline sulfate (called CD4).

After color development, the image-wise developed metallic silver and the remaining silver salts generally must be removed from the photographic material. This is performed in separate bleaching and fixing baths or in a single bath, called blix, which bleaches and fixes the image in a single step. The bleaching bath is a water solution having a pH equal to 5.60 and containing an oxidizing agent, normally a complex salt on an alkali metal or of ammonium and of trivalent iron with an organic acid, e. g. EDTA.Fe.NH₄, wherein EDTA is the ethylenediaminetetracetic acid. While processing, this bath is continuously aired to oxidize the divalent iron which forms while bleaching the silver image and regenerated, as known in the art, to maintain the bleach effectiveness. The bad working of these operations may cause the drawback of the loss of cyan density of the dyes.

Further to the above mentioned oxidizing agents, the blix bath contains known fixing agents, such as for example ammonium or alkali metal thiosulfates. Both bleaching and fixing baths can contain other additives, e. g. polyalkyleneoxide derivatives, as described in GB patent 933,008 in order to increase the effectiveness of the bath, or thioethers known as bleach accelerators.

The present invention is now explained in deeper details with reference to the example below, but it should not be construed as limited thereto.

EXAMPLE

Film A was prepared by coating a cellulose triacetate support base, subbed with gelatin, with the following layers in the following order:

(a) a layer of black colloidal silver dispersed in gelatin having a silver coverage of 0.26 g/m² and a

gelatin coverage of 1.4 g/m²;

(b) an intermediate layer containing 0.7 g/m² of gelatin;

(c) a layer of low sensitivity red-sensitive silver halide emulsion comprising a blend of a low-sensitivity silver bromo iodide emulsion (having 2% silver iodide moles and a mean grain size of 0.3 μm) and a medium sensitivity silver chloro-bromo-iodide emulsion (having 7% silver iodide moles and 5% silver chloride moles and a mean grain size of 0.5 μm) at a total silver coverage of 1.30 g/m² and a gelatin coverage of 1.7 g/m², containing two cyan-dye forming couplers, the coupler I-19 at a coverage of 0.71 g/m² and the coupler A at a coverage of 0.07 g/m², dispersed in a mixture of tricresylphosphate and butylacetanilide;

(d) a layer of high-sensitivity red-sensitive silver halide emulsion comprising a silver bromo-iodide emulsion (having 11% silver iodide moles and a mean grain size of 0.64 μm) at a silver coverage of 0.9 g/m² and a gelatin coverage of 1.2 g/m², containing two cyan-dye forming couplers, the coupler I-19 at a coverage of 0.144 g/m² and the coupler A at a coverage of 0.018 g/m², dispersed in a mixture of tricresylphosphate and butylacetanilide;

(e) an intermediate layer containing 1.0 g/m² of gelatin and 0.074 g/m² of 2,5-diisooctylhydroquinone dispersed in tricresylphosphate;

(f) a layer of medium speed green sensitive silver halide emulsion comprising the blend of silver halide emulsions of layer (c) at a silver coverage of 1.6 g/m² and a gelatin coverage of 1.63 g/m², containing three magenta-dye forming couplers, the coupler B at a coverage of 0.17 g/m², the coupler C at a coverage of 0.58 g/m² and the coupler D at a coverage of 0.05 g/m², dispersed in tricresylphosphate;

(g) a layer of high-sensitivity green sensitive silver bromo-iodide emulsion comprising the emulsion of layer (d) at a silver coverage of 0.8 g/m² and a gelatin coverage of 0.75 g/m² containing three magenta dye forming couplers, the coupler B at a coverage of 0.028 g/m², the coupler C at a coverage of 0.27 g/m² and the coupler D at a coverage of 0.006 g/m², dispersed in tricresylphosphate;

(h) an intermediate layer containing 0.8 g/m² of gelatin;

(i) a yellow filter layer containing 1.1 g/m² of gelatin, yellow colloidal silver at a silver coverage of 0.08 g/m² and 0.1 g/m² of 2,5-diisooctylhydroquinone dispersed in tricresylphosphate;

(l) a layer of medium-sensitivity blue-sensitive silver halide emulsion comprising the blend of silver halide emulsion of layer (c) at a silver coverage of 0.73 g/m² and a gelatin coverage of 1.72 g/m² and the yellow dye forming coupler E at a coverage of 1.58 g/m² dispersed in tricresylphosphate;

(m) a layer of high-sensitivity blue sensitive silver bromo-iodide emulsion (having 11% silver iodide moles and a mean grain size of 0.7 μm) at a silver coverage of 0.55 g/m² and a gelatin coverage of 1.12 g/m², containing the yellow dye-forming coupler E at coverage of 0.22 g/m² dispersed in tricresylphosphate;

(n) a protective layer of 1.4 g/m² of gelatin containing a dispersion of 2-(2'-hydroxy-3, 5'-ditert.butylphenyl)-5-tert.butyl-benzotriazole dispersed in tricresylphosphate;

(o) a top coat layer of 0.7 g/m² of gelatin containing 0.27 g/m² of polymethylmethacrylate beads;

Film B was prepared by coating a cellulose triacetate support base, subbed with gelatin, with the following layers in the following order:

(a) the layer of black colloidal silver dispersed in gelatin of Film A;

(b) the intermediate layer of Film A;

(c) the layer of low sensitivity red-sensitive silver halide emulsion of Film A;

(d) a layer of high-sensitivity red-sensitive silver halide emulsion comprising a bromo-iodide emulsion (having 11% silver iodide moles and a mean grain size of 0.64 μm) at a silver coverage of 0.9 g/m² and a gelatin coverage of 1.2 g/m², containing three cyan-dye forming couplers, the coupler A at a coupler coverage of 0.018 g/m², the coupler (I-19) at a coupler coverage of 0.096 g/m² and the coupler (II-1) at a coupler coverage of 0.048 g/m², dispersed in a mixture of tricresylphosphate and butylacetanilide;

(e) the intermediate layer (e) of Film A;

(f) the medium sensitivity green sensitive layer (f) of Film A;

(g) the high sensitivity green sensitive layer (g) of Film A;

(h) the intermediate layer (h) of Film A;

(i) the yellow filter layer (i) of Film A;

(l) the medium-sensitivity blue-sensitive layer (l) of Film A;

(m) the high-sensitivity blue-sensitive layer (m) of Film A;

(n) the protective layer (n) of Film A;

(o) the top-coat layer (o) of Film A;

Film C was prepared by coating a cellulose triacetate support base, subbed with gelatin, with the following layers in the following order:

(a) the layer of black colloidal silver dispersed in gelatin of Film A;

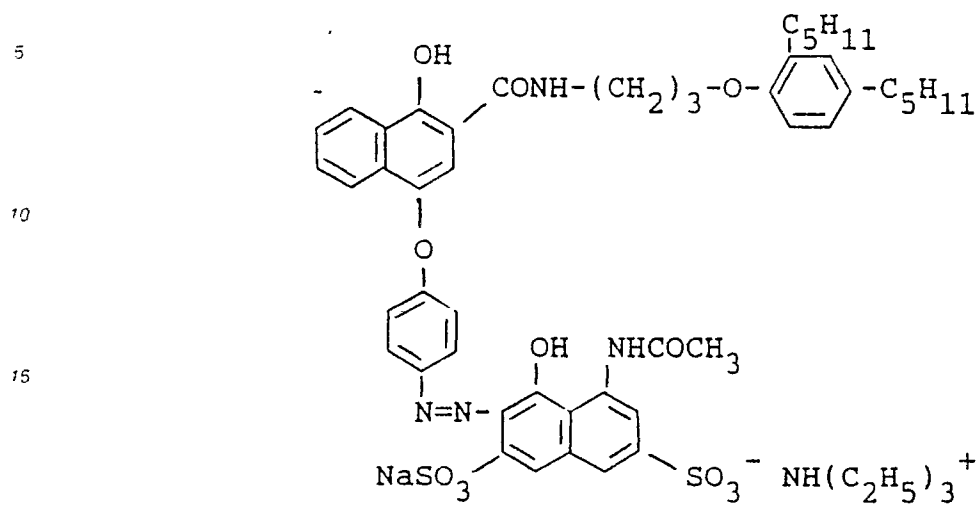
- (b) the intermediate layer of Film A;
- (c) the layer of low sensitivity red-sensitive silver halide emulsion of Film A;
- (d) layer of high-sensitivity red-sensitive silver halide emulsion comprising a bromo-iodide emulsion (having 11% silver iodide moles and a mean grain size of $0.64\ \mu\text{m}$) at a silver coverage of $0.9\ \text{g/m}^2$ and a gelatin coverage of $1.2\ \text{g/m}^2$, containing three cyan-dye forming couplers, the coupler A at a coupler coverage of $0.018\ \text{g/m}^2$, the coupler (I-19) at a coupler coverage of $0.048\ \text{g/m}^2$ and the coupler (II-1) at a coupler coverage of $0.096\ \text{g/m}^2$, dispersed in a mixture of tricresylphosphate and butylacetanilide;
- (e) the intermediate layer (e) of Film A;
- (f) the medium sensitivity green sensitive layer (f) of Film A;
- (g) the high sensitivity green sensitive layer (g) of Film A;
- (h) the intermediate layer (h) of Film A;
- (i) the yellow filter layer (i) of Film A;
- (l) the medium-sensitivity blue-sensitive layer (l) of Film A;
- (m) the high-sensitivity blue-sensitive layer (m) of Film A;
- (n) the protective layer (n) of Film A;
- (o) the top-coat layer (o) of Film A;

Film D was prepared by coating a cellulose triacetate support base, subbed with gelatin, with the following layers in the following order:

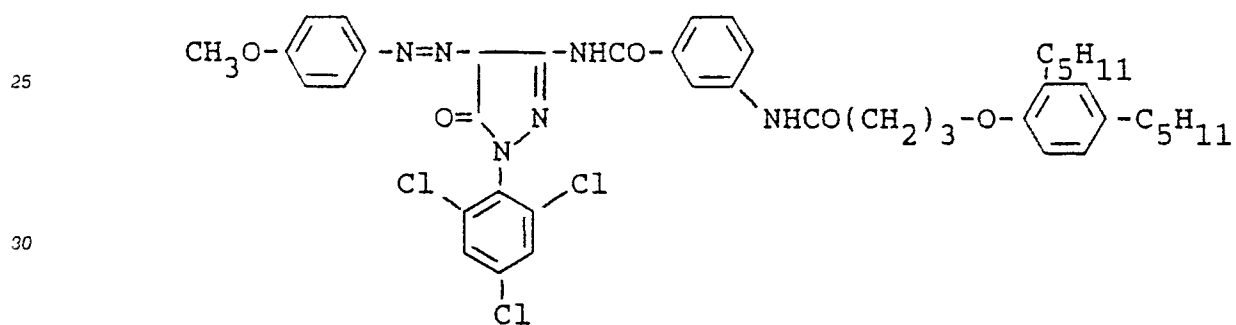
- (a) the layer of black colloidal silver dispersed in gelatin of Film A;
- (b) the intermediate layer of Film A;
- (c) the layer of low sensitivity red-sensitive silver halide emulsion of Film A;
- (d) a layer of high-sensitivity red-sensitive silver halide emulsion comprising a bromo-iodide emulsion (having 11% silver iodide moles and a mean grain size of $0.64\ \mu\text{m}$) at a silver coverage of $0.9\ \text{g/m}^2$ and a gelatin coverage of $1.2\ \text{g/m}^2$, containing two cyan-dye forming couplers, the coupler A at a coupler coverage of $0.018\ \text{g/m}^2$ and the coupler (II-1) at a coupler coverage of $0.144\ \text{g/m}^2$, dispersed in a mixture of tricresylphosphate and butylacetanilide;
- (e) the intermediate layer (e) of Film A;
- (f) the medium sensitivity green sensitive layer (f) of Film A;
- (g) the high sensitivity green sensitive layer (g) of Film A;
- (h) the intermediate layer (h) of Film A;
- (i) the yellow filter layer (i) of Film A;
- (l) the medium-sensitivity blue-sensitive layer (l) of Film A;
- (m) the high-sensitivity blue-sensitive layer (m) of Film A;
- (n) the protective layer (n) of Film A;
- (o) the top-coat layer (o) of Film A.

The couplers used are as follows:

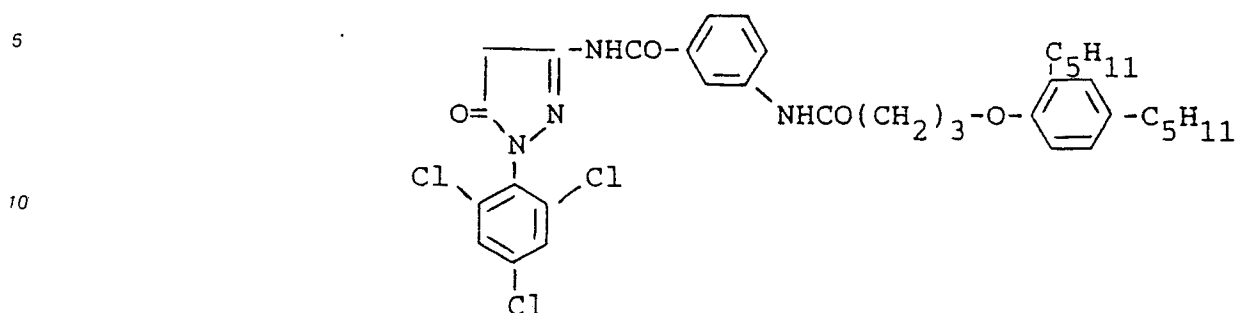
Coupler A:



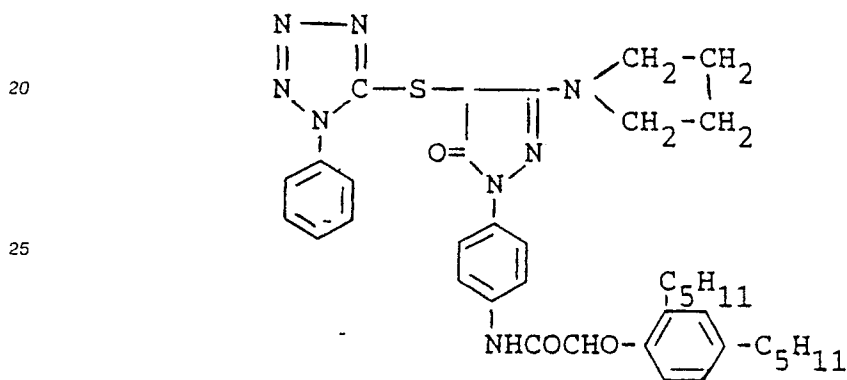
Coupler B:



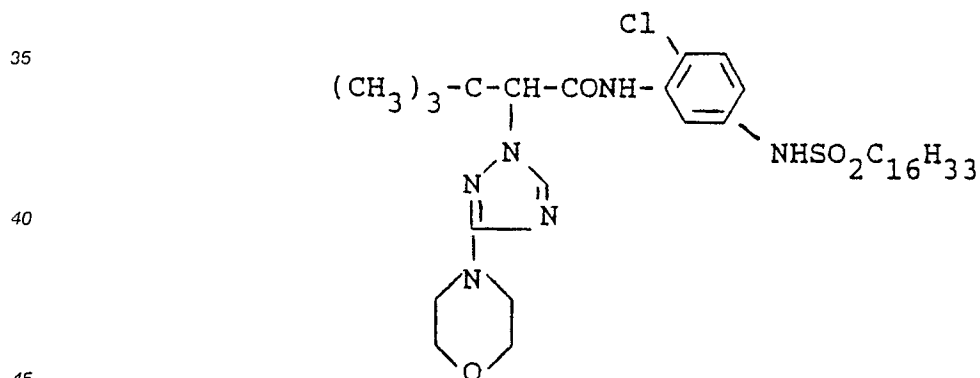
Coupler C:



Coupler D:



Coupler E:



Samples of the four films were exposed to 5500° K light through a grey step wedge, then subjected to a standard Kodak C41 process for color negative films.

50 As regards the evaluation of the sensitometric characteristics of the films having incorporated therein the cyan couplers according to the present invention and the absorption characteristics of the dyes derived from the color development reaction of the cyan couplers of the present invention, said evaluations were made with methods and measurements known in the art.

As regards to the evaluation of the stability of said cyan dyes towards the reduction by ferrous ions present in the bleaching bath, this was made by dipping for 5 minutes a sample of each film after exposure and color development, bleach, fixing and washing processing in a solution, called "bleach-leuco", obtained by adding concentrated ammonia under stirring to a suspension of:

55

ethylenediaminetetracetic acid	32.12 g
ammonium hydroxide conc.	750 ml
ferrous sulfate heptahydrate	27.8 g

5

till obtain a solution and adjusting then the pH thereof to 5.0 with nitric acid. The samples were then dried and the maximum density of the cyan dye scale was read at a normal densitometer.

10 The following table reports the wavelengths of the absorption maxima of the spectrophotometric curves of the cyan dyes formed in the coupling reaction, the fog, sensitivity and maximum density values of the cyan sensitometric HD curves and the color loss percentage according to the bleach-leuco test.

15

20

TABLE

Film	λ_{max} nm	Fog	Sens.*	Dmax	Dmax bleach-leuco	Dye loss %
A	689	.21	1.68	1.97	2.07	+ 5.1
B	685	.21	1.75	2.12	2.10	- 0.9
C	681	.21	1.84	2.12	2.07	- 2.4
D	677	.21	1.87	2.23	1.99	-10.8

35 (*) sensitivity expressed as $-\log E$ (wherein E is Exposure in meter-candle-seconds) measured at 0.2 density.

40

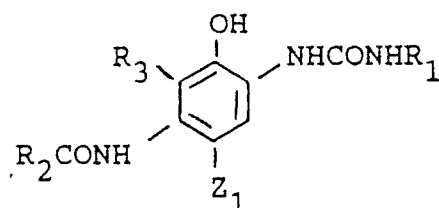
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50 The spectrophotometric and sensitometric curves of the developed cyan images and the bleach-leuco test show how the combination of couplers according to the present invention has absorption maxima shifted towards high wavelengths, as desired, high sensitivity and good resistance to the bleach-leuco processing.

55 Claims

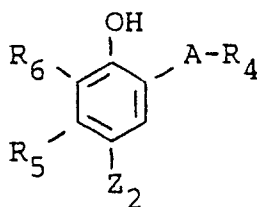
1. A silver halide color photographic material comprising a support having coated thereon one or more silver halide emulsion layers, at least one of said layers comprising in combination at least one of the cyan

couplers of the following Formula (I) and at least one of the cyan couplers of the following Formula (II):



Formula (I)

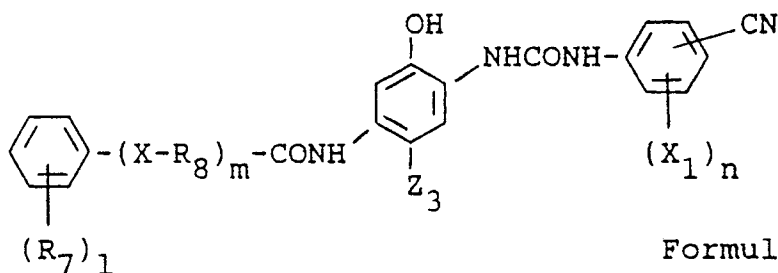
wherein R_1 is an aryl group, R_2 is an alkyl group or an aryl group, R_3 is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group, and Z_1 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.



Formula (II)

wherein A is a -NHCO- group or a -CONH- group, R_4 is an alkyl group, R_5 is an alkyl group, R_6 is a hydrogen atom, a halogen atom, an alkyl group or an alkoxy group or R_5 and R_6 can combine to form a benzene ring, and Z_2 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.

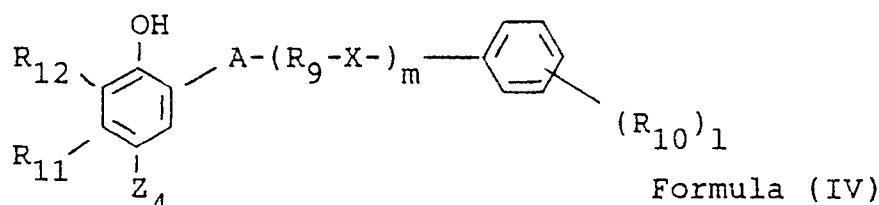
2. The silver halide color photographic material of claim 1, wherein the cyan couplers having Formula (I) are the compounds having the following Formula (III):



Formula (III)

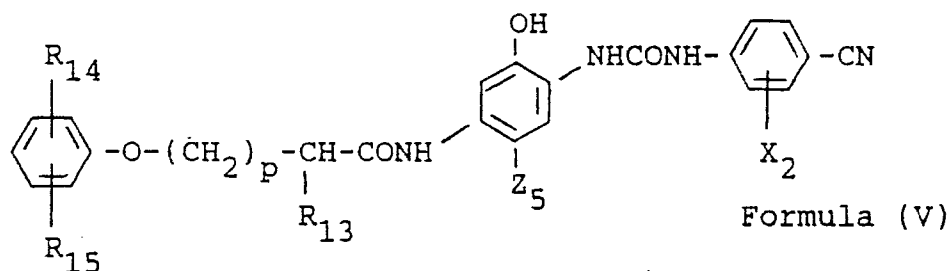
wherein X_1 is a hydrogen atom, a halogen atom or a monovalent organic group, R_7 is a hydrogen atom, a halogen atom, a hydroxyl group, a nitro group, an alkyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, an alkoxy group, an aryloxy group, an alkylcarbonyl group, an arylcarbonyl, an acyloxy group, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfonamido group, a sulfamoyl group, X is an oxygen atom or a sulfur atom, R_8 is a straight-chain or a branched-chain alkylene group, n is an integer of 0 to 3, m is an integer of 0 to 4 and l is an integer of 1 to 4, and Z_3 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with the oxidized product of an aromatic primary amine-type color developing agent.

3. The silver halide color photographic material of claim 1, wherein the cyan couplers having Formula (II) are the compounds having the following Formula (IV):



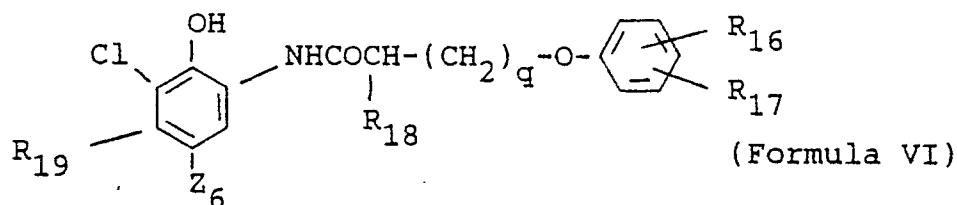
10 wherein A is a $-NHCO-$ group or a $-CONH-$ group, R_9 is a branched-chain or a straight chain alkylene group, R_{10} is a hydrogen atom, a halogen atom, a hydroxyl group, a nitro group, an alkyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, an alkoxy group, an aryloxy group, an alkylcarbonyl group, an arylcarbonyl, an acyloxy group, an alkylsulfonyl group, an arylsulfonyl group, an acyl group, an acylamino group, a sulfonamido group or a sulfamoyl group, X is an oxygen atom or a sulfur atom, R_{11} is an alkyl group, R_{12} is a hydrogen atom, a halogen atom or an alkyl group or R_{11} and R_{12} can combine to form a benzene ring, l is an integer of 1 to 4, m is an integer of 0 to 1, and Z_4 is a hydrogen atom, a halogen atom or a group which can be split off by the reaction of said coupler with oxidized product of an aromatic primary amine-type color developing agent.

20 4. The silver halide color photographic material of claim 1, wherein the cyan couplers having Formula (I) are the compounds having the following Formula (V):



35 wherein X_2 is a hydrogen atom or a halogen atom, R_{13} is a hydrogen atom or an alkyl group, R_{14} and R_{15} may be either the same or different and each is a hydrogen atom, an alkyl group or an alkoxy group, provided that the sum of carbon atoms of R_{13} , R_{14} and R_{15} is from 8 to 20, p is an integer of 0 to 2, and Z_5 is a hydrogen atom or a chlorine atom.

40 5. The silver halide color photographic material of claim 1, wherein the cyan couplers having Formula (II) are the compounds having the following Formula (VI):



50 wherein R_{16} and R_{17} may be either the same or different and each is a hydrogen atom, an alkyl group or an alkoxy group, R_{18} is a hydrogen atom or an alkyl group, provided that the sum of carbon atoms of R_{16} , R_{17} and R_{18} is from 8 to 20, R_{19} is an alkyl group of 1 to 2 carbon atoms, q is an integer of 0 to 2, and Z_6 is a hydrogen atom or a chlorine atom.

55 6. The silver halide color photographic material of claim 1, wherein the cyan coupler having Formula (I) is incorporated in an amount of from 10 to 90 mol % based on the total amount of said couplers represented by Formulae (I) and (II) in said material.

7. The silver halide color photographic material of claim 1, wherein the cyan coupler having Formula (I) is incorporated in an amount of from 25 to 75 mol % based on the total amount of said couplers represented by Formulae (I) and (I) in said material.

8. The silver halide color photographic material of claim 1, wherein said cyan couplers represented by Formulae (I) and (II) are present in a total amount of from 6.5×10^{-3} to 80×10^{-3} mol per mol of silver halide contained in said silver halide emulsion layer.

5 9. The silver halide color photographic material of claim 1 comprising coated on the support base blue, green and red-sensitized silver halide emulsion layers associated with non-diffusing color couplers, wherein the red-sensitive silver halide emulsion layer is associated with the combination of the cyan couplers of Formula (I) and the cyan couplers of Formula (II).

10 10. The silver halide color photographic material of claim 1 comprising coated on the support base blue, green and red-sensitized silver halide emulsion layers associated with non-diffusing color couplers, wherein the red-sensitive silver halide emulsion layer comprises two or more silver halide emulsion layers sensitized to the same spectral region of visible light, the uppermost silver halide emulsion layer of which has the highest sensitivity and the lowermost silver halide emulsion layer has the lowest sensitivity, characterized in that the uppermost highest sensitivity silver halide emulsion layer is associated with the combination of the cyan couplers of Formula (I) and the cyan couplers of Formula (II).

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 10 3931

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. 5)
X	EP-A-0 164 030 (FUJI) * claims 1-3 *	1	G 03 C 7/34
Y	* exemplary compounds I-28 - I-31, II-1,2,7,10 etc. *	1-5	

D,Y	EP-A-0 254 151 (AGFA) * whole document *	1-5	

D,A	EP-A-0 112 514 (KONISHIROKU) * claims; exemplary compounds II-1 - II-22 *	1-7,9	

			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			G 03 C 7/00
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
BERLIN		16-05-1990	STOCK H
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	