(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 520 498 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **92110838.7**

(22) Date of filing: **26.06.92**

(51) Int. Cl.5: **G03C 7/305**

(30) Priority: **28.06.91 US 722807**

(43) Date of publication of application:
30.12.92 Bulletin 92/53

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU MC NL PT SE

(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650-2201(US)

(72) Inventor: **Begley, William James, c/o**
EASTMAN KODAK COMPANY
Patent Legal Staff, 343 State Street
Rochester New York 14650-2201(US)
Inventor: **Chen, Teh-Hsuan, c/o EASTMAN**
KODAK COMPANY
Patent Legal Staff, 343 State Street
Rochester New York 14650-2201(US)

(74) Representative: **Brandes, Jürgen, Dr. rer. nat. et al**
Wuesthoff & Wuesthoff, Patent- und
Rechtsanwälte, Schweigerstrasse 2
W-8000 München 90(DE)

(54) Method of preparation of photographic coupler.

(57) A method of preparing a photographic coupler that comprises a parent coupler moiety (COUP) containing a phenoxy coupling-off group having an animomethyl group in the 2-position of the phenoxy coupling-off group comprises (A) reacting (a) a coupler moiety containing a phenoxy coupling-off group having a hydroxyalkyl or hydroxyaryl group in the 2-position wherein the hydroxy is on the alpha carbon atom of the alkyl or aryl group, with (b) a halogenating agent under ambient conditions; then, (B) reacting the product from step (A) with an amine compound. The product can be reacted with phosgene or a bis-thio compound to form an intermediate that is also useful for forming photographic couplers. The resulting products are useful in photographic silver halide materials and processes.

This invention relates to a method of preparing a photographic coupler that comprises a parent coupler moiety (COUP) containing a phenoxy coupling-off group having an aminoalkyl or aryl group in the 2-position of the phenoxy coupling-off group.

It is known in the photographic art to use photographic couplers to form dye images. It is also known that various couplers can be used to release a photographically useful group (PUG) from a coupler moiety (COUP) in a photographic material and process. Such couplers are described in, for example, *Research Disclosure*, December 1989, Item No. 308119, paragraph VII, and the references listed in this publication.

In preparing such couplers it has been desirable to provide methods that enable tailoring of the substituent groups without complicated multiple synthesis steps under difficult reaction conditions. It has been especially desirable to provide methods that enable formation of such couplers containing substituent groups that are useful in a photographic material and process.

In this regard it has been especially desirable to provide a method of forming a coupler containing a releasable photographically useful group wherein the method enables tailoring of substituent groups. This is especially the case for couplers that have a water solubilizing group on the parent coupler moiety to enable dye formed from the coupler to wash out of the photographic material containing such a coupler upon processing. Such couplers are described in, for example, US-A-4,482,629; and copending serial Nos. 483,600, filed February 22, 1990, titled "Photographic Material and Process Comprising a Compound Capable of Forming a Wash-Out Dye", of Begley and others.

It has been found that such advantages can be provided by a method of preparing a photographic coupler that comprises parent coupler moiety (COUP) containing a phenoxy coupling-off group having an aminomethyl group in the 2-position of the phenoxy coupling-off group

wherein the process comprises (A) reacting (a) a coupler moiety containing a phenoxy coupling-off group having a hydroxyalkyl or hydroxyaryl group in the 2-position; with (b) a halogenating agent wherein the hydroxy is on the alpha carbon atom of the alkyl or aryl group; then, (B) reacting the product from step (A) with an amine compound.

In particular, this method enables the use of substituents on the amine compound and the substitution of the amine upon completion of step (B) that otherwise would not be enabled. For example, a Schiff's base method of forming the compounds as described would not easily enable substitution of a methylamine group on the compound formed.

The coupler moiety (COUP) as described can be any coupler moiety known in the photographic art, preferably a naphtholic coupler moiety or acetanilide coupler moiety. A highly preferred coupler moiety is a naphtholic coupler moiety containing a water solubilizing group, such as $-CONH_2$ or $-CONHCH_3$, in the 2-position of the naphtholic nucleus. Such coupler moieties typically react with oxidized color developing agent in photographic processing to yield colorless compounds or colored compounds.

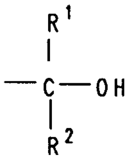
The coupler moiety can be ballasted or unballasted. It can be monomeric, or it can be a dimeric, oligomeric or polymeric coupler.

The coupler moiety is typically a dye-forming coupler such as a colored or colorless dye-forming coupler and can be diffusible or non-diffusible. The coupler moiety is preferably a 2-equivalent coupler of the open-chain ketomethylene, pyrazolone, pyrazolotriazole, pyrazolobenzimidazole, phenol or naphthol type know in the photographic art.

The phenoxy coupling-off group can be any such coupling-off group known in the photographic art provided that the phenoxy group contains a substituted or unsubstituted hydroxyalkyl as described, in the 2-position of the phenoxy group.

The phenoxy coupling-off group can be unsubstituted except for the substituted or unsubstituted hydroxyalkyl group. Optionally the phenoxy coupling-off group can be substituted with groups that do not adversely affect the coupler or the photographic material in which the coupler is used or the reaction as described. Such substituent groups include, for example, groups known to be useful on phenoxy coupling-off groups in the photographic art, such as ballast groups, alkyl, aryl, nitro, sulfonamide, sulfamyl, carbamoyl, ethers, esters, carbonamide, and the like groups.

The described hydroxyalkyl group, preferably containing 1 to 40 carbon atoms, has the hydroxy group on the alpha carbon atom of the alkyl. This hydroxyalkyl group is represented by the formula:



$$-\overset{R^1}{\underset{R^2}{C}}-OH$$

wherein R^1 and R^2 are individually hydrogen or substituents that do not adversely affect the described synthesis, such as alkyl or phenyl, but preferably hydrogen. The hydroxyalkyl group is preferably hydroxymethyl.

The described unsubstituted or substituted hydroxyalkyl group, preferably containing 1 to 40 carbon atoms, also has the hydroxy group on the alpha carbon atom.

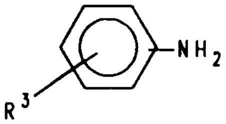
Substituents in the described hydroxyalkyl groups that can adversely affect the described synthesis include other hydroxyl and amine groups.

The halogening agent as described can be any halogenating agent known in the organic compound synthesis art. Such halogenating agents are preferably brominating agents but can be chlorinating agents. Illustrative examples of such halogenating agents include, HBr, phosphorous tribromide, $SOCl_2$, PCl2, and PCl_5 which do not affect the remainder of the molecule.

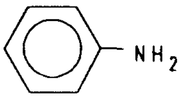
The halogenating reaction is carried out under conditions of pressure and temperature that are dependent upon the halogenating agent used. For example, when using phosphorous tribromide, the pressure and temperature are typical normal atmospheric conditions. When HBr is used, it can be desirable to use elevated temperatures, such as 60 ° C. It is not necessary to carry out this reaction above or below normal atmospheric pressure. Typically the reaction is carried out at a temperature within the range of 0 to 100 ° C.

The halogenating reaction is carried out to completion. Typically an excess of halogenating agent is used in the reaction.

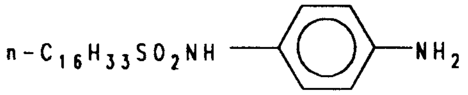
The step (B) as described is carried out with any amine compound that reacts with the product of step (A). The amine compound is preferably an alkylamine or arylamine. The alkylamine is typically an alkylamine comprising 1 to 40 carbon atoms, such as methylamine, ethylamine, n-propylamine, i-propylamine, n-butylamine, t-butylamine, ethanolamine, chloroethylamine, or other substituted alkylamines. The arylamine is typically an unsubstituted or substituted phenylamine containing 6 to 40 carbon atoms. Illustrative examples of such arylamines include aniline, methoxyaniline, chloroaniline or nitroaniline. Illustrative phenylamine compounds are represented by the formula:



R_3 is $-NHSO_2R^4$, $-SO_2NHR^5$, $-NHCOR^6$, $-CONHR^7$, $-CO_2R_8$, $-OR^9$ or hydrogen: wherein R^4 , R^5 , R^6 , R^7 , R^8 , and R^9 individually are substituents that do not adversely affect the described synthesis, such as alkyl, for instance alkyl containing 1 to 40 carbon atoms, or aryl, for instance phenyl. The arylamine is preferably



or



The reaction of the product of step (A) as described with the amine compound is carried out under conditions of pressure and temperature that are dependent upon the amine compound used, 0 ° to 100 ° C being preferred. Typically the reaction is carried out under normal atmospheric conditions of temperature and pressure. Elevated temperatures and pressures above or below may be required depending on the amine. The described reaction is typically carried out at a temperature within the range of 0 to 100 ° C. Less nucleophilic amines such as nitroanilines may require elevated temperatures. The more nucleophilic amines may require reaction at room temperature (20 ° C) or below.)

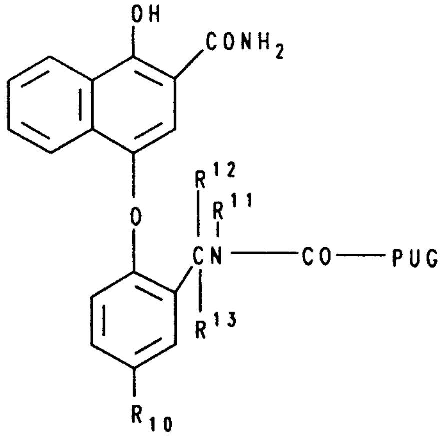
The reaction of the product of step (A) as described with the amine compound is typically carried to completion. The concentrations of reactants can be mixed in stoichiometric ratios; however, typically the amine compound is typically added in excess of that required.

The product of step (B) is typically reacted with phosgene under normal atmospheric conditions and the product of this reaction then reacted with a photographically useful compound. This enables formation of a coupler that is capable of releasing a photographically useful group (PUG) in a photographic material upon processing.

Optionally the product from the reaction in step (B) can be reacted with a bis-mercaptotetrazole compound known in the photographic art, such as bis-phenylmercaptotetrazole or benzotriazole carbonyl chloride. This reaction can also be carried out under normal atmospheric pressure and temperatures preferably within the range of 0 to 100 ° C. This enables formation of a coupler that is capable of releasing a mercaptotetrazole development inhibitor moiety in a photographic material upon processing.

The described bis-mercaptotetrazole moiety can be any such compound known in the organic compound synthesis art, preferably those compounds known in the photographic art that enable formation of a development inhibitor releasing compound that is useful in a photographic silver halide material.

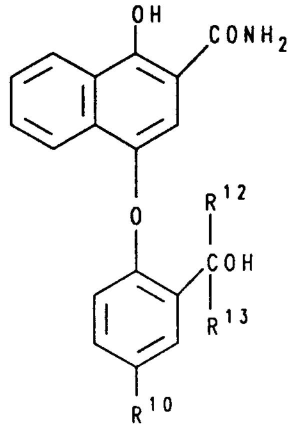
A preferred method as described is a method of forming a photographic coupler represented by the formula:



wherein PUG is a photographically useful group; R^{10} is a hydrogen or a photographic ballast group known in the photographic art; R^{11} is unsubstituted or substituted aryl or alkyl; R^{12} and R^{13} individually are hydrogen or substituents that do not adversely affect the coupler, preferably hydrogen; one of R^{10}, R^{11} , R^{12} or R^{13} is a photographic ballast group preferably R^{11}; comprising

(A) reacting

(a) a coupler moiety represented by the formula:



with

(b) a brominating or chlorinating agent under ambient conditions;

then

(B) reacting the product from step (A) with an unsubstituted or substituted arylamine or alkylamine; then

(C) reacting the product from step (B) with phosgene; then

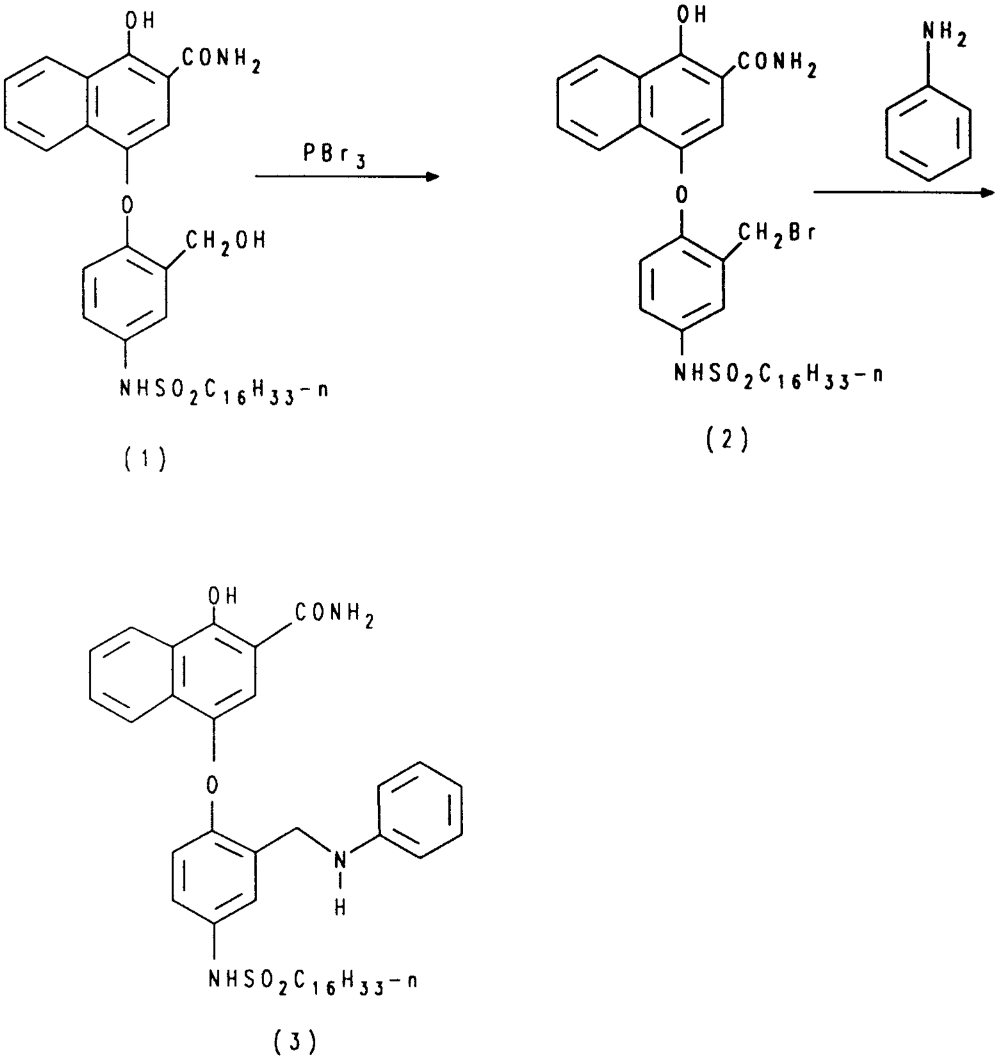
(D) reacting the product from step (C) with a photographically useful compound, preferably a development inhibitor compound.

The photographically useful group (PUG) can be, for example, any of the photographically useful compounds described in copending U.S. Patent Application Serial No. 483,601 of Begley and others filed, February 20, 1990, the disclosure of which is incorporated herein by reference. The PUG can be any group that is typically made available in a photographic element in an imagewise fashion. The PUG can be a photographic reagent or a photographic dye. A photographic reagent herein is a moiety that upon release further reacts with components in the photographic element, such as a development inhibitor, a development accelerator, a coupler (for example, a competing coupler, a dye-forming coupler, or a development inhibitor releasing coupler [DIR coupler]), a dye precursor, a dye, a developing agent (for example, a competing developing agent, a dye-forming developing agent, or a silver halide developing agent), a silver complexing agent, a fixing agent, an image toner, a stabilizer, a hardener, a tanning agent, a fogging agent, an ultraviolet radiation absorber, an antifoggant, a nucleator, a chemical or spectral sensitizer, or a desensitizer.

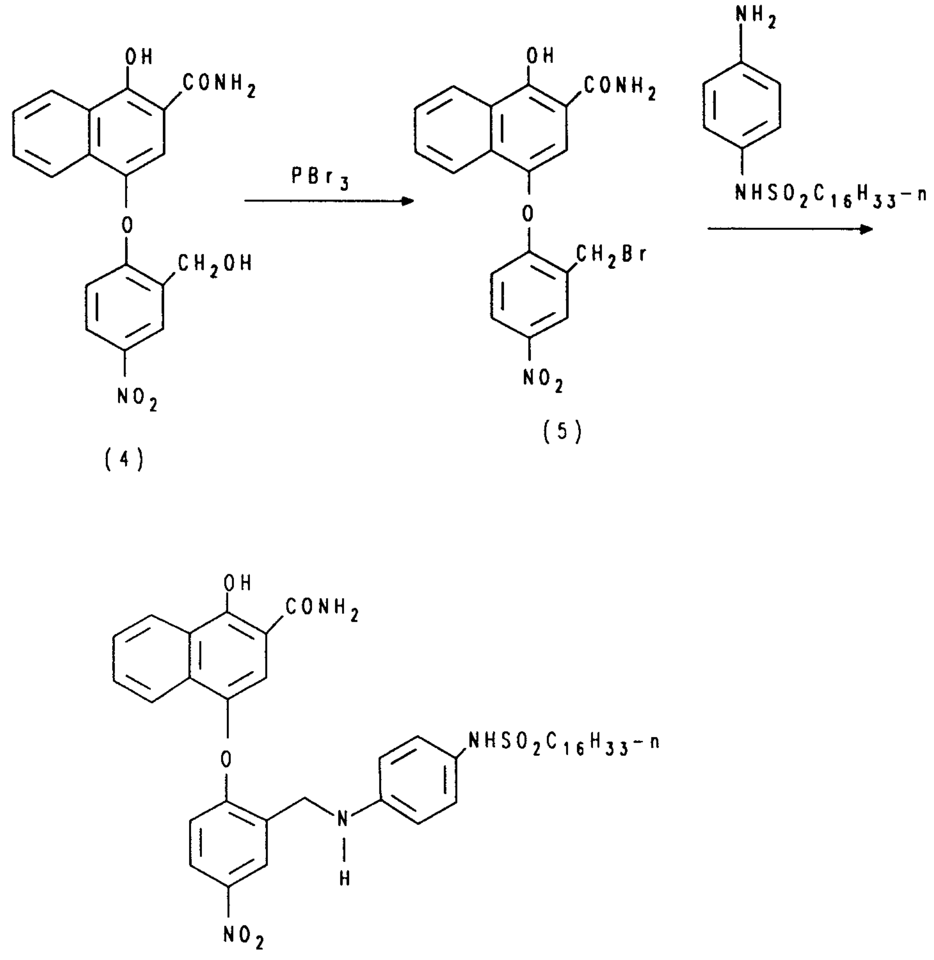
The PUG can be present in the coupling-off group as a preformed species or it can be in a blocked form or as a precursor. The PUG can be, for example, a preformed development inhibitor or the development inhibiting function can be blocked by being the point of attachment to the carbonyl group bonded to the PUG. Other examples are a preformed dye, a dye that is blocked to shift its absorption, and a leuco dye.

Preferred naphtholic compounds are prepared according to the following methods that are illustrative of the described process:

Example A


OH
CONH2
O
CH2OH
NHSO2C16H33-n
(1)
PBr3
OH
CONH2
O
CH2Br
NHSO2C16H33-n
(2)
NH2
OH
CONH2
O
N
H
NHSO2C16H33-n
(3)

Example B



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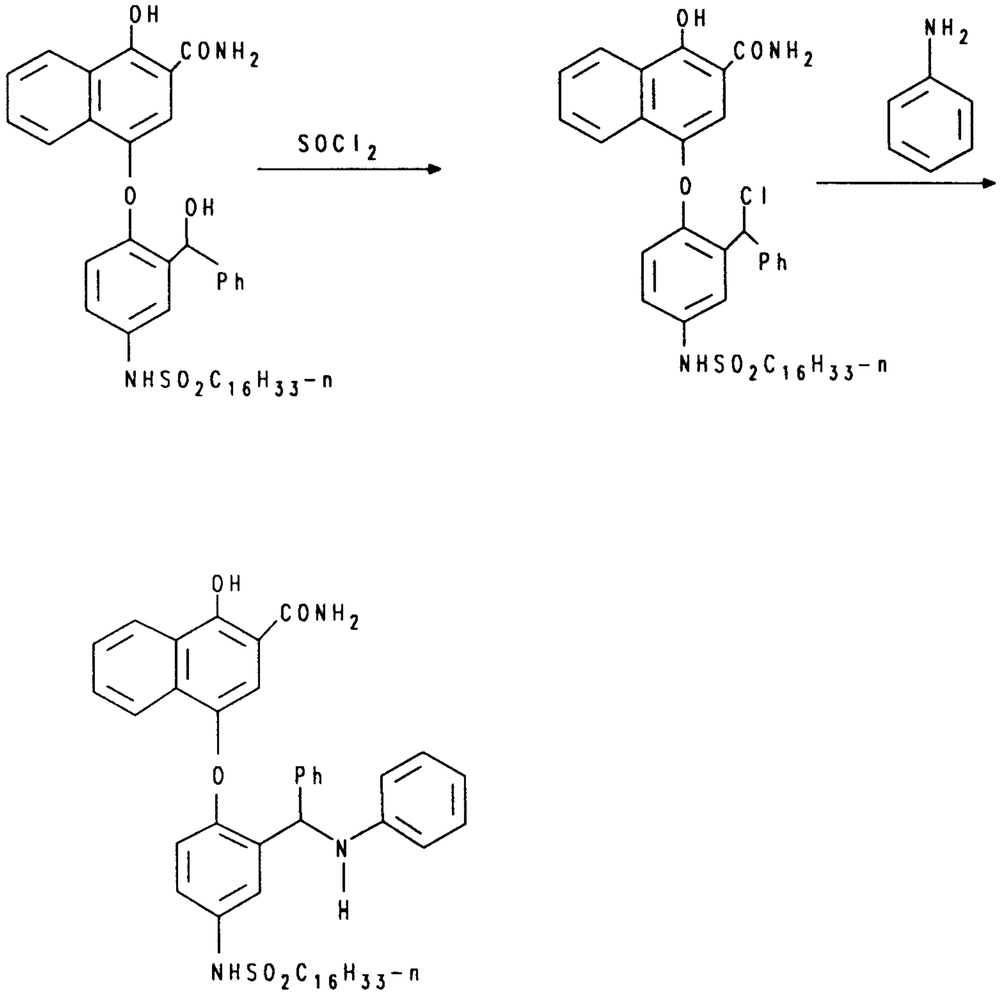
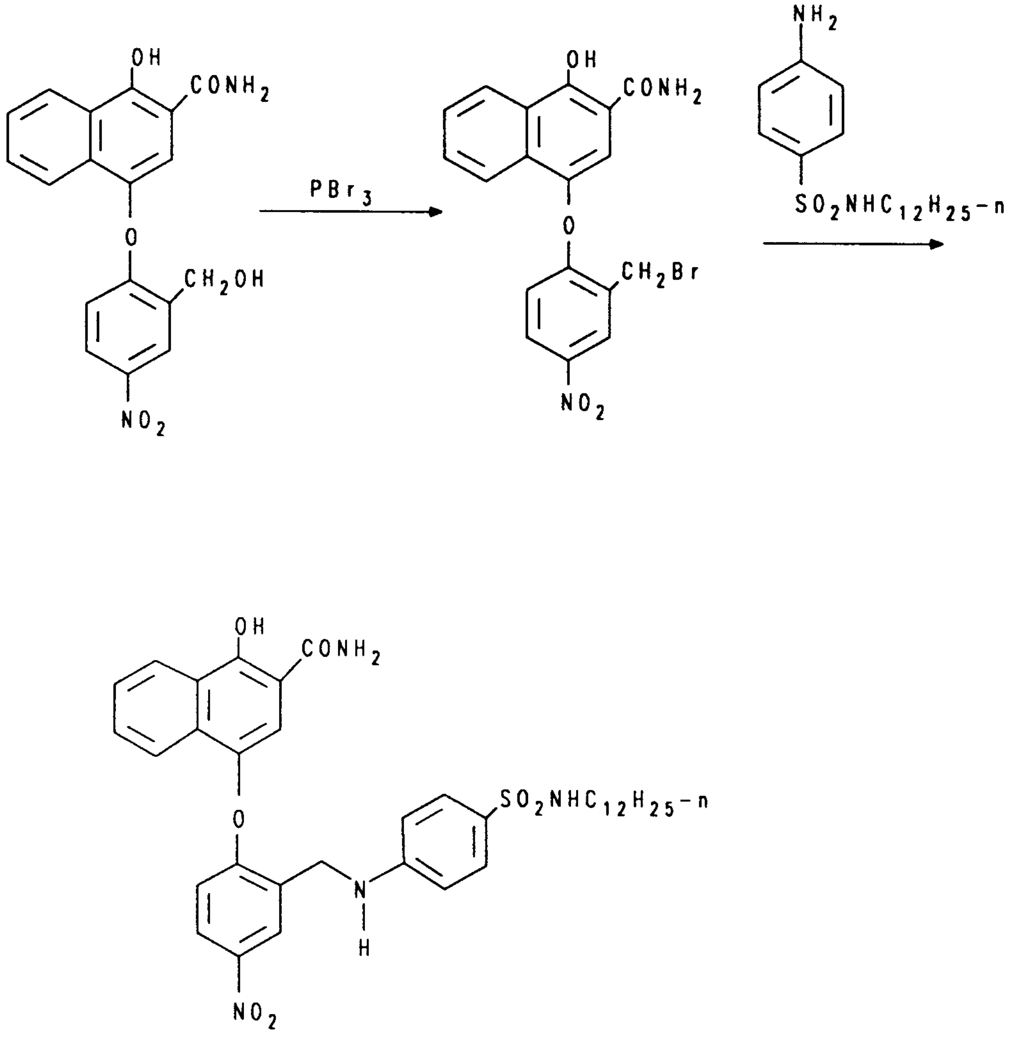
(5)

(6)

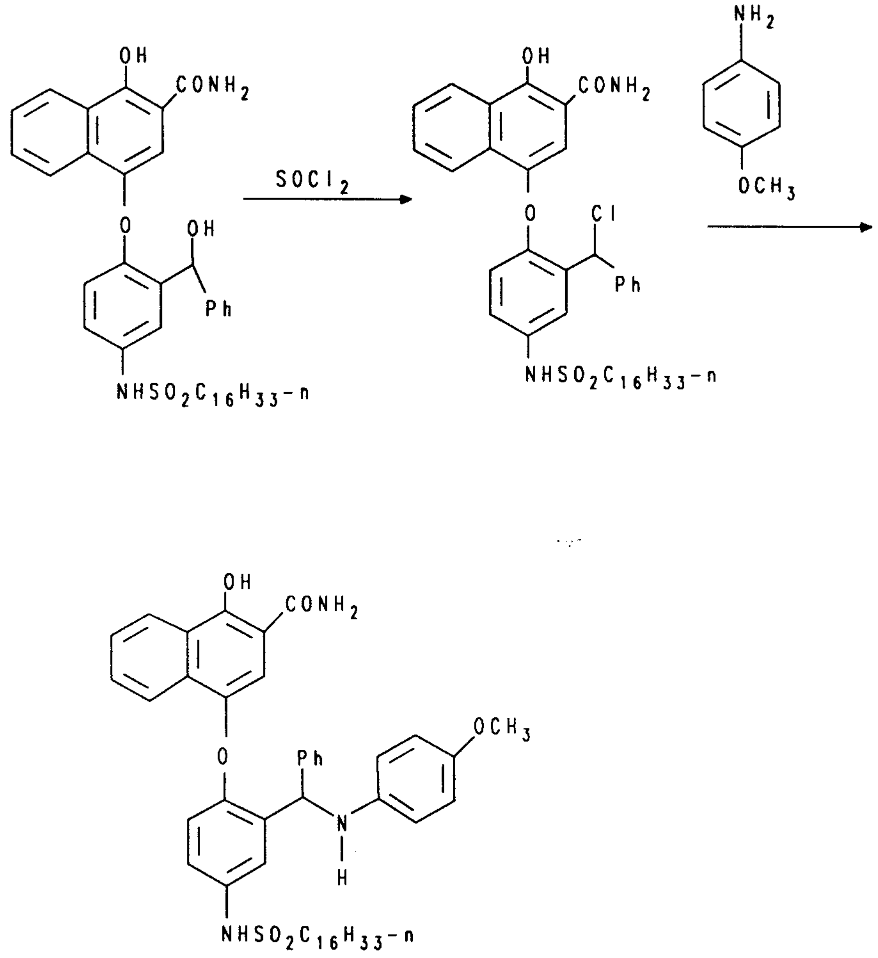
Example C


OH
CONH$_2$
O
OH
Ph
NHSO$_2$C$_{16}$H$_{33}$-n
SOCl$_2$
OH
CONH$_2$
O
Cl
Ph
NHSO$_2$C$_{16}$H$_{33}$-n
NH$_2$
OH
CONH$_2$
O
Ph
N
H
NHSO$_2$C$_{16}$H$_{33}$-n

Example D


OH
CONH2
O
CH2OH
NO2
PBr3
OH
CONH2
O
CH2Br
NO2
NH2
SO2NHC12H25-n
OH
CONH2
O
SO2NHC12H25-n
N
H
NO2

Example E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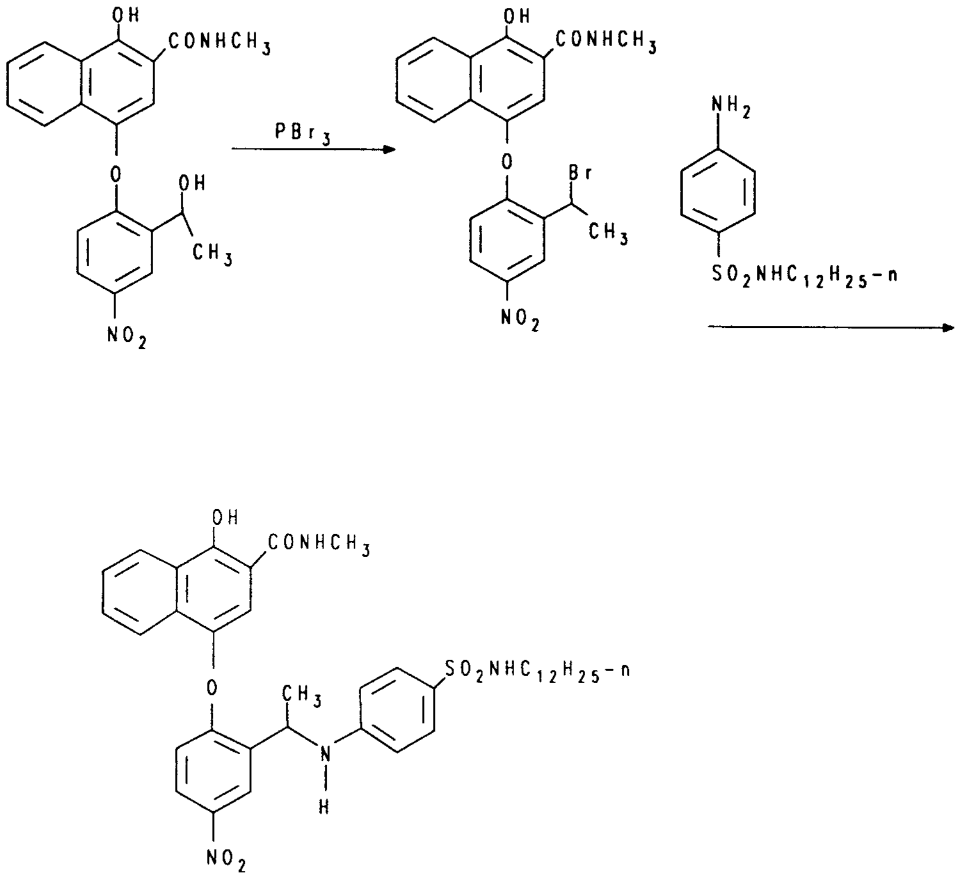
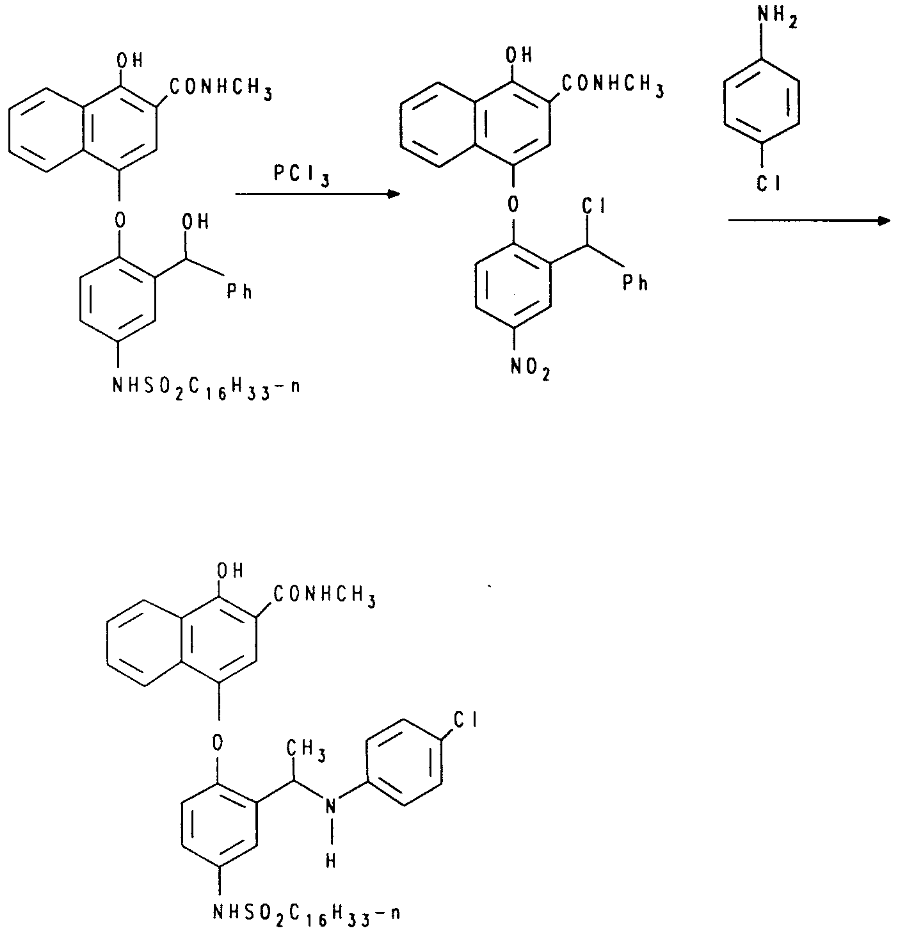
CONH2
O
OH
Ph
NHSO2C16H33-n
SOCl2
OH
CONH2
O
Cl
Ph
NHSO2C16H33-n
NH2
OCH3
OH
CONH2
O
Ph
N
H
OCH3
NHSO2C16H33-n

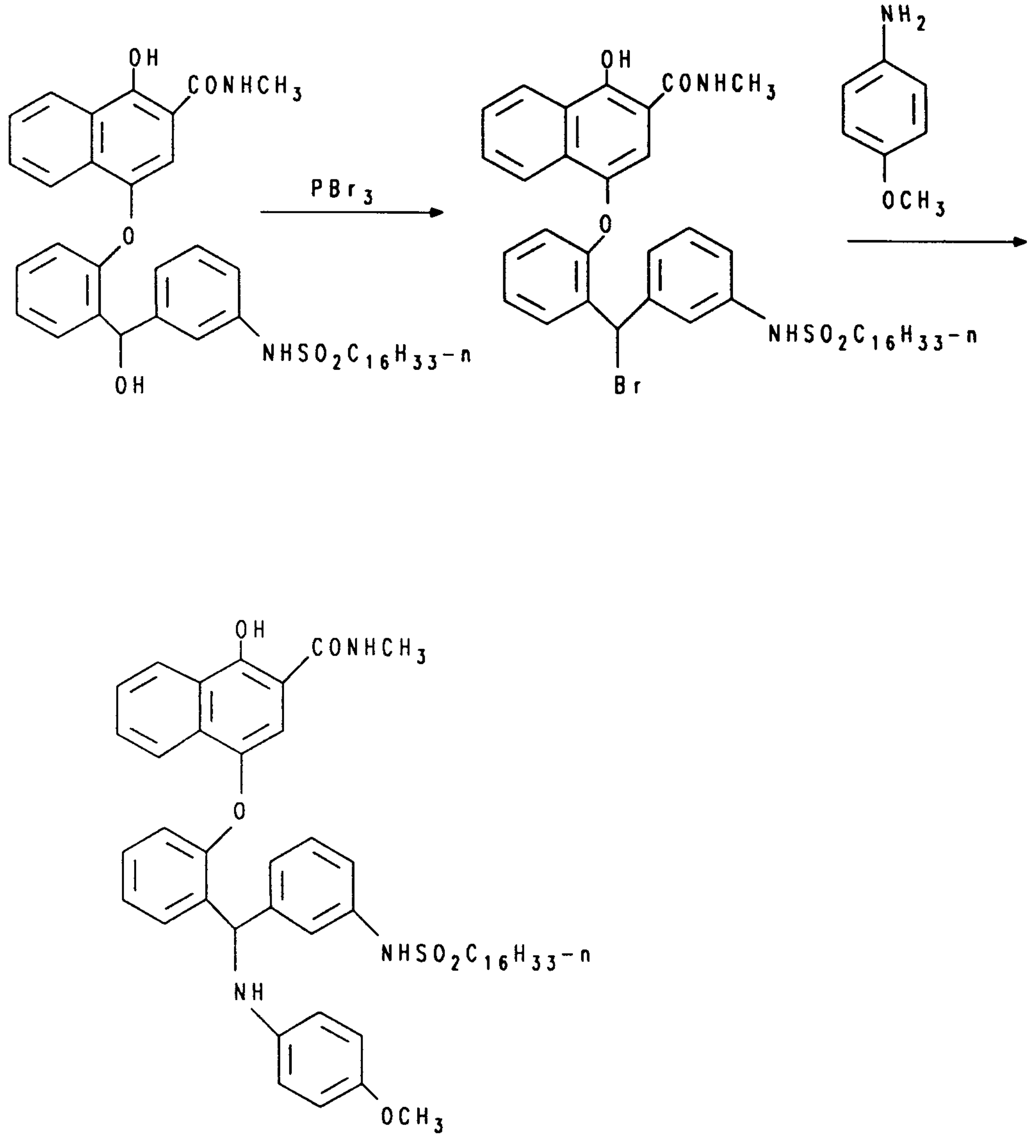
Example F


OH
CONHCH$_3$
O
OH
CH$_3$
NO$_2$
PBr$_3$
OH
CONHCH$_3$
O
Br
CH$_3$
NO$_2$
NH$_2$
SO$_2$NHC$_{12}$H$_{25}$-n
OH
CONHCH$_3$
O
CH$_3$
N
H
SO$_2$NHC$_{12}$H$_{25}$-n
NO$_2$

Example G



Example H



These compounds are photographic couplers that can be used in photographic materials and are compounds that can be used for preparation of other photographic couplers, as described, such as DIR and DIAR couplers.

The image dye-forming couplers can be incorporated in photographic elements and/or in photographic processing solutions, such as developer solutions, so that upon development of an exposed photographic element they will be in reactive association with oxidized color developing agent. Coupler compounds incorporated in photographic processing solutions should be of such molecular size and configuration that they will diffuse through photographic layers with the processing solution. When incorporated in a photographic element, as a general rule, the coupler compounds should be non-diffusible, that is they should be of such molecular size and configuration that they will not significantly diffuse or wander from the layer in which they are coated.

Photographic elements of this invention can be processed by conventional techniques in which color forming couplers and color developing agents are incorporated in separate processing solutions or compositions or in the element.

Photographic elements in which the compounds of this invention are incorporated can be a simple element comprising a support and a single silver halide emulsion layer or they can be multilayer, multicolor elements. The compounds of this invention can be incorporated in at least one of the silver halide emulsion layers and/or in at least one other layer, such as an adjacent layer, where they will come into reactive association with oxidized color developing agent which has developed silver halide in the emulsion layer.

The silver halide emulsion layer can contain or have associated with it, other photographic compounds, such as dye-forming couplers, colored masking couplers, and/or competing couplers. These other photographic couplers can form dyes of the same or different color and hue as the photographic couplers of this invention. Additionally, the silver halide emulsion layers and other layers of the photographic element can contain addenda conventionally contained in such layers.

A typical multilayer, multicolor photographic element can comprise a support having thereon a red-sensitive silver halide emulsion unit having associated therewith a cyan dye image-providing material, a green-sensitive silver halide emulsion unit having associated therewith a magenta dye image-providing material and a blue-sensitive silver halide emulsion unit having associated therewith a yellow dye image-providing material, at least one of the silver halide emulsion units having associated therewith a photographic coupler of the invention. Each silver halide emulsion unit can be composed of one or more layers and the various units and layers can be arranged in different locations with respect to one another.

The couplers of this invention can be incorporated in or associated with one or more layers or units of the photographic element. For example, a layer or unit affected by PUG can be controlled by incorporating in appropriate locations in the element a scavenger layer which will confine the action of PUG to the desired layer or unit. At least one of the layers of the photographic element can be, for example, a mordant layer or a barrier layer.

The light sensitive silver halide emulsions can include coarse, regular or fine grain silver halide crystals or mixtures thereof and can be comprised of such silver halides as silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide and mixtures thereof. The emulsions can be negative-working or direct-positive emulsions. They can form latent images predominantly on the surface of the silver halide grains or predominantly on the interior of the silver halide grains. The emulsion can be of the type used in reversal color photographic materials, color negative photographic materials, such as motion picture films and the like. They can be chemically and spectrally sensitized. The emulsions typically will be gelatin emulsions although other hydrophilic colloids are useful. Tabular grain light sensitive silver halides are particularly useful such as described in *Research Disclosure*, January 1983, Item No. 22534 and US-A-4,434,226.

The support can be any support used with photographic elements. Typical supports include cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polyethylene terephthalate film, polycarbonate film and related films or resinous materials as well as glass, paper, metal and the like. Typically, a flexible support is employed, such as a polymeric film or paper support. Paper supports can be acetylated or coated with baryta and/or an α-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

It is preferred that the coupling-off group contain a releasable PUG. Depending upon the nature of the particular PUG, the couplers can be incorporated in a photographic element for different purposes and in different locations.

In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to *Research Disclosure*, December 1978, Item 17643, published by Industrial Opportunities Ltd., Homewell Havant, Hampshire, P09 1EF, U.K., the disclosures of which are incorporated herein by reference. This publication will be identified hereafter by the term "Research Disclosure".

The photographic elements can be coated on a variety of supports as described in Research Disclosure Section XVII and the references described therein.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVIII and the processed to form a visible dye image as described in Research Disclosure Section XIX. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye.

Preferred color developing agents useful in the invention are p-phenylene diamines. Especially preferred are 4-amino-N,N-diethylaniline hydrochloride; 4-amino-3-methyl-N,N-diethylaniline hydrochloride; 4-amino-3-methyl-N-ethyl-ethyl-β-(methanesulfonamido)-ethylaniline sulfate hydrate; 4-amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate; 4-amino-3-β-(methanesulfonamido)-ethyl-N,N-diethyl-aniline hydrochloride; and 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluenesulfonic acid.

With negative-working silver halide, the processing step described above gives a negative image. To obtain a positive (or reversal) image, this step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form a dye, and then uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

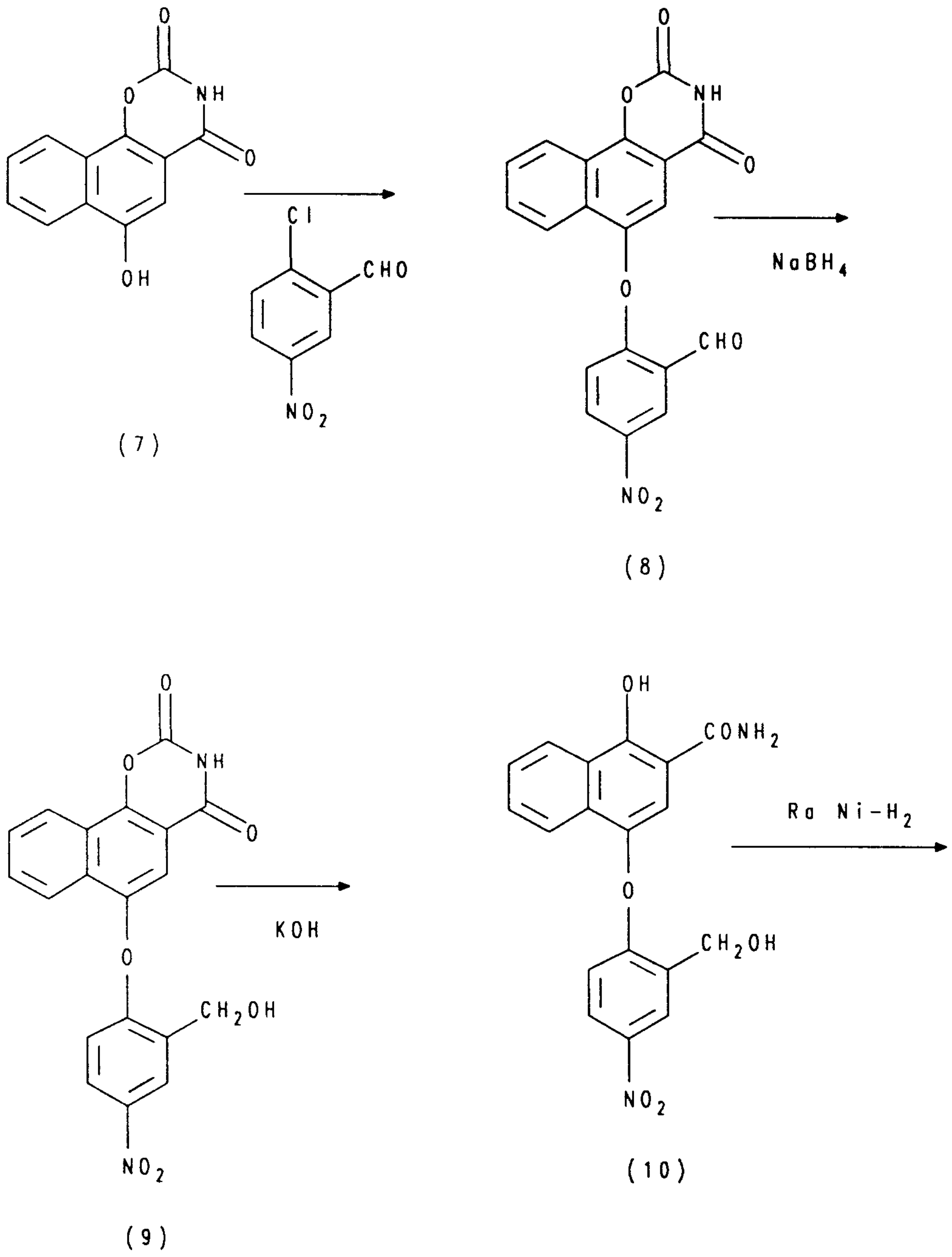
The described photographic materials and processes can be used with photographic silver halide emulsions and addenda known to be useful in the photographic art, as described in, for example, Research Disclosure, December 1989, Item No. 308,119 the disclosures of which are incorporated herein by reference.

Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver and silver halide, washing and drying.

The following examples further illustrate the invention:

Example 1 - Synthesis

The following preparation illustrates preparation of a compound according to the invention:



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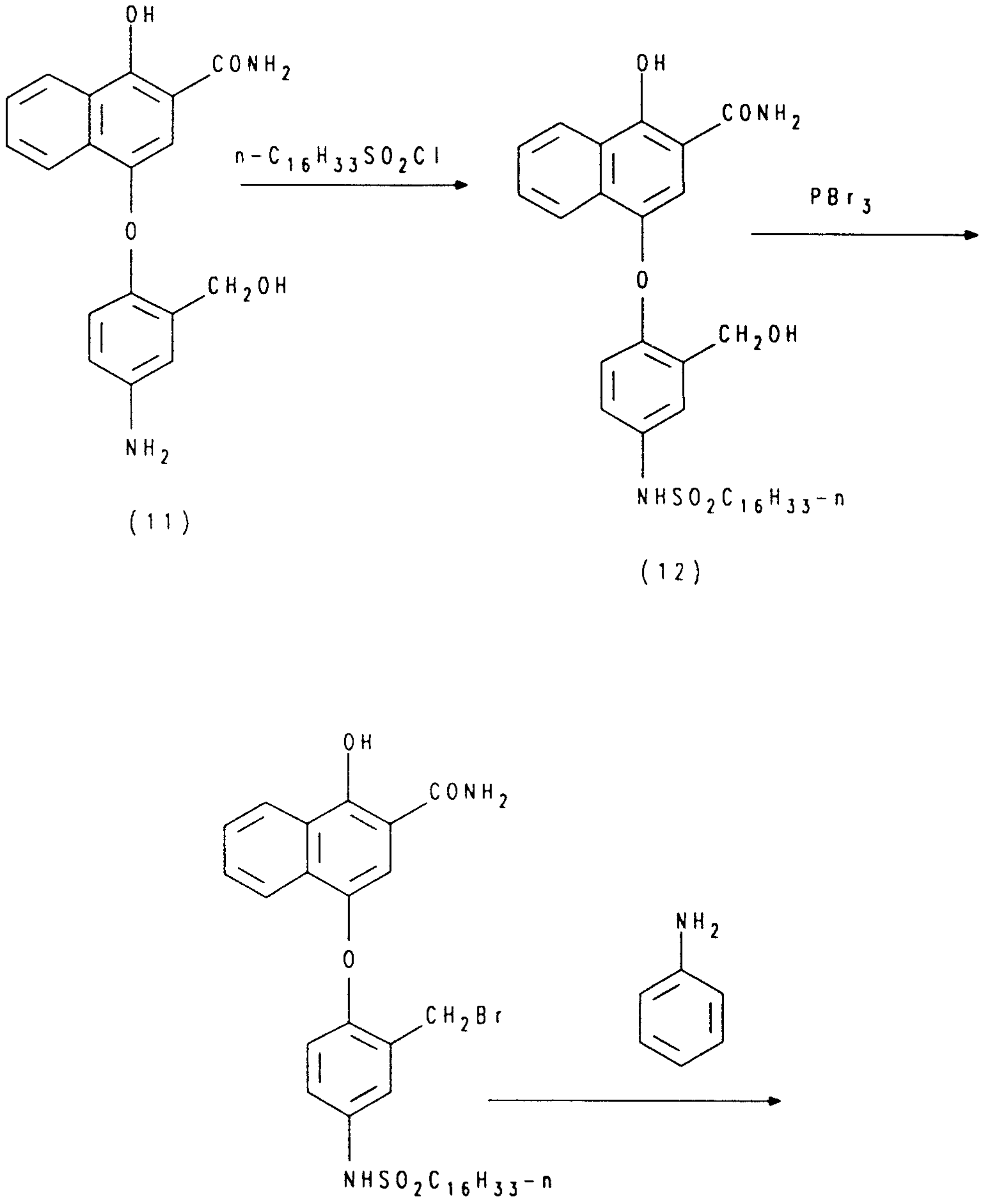
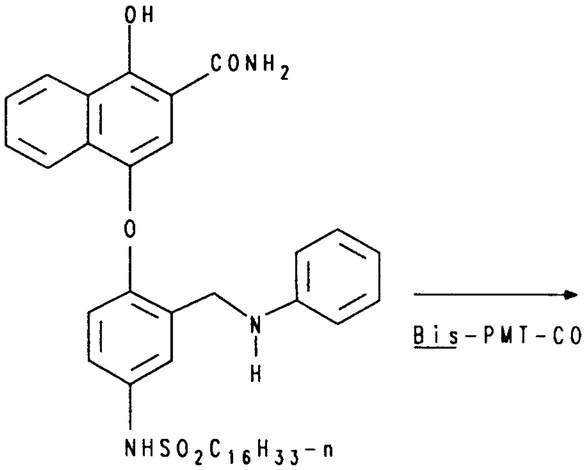
(10)


OH
CONH$_2$
O
CH$_2$OH
NH$_2$
n-C$_{16}$H$_{33}$SO$_2$Cl
NHSO$_2$C$_{16}$H$_{33}$-n
PBr$_3$
CH$_2$Br
NH$_2$

(11) (12) (13)



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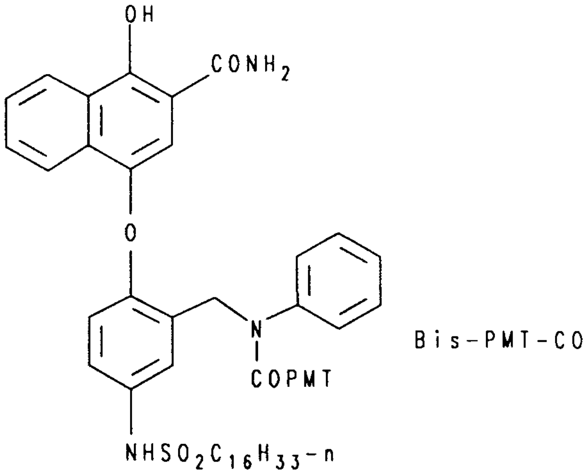


(15)

Experimental

Compound (8):

Compound (7), (20g, 87.26mMole), was taken up in deoxygenated DMSO, (200mL), and stirred under nitrogen. To this solution was added KOH, (10.06g of 85%, 152.71mMole), followed by deoxygenated water, (20mL). The reaction was stirred well at room temperature for approximately 30 minutes. 2-Chloro-5-nitrobenzaldehyde, (16.2g, 87.26mMole), was then added and stirring continued for an additional hour at room temperature. The thick reaction mixture was poured into 2N-HCl, (1L) with efficient stirring. When a suspension of uniform thickness had been achieved, ethyl acetate (200mL), was added and stirring continued for a further 15 minutes. The product, which precipitated out of solution, was filtered off and washed with some ethyl acetate to give pure compound (8), 25.7g, 78%.

Compound (9):

Compound (8), (43.63mMole), was suspended in THF, (100mL), and MeOH, (100mL) added. Sodium borohydride, (1.65g, 43.63mMole), was then added in small amounts with cooling, if necessary. At the end of this addition the resulting dark colored solution was stirred for a further 15 minutes at room temperature and then poured into 2N-HCl with stirring. The yellow solid was filtered off, washed well with water, methanol and finally air dried. Yield 11.0g, 66%.

Compound (10):

Compound (9), (11.0g, 28.92mMole), was suspended in water (140mL), and methanol, (20mL), added. To this suspension was then added KOH, (15.25g of 85%, 231.38mMole). The resulting mixture was refluxed for approximately 20 minutes, cooled to room temperature and then poured into 2N-HCl. The yellow solid which precipitated was filter off, washed with a little water and air dried. Yield, 10g, ≈100%.

Compound (11):

Compound (10), (13.6g, 38.8mMole), was dissolved in THF, (100mL), and methanol, (100mL), added. Raney-Nickel which had been pre-washed with water and methanol was then added and the mixture hydrogenated at 50psi and room temperature. When hydrogen uptake was complete the catalyst was filtered off and the filtrate concentrated to near dryness under reduced pressure. The residue which so results was treated with acetonitrile. The solid which is obtained, was filtered off and air dried to give the product, compound (11), yield 10.1g, 81%.

Compound (12):

Compound (11), (10.1g, 31.14mMole), was dissolved in dry pyridine, (100mL) and to this solution was added n-hexadecylsulfonyl chloride, (11.13g, 34.25mMole). Over a 15 minute period the color of the reaction changed from an intense yellow to light red. The reaction was then concentrated under reduced pressure and the residue taken up in ethyl acetate. The ethyl acetate solution was then washed with 2N-HCl, (X3), dried over $MgSO_4$, filtered and the ethyl acetate solution pass through a short column of silica gel eluding with ethyl acetate. The eluant was concentrated and treated with acetonitrile to give the product, compound (12), yield 15.8g, 83%.

Compound (13):

Compound (12), (15.78mMole), was suspended in dry ether, (150mL), and THF, (30mL), added. Phosphorus tribromide, (2.7mL, 28.36mMole), in dry ether, (30mL), was then added dropwise and the reaction stirred at room temperature for approximately 15 minutes. At the end of this period the reaction solution was diluted with ether, washed with 2N-HCl, (X3), dried over $MgSO_4$, filtered and the solution concentrated to yield a solid. The reaction was assumed to have proceeded in 100% yield to give compound (13). This crude product was used as such in the next step.

Compound (14):

Crude compound (13), (25.78mMole), as described above, was dissolved in DMF, (100mL). To this solution was added potassium iodide, (4.3g, 25.78mMole), followed by aniline, (12mL, 128.9mMole) and the mixture heated gently on a steam bath for approximately 10 minutes. At the end of this period all of the potassium iodide had dissolved leaving a fine precipate of potassium bromide. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, washed with 2N-HCl, (X3), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting semi-solid was treated with acetonitrile to give the product, compound (14), as a white powder, Yield 16.1g, 91%.

Compound (15):

Compound (14), (2.5g, 3.63mMole), was dissolved in THF, (50mL) and bis-phenylmercaptotetrazole carbonyl, (1.4g, 3.63mMole), added. The resulting solution was stirred at room temperature for 1 hour. At the end of this period a further batch of bis-phenylmercaptotetrazole carbonyl, (1.4g, 3.63mMole), was added and stirring continued for 1 more hour. The reaction solution was then concentrated under reduced pressure and the residual oil taken up in ethyl acetate, washed with 2.5%-Na_2CO_3, (X3), 2N-HCl (X3), dried over $MgSO_4$, filtered and concentrated to an oil. This oil was dissolved in a small amount of 35% ethyl acetate in heptane and pressure chromatographed over silica gel eluding with the same solvent mixture. The first

major band, the product, compound (15), was collected.
Yield, 2.0g, 62%.

Calculated for $C_{48}H_{57}N_7O_6S_2$	%C64.62,	%H6.44,	%N10.99	and	%S7.19.
Found:	%C64.33,	%H6.30,	%N10.65	and	%S7.82.

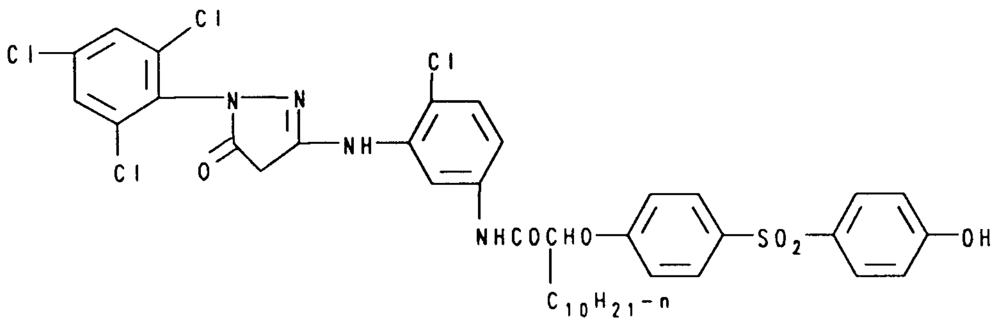
Example 2 - Photographic Utility

Compound I-4(15) was prepared as described in Example 1. Compounds I-1, I-2 and I-3 were also prepared by similar procedures. Photographic elements were prepared by coating the following layers on a cellulose ester film support (amounts of each component are indicated in mg/m^2):

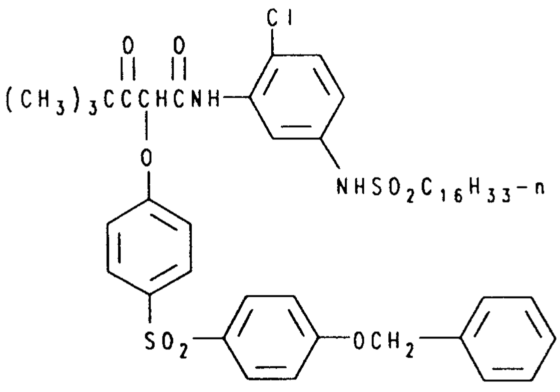
Emulsion layer 1:	Gelatin - 2420: red sensitized silver bromoiodide (as Ag)-1615; yellow image coupler dispersed in dibutyl phthalate (RECEIVER LAYER)
Interlayer:	Gelatin - 860; didodecylhydroquinone - 113
Emulsion layer 2:	Gelatin - 2690; green sensitized silver bromoiodide (as Ag)-1615; magenta image coupler dispersed in tritolyl phosphate; DIR compound of Table 1 dispersed in N,N-diethyl-dodecanamide and coated at levels of 5, 10, 15 and 20 μm/ft^2. (CAUSER LAYER)
Protective Overcoat	Gelatin - 5380; bisvinylsulfonylmethyl ether at 2% total gelatin.

Structures of the image couplers are as follows:

Magenta Image Coupler:



Yellow Image Coupler:



Strips of each element were exposed to green light through a graduated density step tablet, or through a 35% modulation fringe chart for sharpness measurements, and then developed 3.25 minutes at 38°C in the following color developer, stopped, washed, bleached, fixed, washed and dried.

Color Developer:

Distilled water	800 mL
Sodium Metabisulfite	2.18 g
Sodium Sulfite, anhydrous	0.38 g
CD-4 (color developer)*	4.52 g
Potassium Carbonate, anhyd.	34.3 g
Potassium Bicarbonate	2.32 g
Sodium Bromide	1.31 g
Potassium Iodide	1.20 mg
Hydroxylamine Sulfate (HAS)	2.41 g
Diethylenetriaminepentacetic acid, pentasodium salt (40% Soln.)	8.43 g
Distilled water	to 1 L
Adjust pH to 10.0.	

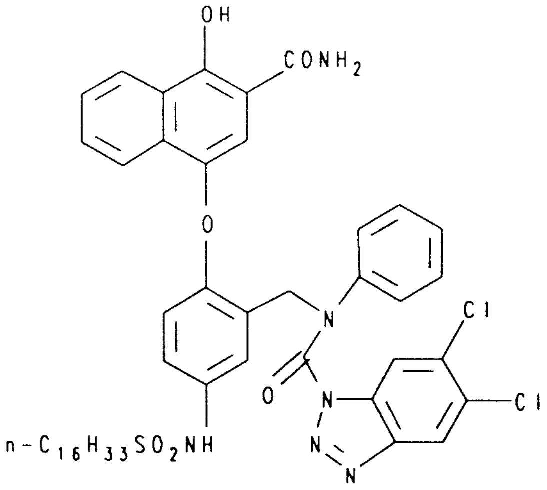
*CD-4 is 4-amino-3-methyl-N-ethyl-N-beta-hydroxyethylaniline sulfate.

Processed images were read with green light to determine the contrast and AMT acutance. The values resulting are reported in the following Table I for a laydown of 10 µmoles of compound/sq. ft. AMT calculations employed the following formula in which the cascaded area under the system modulation curve is shown in equation (21.104) on page 629 of the "Theory of the Photographic Process", 4th Edition, 1977, edited by T. H. James: $AMT = 100 + 66 \mathrm{Log}[\text{cascaded area}/2.669M]$ wherein the magnification factor M is 3.8 for the 35mm system ANT. The use of CMT acutance is described by R. G. Gendron in "An Improved Objective Method of Rating Picture Sharpness: CMT acutance" in the Journal of SMPTE, Vol. 82, pages 1009-12, (1973). AMT is a further modification of CMT useful for evaluation systems which include the viewing of a positive print made from a negative.

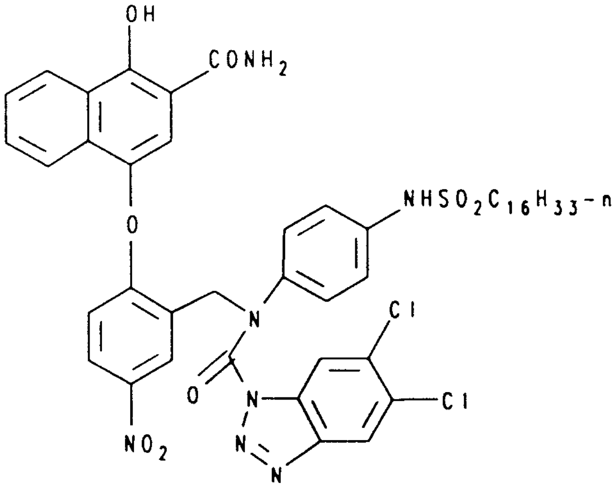
Interimage effect (the degree of color correction) was evaluated after a daylight exposure. Interimage effect, as reported in Table I, was quantified as the ratio of the gamma of the green-sensitive layer (causer) to that of the red-sensitive layer (receiver).

Table I

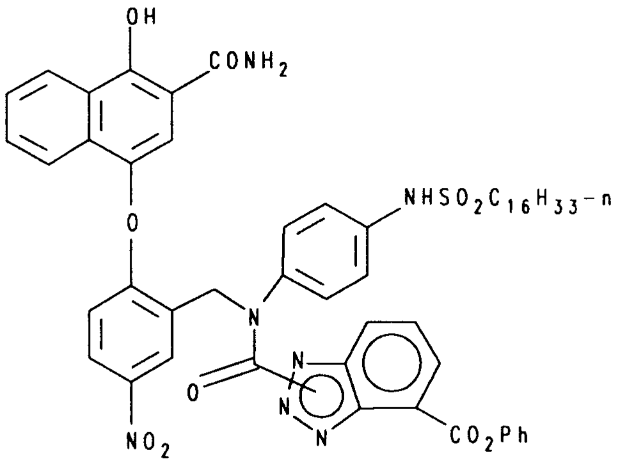
Compound	Gamma Reduction[1]	Gamma Causer Gamma Receiver	Acutance(AMT)
I-1	0.40	2.52	92
I-2	0.71	2.87	94
I-3	1.15	3.01	94
I-4	1.84	1.94	92


OH
CONH$_2$
O
N
Cl
Cl
O
N
N
N
n-C$_{16}$H$_{33}$SO$_2$NH

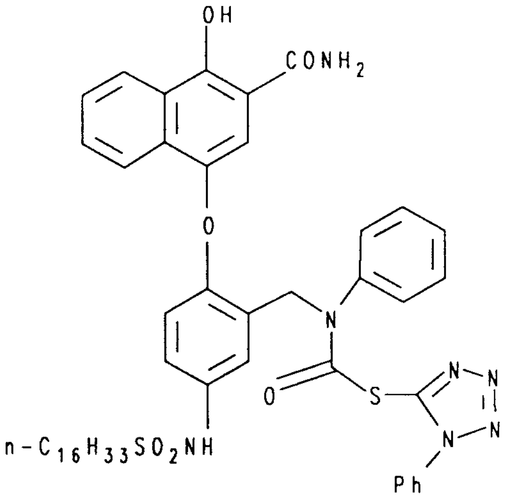
I-1


OH
CONH$_2$
O
NHSO$_2$C$_{16}$H$_{33}$-n
N
Cl
Cl
O
N
N
N
NO$_2$

I-2



I-3



I-4

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. A method of preparing a photographic coupler that comprises a parent coupler moiety (COUP) containing a phenoxy coupling-off group having an aminoalkyl or aryl group in the 2-position of the phenoxy coupling-off group comprising:

(a) reacting a coupler moiety containing a phenoxy coupling-off group having a hydroxyalkyl or aryl group in the 2-position wherein the hydroxy is on the alpha carbon of the alkyl or aryl, with a halogenating compound to form a first product;

(b) reacting said first product from step (a) with an amino compound to form a second product;

(c) reacting said second product with phosgene and then with a photographic development inhibitor compound to form a photographic coupler for releasing said development inhibitor compound in a photographic material upon exposure and processing of the photographic material.

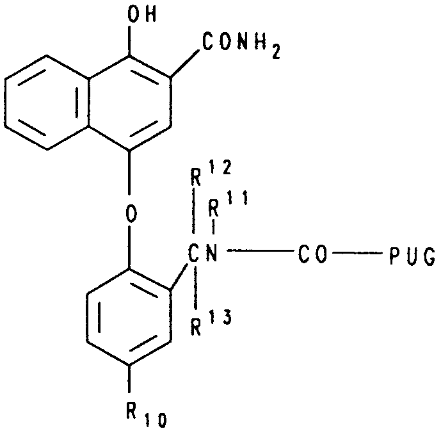
2. A method as in claim 1 wherein the halogenating agent is a brominating or chlorinating agent.

3. A method as in claim 1 wherein the amino compound is an aromatic or aliphatic amino compound.

4. A method as in claim 1 wherein the product of step (B) is reacted with phosgene and then with a photographically useful compound (PUG) to form a coupler capable of release of the photographically useful compound in a photographic material upon exposure and processing of the photographic material.

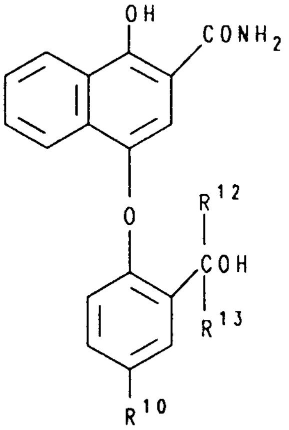
5. A method as in claim 1 wherein the coupler moiety is capable in a photographic material upon exposure and processing of forming a dye that is capable of being washed out of the photographic material.

6. A method as in claim 1 of preparing a photographic coupler represented by the formula:



wherein PUG is a photographically useful group; R^{10} is hydrogen or a photographic ballast; and R^{11} is unsubstituted or substituted aryl or alkyl R^{12} and R^{13} individually are hydrogen or substituents; one of R^{10}, R^{11}, $R^{12'}$ and R^{13} is a photographic ballast group; comprising (A) reacting

(a) a coupler moiety represented by the formula:



with

(b) a brominating or chlorinating agent under ambient conditions; then

(B) reacting the product from step (A) with an unsubstituted or substituted aryl or alkyl amino; then

(c) reacting the product from step (B) with phosgene;

then

(d) reacting the product from step (C) with a photographically useful compound.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 0838

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)
P,X	EP-A-0 443 530 (KODAK) * page 15, line 19 - page 16, line 53 * * page 22, line 44 - line 53 * * page 23, line 36 - line 47; claims 1-8 * -----	1-6	G03C7/305
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 SEPTEMBER 1992	MAGRIZOS S.

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 tbe filing date
D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document