(11) **EP 0 777 151 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:

31.05.2000 Bulletin 2000/22

(51) Int Cl.⁷: **G03C 7/36**

(21) Application number: 96203192.8

(22) Date of filing: 15.11.1996

(54) Photographic element containing yellow dye-forming coupler comprising a dye light stability enhancing ballast and process

Photographisches Element enthaltend einen einen gelben Farbstoff bildenden Kuppler enthaltend eine Ballastgruppe, die die Lichtstabilität des Farbstoffes erhöht und Verfahren

Elément photographique contenant un coupleur formant un colorant jaune comprenant un groupe ballast augmentant la stabilité du colorant à la lumière et procédé

(84) Designated Contracting States: **DE FR GB**

(30) Priority: **30.11.1995 US 565517 15.07.1996 US 680743 15.07.1996 US 680191**

- (43) Date of publication of application: **04.06.1997 Bulletin 1997/23**
- (73) Proprietor: EASTMAN KODAK COMPANY Rochester, New York 14650 (US)
- (72) Inventors:
 - Lussier, Barbara Boland Rochester, New York 14650-2201 (US)

- DiCillo, John Rochester, New York 14650-2201 (US)
- (74) Representative: Nunney, Ronald Frederick Adolphe et al Kodak Limited, Patents, W92-3A, Headstone Drive Harrow, Middlesex HA1 4TY (GB)
- (56) References cited:
 - PATENT ABSTRACTS OF JAPAN vol. 5, no. 84 (P-064), 2 June 1981 & JP 56 030126 A (KONISHIROKU PHOTO IND. CO. LTD.), 26 March 1981,

P 0 777 151 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

Field of the Invention

⁵ **[0001]** This invention relates to color photographic materials or elements comprising a yellow dye-forming coupler which forms a dye upon development which exhibits improved stability against dye fade upon exposure to light.

Background of the Invention

[0002] A typical photographic element contains multiple layers of light-sensitive photographic silver halide emulsions with one or more of these layers being spectrally sensitized to blue light, green light, and red light, respectively. The blue, green, and red light sensitive layers will typically contain yellow, magenta or cyan dye forming couplers, respectively.

[0003] For forming color photographic images, the color photographic material is exposed imagewise and processed in a color developer bath containing an aromatic primary amine color developing agent. Image dyes are formed by the coupling reaction of these couplers with the oxidized product of the color developing agent. Generally, image couplers are selected to provide image dyes with good stability towards heat and light and which desirably have an absorption curve with a suitable peak absorption and low unwanted side absorptions in order to provide color photographic images with good color reproduction.

[0004] The present invention is concerned with improving the light stability of yellow image dyes. Couplers that form yellow dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,298,443, 2,407,210, 2,875,057, 3,048,194, 3,265,506, 3,447,928, 4,022,620, 4,443,536, and "Farbkuppler-eine LiteratureUbersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Other examples of yellow dye-forming couplers are detailed in Research Disclosure No. 365, Item 36544, September 1994, Section X-B(6). Such couplers are typically open chain ketomethylene compounds.

[0005] The ability of yellow image dyes to resist light fade is important to the longevity of color images, especially those which are destined to be subject to constant daylight exposure such as professional portraits and the like. Yellow images will fade and images formed with yellow dye as a component may change color if the rate of fade for the yellow dye is not sufficiently matched with the other dyes of the photographic element.

[0006] Heretofore, one method of improving the light stability of yellow image dyes has been to add one or more stabilizing addenda to the coupler dispersion. Compounds suitable for this purpose are described more fully in Research Disclosure No. 365, Item 36544, September 1994, Section X-D. Examples of suitable such compounds are shown as Compounds 1, 2, and 3 and P1 in conjunction with Table IV.

[0007] U.S. Patent No. 4,248,962 relates to a pyrazolotriazole magenta dye-forming coupler designed to release a photographically useful group upon coupling. The patent proposes a timing group which will undergo an intramolecular nucleophilic displacement reaction to release a photographically useful group. Among the many proposed couplers is one (coupler 44) which contains a ballast having an acetate substituent on a phenoxy group connected through a linking group to a phenyl ring in the ballast. There is no indication that any dye light stability is inferred by the presence of the particular ballast employed in that example.

[0008] Japanese published application 56-30126 discloses acylacetanilide yellow couplers containing a 2-chloro-5-carboxy anilino ring. There is no disclosure therein that couplers of this type can provide an improvement in dye light stability.

[0009] A problem to be solved is to provide a yellow image dye-forming coupler which forms a dye upon development which exhibits improved stability upon exposure to light. Desirably, the coupler is one for which the dye light stability may be further improved by the addition of a stabilizing addenda.

Summary of the Invention

[0010] The invention provides a photographic element comprising a light sensitive silver halide emulsion layer having associated therewith an open chain α -carbonyl acetanilide yellow dye-forming coupler having the formula:

50

45

20

wherein

5

10

15

20

25

30

35

 R_1 is selected from the group consisting of alkyl, aryl, heterocyclic, and amino groups, provided that R_1 may form a ring bonded to another carbon atom which is a member of Ring "A";

each R_2 is independently selected from the group consisting of those substituents having a Hammett's sigma value of 0 or less, and m is from 0 to 4;

each R_3 and R_4 for each of the n carbon atoms is independently selected from the group consisting of hydrogen, alkoxy, aryl, heterocyclic, aryloxy, amino and alkyl groups, and n is 0 to 16;

each R_5 is independently selected from the group consisting of halogen, amino, alkyl groups, and groups linked to the "B" ring by oxygen or sulfur, and p is 0 to 3, provided that two R_5 groups may join to form a ring;

each L is independently a divalent linking group and q is 0 to 3; and

Ring "A" is bonded indirectly to the 3-, 4-, or 5-position of Ring "B",

R₆ is selected from the group consisting of alkyl, aryl, and amino groups; and

- (1) when an R_5 is halogen, Z is hydrogen or a coupling-off group selected from the group consisting of:
 - (a) an aryloxy or arylthio group;
 - (b) a heterocyclic group containing, in a five or six membered ring, one or two nitrogen atoms, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring; and
 - (c) a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group; and
- (2) when no R_5 is halogen, Z is hydrogen, or a group capable of coupling-off when the coupler reacts with an oxidized color developing agent,

atoms. Particularly suitable are alkyl (including cycloalkyl and branched alkyl), amino, fused alkyl, and aryl groups. Particularly suitable are methyl, isopropyl, fused alkyl, t-butyl, dimethylamino, diethylamino, phenyl, and fused amino.

[0011] Each R₂ is a substituent on the phenoxy ring "A", and there may be present up to four of these substituents. This substituent may be broadly selected from those substituents which have a Hammett's sigma value of 0 or less. Hammett's sigma values are provided in <u>C. Hansch and A. J. Leo,</u> "Substituent Constants for Correlation Analysis in Chemistry and Biology", Wiley, New York, N.Y., 1979. Generally, values less than 0 indicate that a substituent has an electron donating effect relative to hydrogen. Thus, R₂ is electron donating. It is further provided that at least one R₂ group is located ortho to the acyloxy group containing R₁. This group desirably contains branching. Suitably, R₂ is an alkyl, alkoxy or amino compound. Satisfactory compounds include thioalkyl, dialkylamino, and branched alkyl and alkoxy groups. Appropriate examples include t-butyl, t-pentyl, t-octyl, and isopropyl.

[0012] Where n>1 the R_3 and R_4 substituents bonded to each of the n carbon atoms may be independently selected. Besides hydrogen, suitable R_3 and R_4 substituents may include alkyl, alkoxy (including polyalkoxy), aryl, aryloxy, heterocyclic, and amino groups. Alkyl or alkoxy groups of 1-18 carbon atoms and hydrogen are satisfactory substituents. If desired, R_3 or R_4 may form a ring with another R_3 or R_4 group.

[0013] R_5 is a substituent which may or may not be present as indicated by the subscript "p". Each R_5 is a substituent which may be a halogen, an amino group, an alkyl group, or a group linked to the "B" ring by an provided that if L is other than

55

wherein R is hydrogen or an alkyl group and R' is an alkylene group, then there is present at least one R_2 substituent on ring "A" ortho to the acyloxy group to which R1 is attached.

[0014] The photographic element of the invention forms a yellow image dye which exhibits an improved stability to light degradation.

Detailed Description of the Invention

20

25

30

35

40

[0015] R₁ is the substituent attached to the acyloxy group on the ring "A". It may be an alkyl, aryl, heterocyclic, or an amino group. Also, R₁ may form a ring bonded to another carbon atom which is a member of Ring "A". Desirably R₁ contains at least 4 carbon atom of oxygen or sulfur. Suitably, one or more of the R₅ substituents may occupy the 2-, 4-, or 6- position of the ring "B". Suitably, R₅ may be bonded to the ring "B" by an acyloxy, alkylthio, alkyl, amino, or oxy group. Particularly suitable groups are alkylacyloxy, arylacyloxy, trifluoromethyl, alkylthio, alkoxy, aryloxy, alkyl, or amino groups. The value of "p" may range from 0 to 3, suitably 1 to 3.

[0016] R_6 is an amino group, an alkyl group or an aryl group. More suitably, R_6 may be a secondary or tertiary alkyl group, a phenyl group, a phenyl amino group, or an alkyl amino group. Typically, the secondary alkyl group may be an isopropyl group, the tertiary alkyl group may be t-butyl, t-pentyl, t-octyl, or 1-methyl-1-cyclopropyl. The phenyl group may be phenyl or phenyl substituted, for example, with alkoxy, alkyl or amido groups. The amino may be a phenylamino or alkylamino group.

[0017] The group L is optionally present. As indicated by the value of q of up to three, there may be present as many as three L groups. Each of the L groups may be independently selected to provide a linkage between the ring "B" and the remainder of the coupler. In the broadest sense, L may be any divalent group linking the ballast directly or indirectly with a noncoupling position of the rest of the coupler. Each L may be represented, for example, by one of the groups:

wherein R is hydrogen or an alkyl group and R' is an alkylene group. Specifically useful are:

15 and

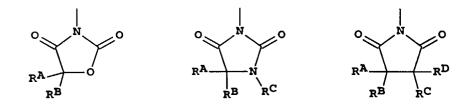
25

30

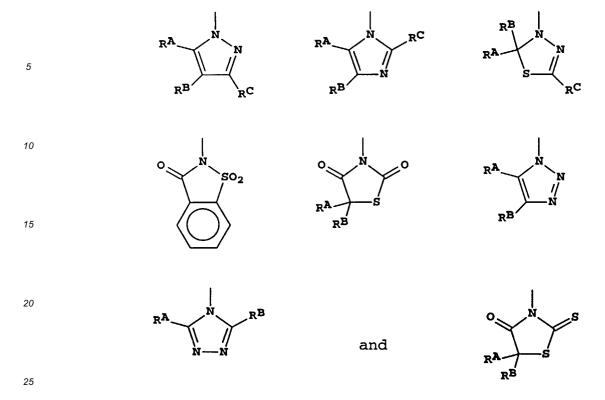
35

[0018] With regard to Z,

- (1) when an R_5 is halogen, Z is hydrogen or a coupling-off group selected from the group consisting of:
 - (a) an aryloxy or arylthio group;
 - (b) a heterocyclic group containing, in a five or six membered ring, one or two nitrogen atoms, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring; and
 - (c) a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group; and
- (2) when no R₅ is halogen, Z is hydrogen, or a group capable of coupling-off when the coupler reacts with an oxidized color developing agent. In the latter case, any suitable coupling-off group of the art may be employed as described more fully hereafter. Typical such group include aryloxy, arylthio and nitrogen heterocyclic groups. If desired, the coupling-off group may include a so-called timing group together with a photographically useful group ("PUG") which can permit the PUG to diffuse away from the coupler's initial location to perform a function such as inhibiting development, assisting bleaching etc. Such groups are more fully described hereafter.
- [0019] It is suitable that the group Z represents a heterocyclic group containing, a nitrogen atom in a five or six membered ring, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring. Examples of such a heterocyclic group contain one or more nitrogen atoms in the ring and possibly an oxygen atom. The use of dione formulas is convenient. Examples of suitable groups are pyrazole, imidazole, hydantoin, urazole, and oxazole groups such as the following:



55



wherein each R^A , R^B , R^C and R^D is an independently selected group such as hydrogen, or an alkyl (e.g. methyl, ethyl ,propyl, phenylmethyl, sulfonamidoalkyl), aryl, or alkoxy (e.g. methoxy, ethoxy) group. Particularly useful as Z are the following:

30

55

[0020] When an R_5 is halogen, group Z may represent a heterocyclic group containing in a five or six membered ring one or two nitrogen atoms and possibly an oxygen atom, where the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring. The use of dione formulas is convenient. Examples of suitable groups are pyrazole, imidazole, hydantoin, succinimide, thiazole, thiazolidino, thiadiazole, saccharin, rhodanine, and oxazole groups such as the following:

and

wherein each R^A , R^B , R^C and R^D is an independently selected group such as hydrogen, or an alkyl (e.g. methyl, ethyl ,propyl, phenylmethyl, sulfonamidoalkyl), aryl, or alkoxy (e.g. methoxy, ethoxy) group.

[0021] When it is desired to release a development inhibitor group, a benzotriazole group is useful as Z.

[0022] Other useful coupling-off groups are arylthio such as phenylthio groups and aryloxy such as phenoxy groups.

[0023] Examples of suitable couplers of the invention are as follows:

15

5

10

20

25

30

35

40

45

50

C14H29 CH3SO2NH SO2CH3

Y-2 Ċ₁₂H₂₅

Y-3

Y-6
$$\begin{array}{c} & & & & \\ & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$$

Y-8 Y-8

Y-10 Y-11 Y-12 NH-| SO₂

$$\begin{array}{c} & & & \\ & &$$

Y-21
$$\begin{array}{c}
0 & 0 & 0 \\
NH & 0 & NH \\
0 & 0 & 0
\end{array}$$

C₁₂H₂₅ 5 Y-24 10 OC4H9 15 20 Y-25 25 С₁₂н₂₅ 30 35 Y-26 C8H17 40 45 50 C₁₂H₂₅ Y-27 55

СН30

30

35

40

45

50

55

[0024] Unless otherwise specifically stated, substituent groups which may be substituted on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for photographic utility. When the term "group" is applied to the identification of a substituent containing a substitutable hydrogen, it is intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any group or groups as herein mentioned. Suitably, the group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, or sulfur. The substituent may be, for example, halogen, such as chlorine, bromine or fluorine; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain alkyl, such as methyl, trifluoromethyl, ethyl, t-butyl, 3-(2,4-di-t-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, sec-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-t-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-t-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-t-pentyl-phenoxy)acetamido, alpha-(2,4-di-t-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-t-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-t-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-t-pentylphenyl)carbonylamino, p-dodecyl-phenylcarbonylamino, p-toluylcarbonylamino, N-methylureido, N,Ndimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioctyl-N'-ethylureido, Nphenylureido, N,N-diphenylureido, N-phenyl-N-p-toluylureido, N-(m-hexadecylphenyl)ureido, N,N-(2,5-di-t-pentylphenyl)-N'-ethylureido, and t-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, p-toluylsulfonamido, p-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropyl-sulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]sulfamoyl, Nmethyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N.N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; carbonyl, such as acetyl, (2,4-di-t-amylphenoxy)acetyl, phenoxycarbonyl, p-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-t-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexyl-

sulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-toluylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and p-toluylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, p-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbonyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1 (N-phenylimido)ethyl, N-or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

[0025] If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups, etc. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

[0026] If desired, the photographic element can be used in conjunction with an applied magnetic layer as described in Research Disclosure, November 1992, Item 34390 published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, and as described in Hatsumi Kyoukai Koukai Gihou No. 94-6023, published March 15, 1994, available from the Japanese Patent Office, the contents of which are incorporated herein by reference. When it is desired to employ the inventive materials in a small format film, Research Disclosure, June 1994, Item 36230, provides suitable embodiments.

[0027] In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to <u>Research Disclosure</u>, September 1994, Item 36544, available as described above, which will be identified hereafter by the term "Research Disclosure". The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure.

[0028] Except as provided, the silver halide emulsion containing elements employed in this invention can be either negative-working or positive-working as indicated by the type of processing instructions (i.e. color negative, reversal, or direct positive processing) provided with the element. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through V. Various additives such as UV dyes, brighteners, antifoggants, stabilizers, light absorbing and scattering materials, and physical property modifying addenda such as hardeners, coating aids, plasticizers, lubricants and matting agents are described, for example, in Sections II and VI through VIII. Color materials are described in Sections X through XIII. Scan facilitating is described in Section XIV. Supports, exposure, development systems, and processing methods and agents are described in Sections XV to XX. Desirable photographic elements and processing steps including other components suitable for use in photographic elements of the invention are also described in Research Disclosure, Item 37038, February 1995.

[0029] It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England, incorporated herein by reference. [0030] With negative-working silver halide, the processing step described above provides a negative image. The described elements can be processed in the known Kodak C-41 color process as described in The British Journal of Photography Annual of 1988, pages 191-198. Where applicable, the element may be processed in accordance with color print processes such as the RA-4 process of Eastman Kodak Company as described in the British Journal of Photography Annual of 1988, Pp 198-199. Such negative working emulsions are typically sold with instructions to process using a color negative method such as the mentioned C-41 or RA-4 process. To provide a positive (or reversal) image, the color development step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and followed by uniformly fogging the element to render unexposed silver halide developable. Such reversal emulsions are typically sold with instructions to process using a color reversal process such as E-6. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

[0031] Preferred color developing agents are p-phenylenediamines such as:

4-amino-N,N-diethylaniline hydrochloride,

20

30

35

40

45

- 4-amino-3-methyl-N,N-diethylaniline hydrochloride,
- 4-amino-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline sesquisulfate hydrate,
- 4-amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline sulfate,

- 4-amino-3-(2-methanesulfonamido-ethyl)-N,N-diethylaniline hydrochloride and 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.
- **[0032]** Development is usually followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.
- **[0033]** The entire contents of the various patent applications, patents and other publications referred to in this specification are incorporated herein by reference.

Synthetic Example

5

10

50

[0034] The synthesis of the couplers of the invention is accomplished using conventional reactions. The following is a typical method for preparing coupler Y-2 of the invention which may be employed in an analogous manner to prepare other couplers of the invention.

Synthesis of Example Yellow Coupler Y-2:

Preparation of 2-(4,4-dimethyl-3-oxovaleramido)-4-nitroanisole.

[0035] Methyl-4,4-dimethyl-3-oxovalerate (15.8 g, 0.1 mol) and 2-methoxy-5-nitroaniline (16.8 g, 0.01 mol) were taken up in toluene (150 mL) in a round bottomed flask fitted with a Dean-Stark trap. The mixture was heated to a vigorous reflux while the MeOH side-product was distilled off and removed. After 4 hours, the mixture was cooled and the toluene removed *in vacuo*. The residue was recrystallized from acetonitrile to yield 27 g of the desired condensation

product.

20

Preparation of 2-(4,4-dimethyl-3-oxovaleramido)-4-aminoanisole hydrochloride.

- [0036] A solution of 2-(4,4-dimethyl-3-oxo-valeramido)-4-nitroanisole (20 g) in EtOH (100 mL) with 1 g Pd/C was catalytically reduced under hydrogen to give the corresponding amine in quantitative yield. After filtering the mixture, HCl gas was bubbled through the solution. Upon cooling, white crystals of 2-(4,4-dimethyl-3-oxo-valeramido)-4-aminoanisole hydrochloride formed. The crystals were collected and dried *in vacuo* to yield 17 g of product.
- Preparation of 2-(4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2- (4-aceto-3-tert-butyl-aryloxy)acetamido] anisole.

[0037] A solution of 2-dodecyl-2-(4-aceto-3-tert-butylaryloxy)-acetylchloride (19.4 g, 0.043 mol) in acetonitrile (100 mL) was added to a solution of 2-(4,4-dimethyl-3-oxovaleramido)-4-aminoanisole hydrochloride (13.1 g, 0.043 mol) in acetonitrile (50 mL). Diisopropylethylamine (11.2 g, 0.086 mol) was added dropwise. After 1 hour, EtOAc (100 mL) was added. The mixture was submitted to an aqueous, acidic workup. The organics were dried over MgSO4, filtered and the solvents removed *in vacuo*. The isolated product (27 g) was suitably pure for use in the next step.

Preparation of 2-(2-chloro-4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2-(4-aceto-3-tert-butylaryloxy) acetamido]anisole.

[0038] To a solution of 2-(4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2-(4-aceto-3-*tert*-butylaryloxy)acetamido]anisole (25.0 g, 0.0367 mol) in dichloromethane (150 mL) was added sulfuryl chloride (2.9 mL, 0.0367 mol). The mixture was stirred for 30 minutes at room temperature. The solvent was removed *in vacuo*. The product was formed quantitatively and was suitably pure for use in the next reaction.

Preparation of 2-[4,4-dimethyl-2-(4,4-dimethyloxazolidinedione)-3-oxovaleramido]-4-[2-dodecyl-2-(4-aceto-3-tert-butylaryloxy)acetamido]anisole.

[0039] A solution of 2-(2-chloro-4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2-(4-aceto-3-tert-butylaryloxy)-acetamido]anisole (15.0 g, 0.021 mol), 4,4-dimethyloxazolidinedione (3.4 g, 0.026 mol) and triethylamine (2.2g, 0.023 mol) in acetonitrile (200 mL) was stirred and heated to reflux. After 4 hours, the mixture was cooled to room temperature and submitted to aqueous, acidic workup. The organics were extracted into EtOAc, dried over MgSO4, filtered and the solvent stripped in *vacuo*. The residue was recrystallized from isopropyl ether to yield 15.2 g (90%) of the desired yellow coupler. The results of NMR analysis were consistent with the compound Y-2. 1H NMR (CDCI3/TMS): d = 0.9 (t, 3 H), 1.4 (m, 46 H), 2.3 (s, 3H), 3.9 (s, 3 H), 4.6 (t, 1 H), 5.6 (s, 1 H), 6.9 (m, 4H), 7.8 (d, 1 H), 8.1 (m,br, 2 H), 9.0 (s, 1H). MS (FDMS) m/e = 807

C45 H65 N3 O10					
calc 66.89 H 8.11 N 5.2					
found	66.85	H 8.01	N 5.0		

Photographic Examples

Preparation of Photographic Elements

[0040] Dispersions of the couplers were prepared in the following manner, exemplified with representative coupler Y2. In one vessel, 1.55 g of the coupler, Y2, 0.72g of dibutyl phthalate, 0.6g of 2-(2-butoxyethoxy)ethyl acetate and 4.6g of ethylacetate were combined and warmed to 60°C to dissolve. In a second vessel, 21.2g of 11.55% gelatin, 2.44g of Alkanol XC™ (surfactant and trademark of E. I. Dupont Co., USA) and 9.62g of water were combined and warmed to 40°C. The two mixtures were combined and passed three times through a Gaulin colloid mill.

[0041] The photographic elements were prepared by coating the following layers in the order listed on a resin-coated paper support:

1st layer	
Gelatin	3.23 g/m ²

55

40

45

(continued)

2nd layer				
Coupler dispersion AgCl emulsion	8.8 x 10 ⁻⁴ mole coupling moieties/m ² 0.28g Ag/m ² and blue-sensitized			
3rd layer				
Gelatin Bis (vinylsulfonylmethyl)ether	1.4 g/m ² 0.14 g/m ²			

Exposing and processing of Photographic Elements

5

10

15

20

25

30

35

40

55

[0042] The photographic elements were subjected to stepwise exposure to blue light and processed as follows at 35° C:

Color Developer	45 seconds
Bleach-Fix	45 seconds
Wash (running water)	90 seconds

[0043] The developer and bleach-fix were of the following compositions:

Triethanolamine	700 ml
Hierianolanine	12.41 (
Blankophor REU TM (Mobay Corp)	2.3 g
Lithium polystyrene sulfonate (30%)	0.3 g
N,N-diethylhydroxylamine (85%)	5.4 g
Lithium sulfate	2.7 g
N-{2-[(4-amino-3-methylphenyl)ethylamino]-ethyl}-methanesulfonamide, sesquisulfate	5.0 g
1-hydroxyethyl-1,1-diphosphonic acid (60%)	0.81 g
Potassium carbonate, anhydrous	21.16
Potassium chloride	1.6 g
Potassium bromide	7.0 g
Water to make	1.0 L

	Bleach-Fix		
	Water	700 mL	
	Solution of Ammonium thiosulfate(56.4% plus Ammonium sulfite (4%)	127.4 g	
45	Sodium metabisulfite		
	Acetic Acid (glacial)	10.2 g	
	Solution of Ammonium ferric ethylenediaminetetraacetate (44%) + ethylenediaminetetraacetic acid (3.5%)	110.4 g	
50	Water to make	1.0 L	
	pH at 26.7° C adjusted to 6.7	1	

Photographic Tests

[0044] Yellow dyes were formed upon processing of the photographic elements. The coatings were assessed sensitometrically for the following characteristics:

D-max (the maximum density to blue light), Dmin (the minimum density to blue light),

[0045] Contrast (the ratio of (S-T)/0.6 where S is the density at a log exposure 0.3 units greater than the Speed value, and T is the density at a log exposure 0.3 units less than the Speed value),

[0046] Speed (the relative reciprocal of exposure required to yield a density to blue light of 1.0), and Lambda-max (the wavelength of peak absorption at a density of 1.0).

[0047] The data is reported in Table I. The data shows that the couplers of the invention are comparable or superior in sensitometry to the comparison couplers.

Table I

Table I						
Sensitometric Data						
Coupler	Туре	Dmax	Dmin	Contrast	Speed	λmax
Y-1	Inv	2.75	0.06	2.65	182.4	439
Y-2	Inv	2.75	0.09	2.65	188.4	439
Y-3	Inv	2.74	0.08	2.64	198.1	438
Y-4	Inv	2.76	0.09	2.80	199.5	437
Y-5	Inv	2.83	0.05	2.84	186.9	436
Y-6	Inv	2.81	0.08	2.59	197.0	440
C-1	Comp	2.70	0.05	2.55	191.7	446
C-2	Comp	2.62	0.05	2.60	188.2	438
C-3	Comp	2.42	0.06	2.40	177.6	441
C-4	Comp	2.71	0.04	2.51	178.4	442

[0048] The comparative couplers were as follows:

55

50

5

10

15

20

25

30

35

40

C-2

$$N_{H}$$
 $C_{16}H_{33}$

C-3

$$C_{14}H_{29}$$
 $C_{12}H_{25}$
 $C_{13}H_{25}$
 $C_{14}H_{25}$
 $C_{15}H_{25}$
 $C_{15}H$

[0049] Couplers C-1 and C-2 represent couplers actually in use in commercial photographic film. Couplers C-3 and C-4 are provides as additional comparisons.

Light Stability Test

[0050] The coating strips were exposed to a high intensity Xenon light source at a luminous flux level of 50 Klux with a WRATTEN 2C filter interposed between the light source and sample. After 2 weeks and 4 weeks, the strips were removed and the decrease in density from initial densities of 1.7, 1.0 and 0.5 were measured. The data is recorded in Table 2 as a measure of the per cent dye retained for each sample dye. These results compare the light fastness of dyes from couplers of the present invention with those of the comparisons.

Table II

Coupler	Туре	Dye Retained from Initial Density 1.0		
		14-Day	28-Day	
Y-1	Inv	96%	85%	
Y-2	Inv	96%	86%	

Table II (continued)

Coupler	Туре	Dye Retained from Initial Density 1.0		
		14-Day	28-Day	
Y-3	Inv	91%	79%	
Y-4	Inv	91%	82%	
Y-5	Inv	94%	79%	
Y-6	Inv	95%	85%	
C-1	Comp	51%	17%	
C-2	Comp	72%	40%	
C-3	Comp	78%	40%	
C-4	Comp	91%	77%	

15

20

25

30

5

10

[0051] As can be seen from Table II, the couplers of the invention have superior light fastness as compared to couplers C-1 and C-2 typically used in the art and are advantageous over comparisons C-3 and C-4. The amount of dye remaining after exposure averages 82.6% for the inventive couplers compared to an average of 43.5% for the comparative couplers. At 14 days the corresponding values are 93.8 and 73.0, respectively. The inventive couplers are stable enough that they can be used without light stabilizing addenda when a neutral fade position with typical magenta and cyan dyes is desired.

[0052] Neutral fade could also be achieved even if extremely stable magenta and cyan dyes were utilized by incorporating light stabilizing addenda along with the yellow couplers of this invention in an analogous photographic format to that described above with the following weight ratios: Yellow coupler: coupler solvent such as dibutylphthalate: auxiliary solvent such as 2-(2-butoxyethoxy)ethylacetate: stabilizer addenda 54:15:18:13. The stabilizer addenda typically used are those exemplified by compounds 1-3 but are not limited to these. Also suitable are polymeric stabilizing addenda. The polymers can be homopolymers or copolymers which are miscible with the coupler and coupler solvent which are present, for example, as a latex or as an organic solution. Especially useful are polymers containing monomers derived from styrene and/or acrylics such as acrylamide (particularly t-butyl acrylamide such as P1 below where x=99 and y=1), acrylates, methacrylamides, and methacrylates.

[0053] Table III describes 2-week and 4-week light fade data for dyes formed from representative couplers using compound 1 as stabilizing addenda.

35

40

45

₩

Compound 1

Compound 2

HO CHOCK OF SHOCK OF

Compound 3

50

NH O NH SO₃Na

55

P1

ADD-1

10

5

Table III

15

20

25

Coupler + Compound 1 Coupler Type Dye Retained from Initial Density 1.0 14 day 28 day Y-1 97% 90% Inv Y-2 Inv 100% 93% Y-3 Inv 96% 86% Y-4 Inv 93% 84% Y-5 93% 90% Inv Y-6 Inv 95% 85% C-1 Comp 88% 69% C-3 Comp 91% 71%

[0054] As shown in Table III, the couplers of this invention yield dyes which show highly superior resistance to light fade when coated with stabilizing addenda.

[0055] This can be particularly useful if one desires to use certain emulsion additives to achieve unique photographic features, as is sometimes done in the art. Although the presence of these emulsion additives give desirable photographic features, they can sometimes be detrimental to dye stability. Coupler Y-2 was coated in a format similar to that described above with the weight ratio of coupler: dibutylphthalate: stabilizing addenda of 3:2:1. Emulsion addenda ADD-1 was present in the emulsion in the amount of 0.88 mg/ft². The data in Table IV thus show that coupler Y-2 is still quite stable even without stabilizing addenda and can be made even more stable in the presence of stabilizing addenda.

35

Table IV

40

45

50

Table IV						
Dye Retained from Initial Density 1.0 Coupler + Addenda Emulsion with ADD-1						
Coupler	Туре	Addenda	21 days			
C-2	Comp	None	53%			
Y-2	Inv	None	77%			
C-2	Comp	Cmpd. 1	75%			
Y-2	Inv	Cmpd. 1	84%			
C-2	Comp	Cmpd. 2	74%			
Y-2	Inv	Cmpd. 2	87%			
C-2	Comp	Cmpd. 3	74%			
Y-2	Inv	Cmpd. 3	87%			
C-2	Comp	P1	74%			
Y-2	Inv	P1	80%			

Claims

5

10

15

20

25

30

35

40

45

50

55

1. A photographic element comprising a light sensitive silver halide emulsion layer having associated therewith an open chain α-carbonyl acetanilide yellow dye-forming coupler having the formula:

R₆

R₆

R₇

R₈

R₈

R₈

R₈

R₈

R₈

R₈

R₁

R₁

R₁

R₁

R₁

R₂

R₂

R₂

R₂

R₃

R₄

R₄

R₄

R₅

R₄

R₅

R₇

R₈

R₈

R₁

wherein

 R_1 is selected from the group consisting of alkyl, aryl, heterocyclic, and amino groups, provided that R_1 may form a ring bonded to another carbon atom which is a member of Ring "A";

each R_2 is independently selected from the group consisting of t ose substituents having a Hammett's sigma value of 0 or less, and m is from 0 to 4;

each R_3 and R_4 for each of the n carbon atoms is independently selected from the group consisting of hydrogen, alkoxy, aryl, heterocyclic, aryloxy, amino and alkyl groups, and n is 0 to 16;

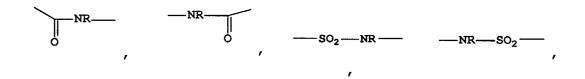
each R_5 is independently selected from the group consisting of halogen, amino, alkyl groups, and groups linked to the "B" ring by oxygen or sulfur, and p is 0 to 3, provided that two R_5 groups may join to form a ring; each L is independently a divalent linking group and q is 0 to 3; and

Ring "A" is bonded indirectly to the 3-, 4-, or 5-position of Ring "B",

R₆ is selected from the group consisting of alkyl, aryl, and amino groups; and

- (1) when an R_5 is halogen, Z is hydrogen or a coupling-off group selected from the group consisting of:
 - (a) an aryloxy or arylthio group;
 - (b) a heterocyclic group containing, in a five or six membered ring, one or two nitrogen atoms, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring; and
 - (c) a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group; and
- (2) when no R_5 is halogen, Z is hydrogen, or a group capable of coupling-off when the coupler reacts with an oxidized color developing agent

provided that if L is other than



wherein R is hydrogen or an alkyl group and R' is an alkylene group, then there is present at least one R₂ substituent on ring "A" ortho to the acyloxy group to which R1 is attached.

- 2. The element of claim 1 wherein said coupling-off group is as defined in (1)(b) or (1)(c) of claim 1 when an R_5 is halogen, or is a heterocyclic group containing, a nitrogen atom in a five or six membered ring, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring when no R_5 is halogen.
 - **3.** The element of claim 1 wherein said coupling-off group is a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group.
 - 4. The element of claim 1 wherein said coupling-off group is an aryloxy or arylthio group.
 - **5.** The element of claim 1 wherein m is at least 1.
 - **6.** The element of claim 5 wherein there is at least one R₂ substituent on ring "A" ortho to the acyloxy group to which R₁ is attached.
 - 7. The element of claim 6 wherein said at least one R₂ substituent on ring "A" ortho to the acyloxy group to which R₁ is attached contains branching.
 - **8.** The element of claim 7 wherein said at least one R₂ substituent on ring "A" ortho to the acyloxy group to which R₁ is attached is a branched alkyl group.
- **9.** The element of claim 8 wherein said at least one R₂ substituent on ring "A" ortho to the acyloxy group to which R₁ is attached is selected from the group consisting of i-propyl, t-butyl, t-amyl, and t-octyl groups.
 - 10. The element of claim 1 wherein R₁ contains at least 4 carbon atoms.
- 11. The element of claim 1 wherein at least one R₅ is bonded at the 2-,4-, or 6-position of ring "B".

Patentansprüche

1. Fotografisches Element, das eine lichtempfindliche Silberhalogenidemulsionsschicht umfasst, die mit einem einen gelben Farbstoff bildenden offenkettigen α-Carbonylacetanilid-Kuppler der folgenden Formel versehen ist:

dadurch gekennzeichnet, dass

- R₁ aus der Gruppe der Alkylgruppen, Arylgruppen, heterocyclischen Gruppen und Aminogruppen ausgewählt wird, vorausgesetzt, dass R₁ mit einem Kohlenstoffatom des Rings "A" einen Ring bilden kann;
- jede Gruppe R_2 unabhängig von jeder anderen aus der Gruppe der Substituenten ausgewählt wird, die einen

15

5

25

. .

P

40

50

- Hammettschen $\sigma_{\text{\tiny D}}$ -Wert von 0 oder kleiner haben, und m einen Wert zwischen 0 und 4 hat;
- jede Gruppe R₃ und R₄ an jedem der n Kohlenstoffatome unabhängig von jeder anderen aus der Gruppe von Wasserstoff, Alkoxygruppen, Arylgruppen, heterocyclischen Gruppen, Aryloxygruppen, Aminogruppen und Alkylgruppen ausgewählt wird und n einen Wert von 0 bis 16 hat;
- jede Gruppe R₅ unabhängig von jeder anderen aus der Gruppe von Halogen, Aminogruppen, Alkylgruppen und Gruppen ausgewählt wird, die über Sauerstoff oder Schwefel an den "B"-Ring gebunden sind, und p zwischen 0 und 3 liegt, sofern zwei R₅-Gruppen zu einem Ring zusammentreten können;
- jedes L unabhängig von jedem anderen eine zweiwertige Brückengruppe ist und q zwischen 0 und 3 liegt; und
- Ring "A" indirekt mit der Position 3, 4 oder 5 von Ring "B" verknüpft ist,

5

10

15

20

25

30

40

45

- R₆ aus der Gruppe der Alkyl-, Aryl- und Aminogruppen ausgewählt wird; und
 - (1), wenn eine R₅-Gruppe Halogen ist, ist Z Wasserstoff oder eine Kupplungs-Abgangsgruppe, die aus der folgenden Gruppe von Gruppen ausgewählt wird:
 - a) einer Aryloxygruppe oder Alkylthiogruppe;
 - b) einem Heterocyclus, der in einem Fünf- oder Sechsring ein oder zwei Stickstoffatome enthält, wobei die Gruppe Z an den Kuppler-Rest durch ein Ringstickstoffatom gebunden ist; und
 - c) einer Benzotriazol-Gruppe, wobei die Gruppe Z an den Kuppler-Rest durch ein Stickstoffatom der Triazolgruppe gebunden ist; und
 - (2) wenn keine R₅-Gruppe Halogen ist, ist Z Wasserstoff oder kann als Kupplungs-Abgangsgruppe fungieren, wenn der Kuppler mit einem oxydierten Farbentwickler reagiert, sofern L nicht als eine der folgenden Gruppierungen mit Wasserstoff oder einer Alkylgruppe für R und einer Alkylengruppe für R' vorliegt,

dann muss sich an Ring "A" mindestens ein R_2 -Substituent in ortho-Stellung zur den R_1 -Rest tragenden Acyloxy-Gruppe befinden.

- 2. Fotografisches Element nach Anspruch 1, dadurch gekennzeichnet, dass die Kupplungs-Abgangsgruppe wie in (1) b) oder (1) c) von Anspruch 1 definiert ist, wenn R₅ Halogen ist, oder eine heterocyclische Gruppe ist, die ein Stickstoffatom in einem Fünf- oder Sechsring enthält, und dass die Gruppe Z an den Kuppler-Rest durch ein Ringstickstoffatom gebunden ist, wenn keine der R₅-Gruppen Halogen ist.
- 55 **3.** Fotografisches Element nach Anspruch 1, dadurch gekennzeichnet, dass die Kupplungs-Abgangsgruppe eine Benzotriazol-Gruppe ist und die Gruppe Z an den Kuppler-Rest durch ein Stickstoffatom der Triazolgruppe gebunden ist.

- **4.** Fotografisches Element nach Anspruch 1, dadurch gekennzeichnet, dass die Kupplungs-Abgangsgruppe eine Aryloxy- oder Arylthiogruppe ist.
- 5. Fotografisches Element nach Anspruch 1, dadurch gekennzeichnet, dass m mindestens gleich 1 ist
- **6.** Fotografisches Element nach Anspruch 5, dadurch gekennzeichnet, dass sich mindestens ein R₂-Substituent an Ring "A" in ortho-Stellung zur den R₁-Rest tragenden Acyloxy-Gruppe befindet.
- 7. Fotografisches Element nach Anspruch 6, dadurch gekennzeichnet, dass der mindestens eine R₂-Substituent, in ortho-Stellung zur den R₁-Rest tragenden Acyloxy-Gruppe an Ring "A", verzweigt ist.
- **8.** Fotografisches Element nach Anspruch 7, dadurch gekennzeichnet, dass der mindestens eine R₂-Substituent, in ortho-Stellung zur den R₁-Rest tragenden Acyloxy-Gruppe an Ring "A", eine verzweigte Alkylgruppe ist.
- 9. Fotografisches Element nach Anspruch 8, dadurch gekennzeichnet, dass der mindestens eine R₂-Substituent, in ortho-Stellung zur den R₁-Rest tragenden Acyloxy-Gruppe an Ring "A", aus der Gruppe der i-Propyl-, t-Butyl-, t-Amyl- und t-Octyl-Reste gewählt wird.
 - **10.** Fotografisches Element nach Anspruch 1, dadurch gekennzeichnet, dass R₁ mindestens 4 Kohlenstoffatome enthält.
 - **11.** Fotografisches Element nach Anspruch 1, dadurch gekennzeichnet, dass mindestens ein R₅-Substituent in Position 2, 4 oder 6 an Ring "B" gebunden ist.

Revendications

5

10

20

25

30

35

40

45

50

55

1. Elément photographique comprenant une couche d'émulsion aux halogénures d'argent photosensibles à laquelle est associé un coupleur formateur de colorant jaune à base d'α-carbonylacétanilide en chaîne ouverte répondant à la formule :

où:

R₁ est choisi dans le groupe constitué du groupe alkyle, du groupe aryle, d'un hétérocycle et d'un groupe amino. à condition que R₁ puisse former un noyau lié à un autre atome de carbone qui est un membre du noyau "A" :

chaque groupe R_2 est choisi séparément dans le groupe constitué des substituants ayant une valeur sigma de Hammett inférieure ou égale à 0; et m est compris entre 0 et 4;

chaque groupe R_3 et R_4 rattaché à chacun des n atomes de carbone est choisi séparément dans le groupe constitué de l'hydrogène, des groupes alkoxy, aryle, d'un hétérocycle, des groupes aryloxy, amino et alkyle, et n est compris entre 0 et 16 ;

chaque groupe R_5 est choisi séparément dans le groupe constitué d'un halogène, d'un groupe amino, d'un groupe alkyle et des groupes liés au noyau "B" par un oxygène ou un soufre, et p est compris entre 0 et 3, à condition que deux groupes R_5 puissent se lier pour former un noyau ;

chaque groupe L représente séparément un groupe de liaison divalent et q est compris entre 0 et 3 ; et le noyau "A" est lié indirectement à la position 3, 4 ou 5 du noyau "B",

le groupe R₆ est choisi dans le groupe constitué des groupes alkyle, aryle et amino ; et

- (1) lorsqu'un groupe R_5 est un halogène, Z est un hydrogène ou un groupe qui se sépare au couplage choisi dans le groupe constitué de :
 - (a) un groupe aryloxy ou arylthio;

5

10

15

20

25

30

35

45

- (b) un hétérocycle contenant, dans un noyau à cinq ou six membres, un ou deux atomes d'azote, dans lequel le groupe Z est lié au reste du coupleur par l'intermédiaire d'un atome d'azote contenu dans le noyau ; et
- (c) un groupe benzotriazole dans lequel le groupe Z est lié au reste du coupleur par l'intermédiaire d'un atome d'azote contenu dans le groupe triazole ; et
- (2) lorsqu'aucun des groupes R₅ ne représente un halogène, Z est un hydrogène ou un groupe capable de se séparer au couplage lorsque le coupleur réagit avec un développateur chromogène oxydé à condition que si le groupe L est autre que

_____ ou ______

dans lesquels R représente un hydrogène ou un groupe alkyle et R' représente un groupe alkylène, il y ait au moins un substituant R_2 sur le noyau "A" en position ortho par rapport au groupe acyloxy auquel R_1 est rattaché.

- 2. Elément photographique selon la revendication 1, dans lequel ledit groupe qui se sépare au couplage est tel que défini en (1)(b) ou (1)(c) de la revendication 1, lorsqu'un substituant R₅ représente un halogène, ou est un hétérocycle contenant un atome d'azote dans un noyau à cinq ou six membre, dans lequel le groupe Z est lié au reste du coupleur par l'intermédiaire d'un atome d'azote contenu dans le noyau, lorsqu'aucun des substituants R₅ ne représente un halogène.
 - 3. Elément photographique selon la revendication 1, dans lequel ledit groupe qui se sépare au couplage est un groupe benzotriazole dans lequel le groupe Z est lié au reste du coupleur par l'intermédiaire d'un atome d'azote contenu dans le groupe triazole.
- 50 **4.** Elément photographique selon la revendication 1, dans lequel ledit groupe qui se sépare au couplage est un groupe aryloxy ou arylthio.
 - 5. Elément photographique selon la revendication 1, dans lequel m est au moins égal à 1.
- 6. Elément photographique selon la revendication 5, dans lequel au moins un substituant R₂ sur le noyau "A" est en position ortho par rapport au groupe acyloxy auquel R₁ est rattaché.
 - 7. Elément photographique selon la revendication 6, dans lequel ledit au moins un substituant R_2 sur le noyau "A"

en position ortho par rapport au groupe acyloxy auquel R₁ est rattaché contient une ramification.

- **8.** Elément photographique selon la revendication 7, dans lequel ledit au moins un substituant R₂ sur le noyau "A" en position ortho par rapport au groupe acyloxy auquel R₁ est rattaché est un groupe alkyle ramifié.
- 9. Elément photographique selon la revendication 8, dans lequel ledit au moins un substituant R₂ sur le noyau "A" en position ortho par rapport au groupe acyloxy auquel R₁ est rattaché est choisi dans le groupe constitué des groupes i-propyle, t-butyle, t-amyle et t-octyle.
- **10.** Elément photographique selon la revendication 1, dans lequel le substituant R₁ contient au moins 4 atomes de carbone.
 - **11.** Elément photographique selon la revendication 1, dans lequel au moins l'un des substituants R₅ est lié à la position 2, 4 ou 6 du noyau "B".