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(54) **Use of a coupler comprising a coupler moiety having a releasable bleach accelerator moiety.**

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(56) References cited :
US-A- 3 893 858
US-A- 4 075 021
US-A- 4 163 669
US-A- 4 293 691
US-A- 4 387 159
US-A- 4 842 994
PATENT ABSTRACTS OF JAPAN, vol. 7, no. 18 (P-170)[1163], 25th January 1983; & JP-A-57 173 836
RESEARCH DISCLOSURE, vol. 114, October 1973, pages 66-67, reference no. 11449, Havant, Hants, GB; "Bleach accelerator releasing couplers"

(56) References cited :
JP-A-55 029805 and partial English translation thereof
JP-A-53 057831 and partial English translation thereof
Research Disclosure, June 1984, vol. 242, item 24241, pp. 286-292

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Description

This invention relates to photographic materials and processes which utilize a compound capable of releasing a bleach accelerator moiety.

Photographic materials useful for forming dye images by means of a process which includes a bleaching step are known and used commercially. Such materials and processes are described in, for example. *The Theory of the Photographic Process*, 4th Edition, Edited by T. H. James, 1977, pages 462-463 and pages 335-361. The use in such photographic materials of a bleach accelerator releasing coupler is described in *Research Disclosure*, 1973, Item No. 11449. The bleach accelerator releasing coupler, also known as a BARC, has contained a heterocyclic group as the bleach accelerator moiety which is released during processing of the photographic element. These bleach accelerator releasing couplers cause an undesired degree of adverse development effects.

Couplers which have a thioether group at the coupling position have been known in the photographic art. Examples of such couplers are described in, for example, U.S. Patent 4,387,159, Japanese Published Patent Application 57-173836, U.S. Patent 3,227,554 and U.S. Patent 4,293,691. These compounds have been useful as development inhibitor releasing (DIR) couplers. Almost all of the couplers that are designed as development inhibitor releasing couplers have a thioether group and are oleophilic in order to help maintain the coupler in one location in the hydrophilic emulsion layers of the photographic material. Typically such couplers have ballast groups for this purpose. These have not required a balance of a strong affinity for silver and a balance of water solubility as is the case with bleach accelerator compounds.

The present invention provides use of a coupler comprising a coupler moiety having a releasable bleach accelerator moiety represented by the formula:

$$-(TIME)_n-S-R_1-R_2$$

wherein

TIME is a timing group;

n is 0 or 1;

R_1 is a linking group consisting of alkylene comprising 1 to 8 carbon atoms; and,

R_2 is a water solubilizing group,

as a bleach accelerator releasing coupler in a photographic element comprising a support, a photographic silver halide emulsion layer and the bleach accelerator releasing coupler incorporated in the emulsion layer or a layer adjacent thereto.

The releasable bleach accelerator moiety is in a location on the compound carrying the moiety which enables release of the bleach accelerator moiety at time during processing of the photographic element which enables acceleration of the bleaching step. The bleach accelerator releasing compound is preferably a coupler having the bleach accelerator moiety in the coupling position. The coupler can be, but need not be, a dye-forming coupler.

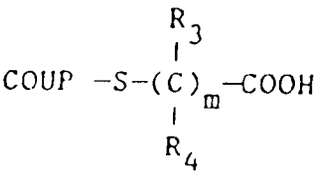
One embodiment of the invention is a silver halide photographic element containing a bleach accelerator releasing compound which has a releasable bleach accelerator moiety as described.

Herein the term "coupler" refers to the entire compound including the coupler moiety and the bleach accelerator moiety $(TIME)_n-S-R_1-R_2$. The term coupler moiety herein refers to that portion of the compound other than the bleach accelerator moiety.

The particular R_1 group linking the sulfur atom and the water solubilizing group R_2 can be varied to control such parameters as water solubility, diffusivity, silver affinity, silver ion complex solubility, silver development effects and other sensitometric effects. Since these parameters can be controlled by modification of R_1, they need not be emphasized in selecting a particular coupler moiety and the particular water solubilizing group, but provide freedom in selecting such moieties and groups for a particular photographic element and process.

In processing, the bleach accelerator fragment is released at an appropriate time as a unit. That is, $-S-R_1-R_2$ is released as a unit. The rate and total time of difussion of the bleach accelerator fragment in the photographic element must be such as to enable bleach acceleration in the appropriate layers of the photographic element during processing. The timing group, when present, also releases $-S-R_1-R_2$ as a unit. Selection of R_1 and R_2 can also influence the rate and total time of release of the bleach accelerator moiety from the remainder of the compound, preferably the remainder of the coupler. It is necessary that the bleach accelerator moiety not adversely effect the processing steps and the photographic element. Selection of a sufficiently water soluble bleach accelerator moiety by selection of optimum R_1 and R_2 groups minimizes development inhibition activity of the bleach accelerator moiety while enhancing bleach accelerator activity. This helps separate those compounds which are useful bleach accelerator releasing compounds from those compounds which are useful development inhibitor releasing compounds.

Preferred photographic couplers used in the invention are represented by the formula:

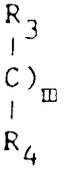


wherein

COUP is a coupler moiety;

m is 1 to 8;

R_3 and R_4 are individually hydrogen or alkyl containing 1 to 4 carbon atoms; and wherein the total number of carbon atoms in



is 1 to 8.

Alkyl includes straight or branched chain alkyl, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, and t-butyl.

The coupler moiety can be any moiety that will react with oxidized color developing agent to enable release of the bleach accelerator moiety. The coupler moiety includes coupler moieties which are useful in conventional dye-forming couplers whrch yield dyes on reaction with oxidized color developing agents as well as coupler moieties which yield colorless products on reaction with oxidized color developing agents.

The coupler moiety can be unballasted or ballasted with an oil-soluble group. It can be monomeric, or it can form part of a dimeric, oligomeric or polymeric coupler, in which case more than one bleach accelerator moiety can be contained in the coupler. Each coupling position can release a bleach accelerator moiety.

It will be appreciated that, depending upon the particular coupler moiety, the particular color developing agent and the type of processing, the reaction product of the coupler moiety and oxidized color developing agent can be: (1) colored and nondiffusible, in which case it will remain in the location where it is formed; (2) colored and diffusible, in which case it may be removed during processing from the location where it is formed or allowed to migrate to a different location; or (3) colorless and diffusible or nondiffusible, in which case it will not contribute to image density. In cases (2) and (3) the reaction product may be initially colored and/or nondiffusible but converted to colorless and/or diffusible products during the course of processing.

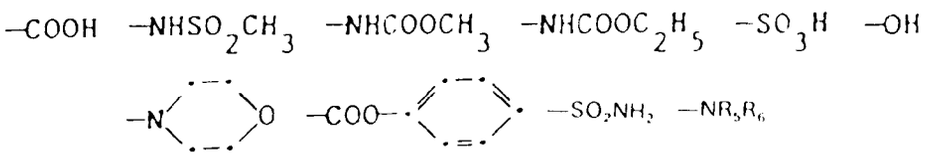
The bleach accelerator moiety is attached at the coupling position of the coupler moiety which enables the bleach accelerator moiety to be displaced upon reaction of the coupler with oxidized color developing agent.

In bleach accelerator releasing organic compounds as described, preferably bleach accelerator releasing couplers, the bleach accelerator moiety can be bonded to the remainder of the organic compound through a timing group (TIME). TIME in the described structures is a group which enables the time release of -S-R_1-R_2 from COUP. The timing mechanism can be any timing mechanism which is useful for releasing photographically useful groups from coupler moieties. For example, the timing mechanism can be as described in, for example U.S. Patent 4,248,962 or U.S. 4,409,323.

Release of the bleach accelerator moiety can involve a single reaction or it can involve sequential reactions. For example, two or more sequential reactions may be required within a TIME group to effect release of the bleach accelerator moiety. As another example, the TIME group can have two bleach accelerator moieties bonded to different locations on the TIME group so that upon release of the TIME group from the coupler moiety two reactions can occur sequentially enabling sequential release of the two bleach accelerator moieties. Another example is a reaction in the TIME group which may release a second coupler moiety which contains another timing group to which a photographically useful group is attached and from which it is released after the second coupler moiety reacts with oxidized color developing agent.

The TIME group can contain moieties and substituents which will permit control of one or more of the rates of reaction of COUP with oxidized color developing agent, the rate of diffusion of -TIME-S-R_1-R_2 once it is released from COUP and the rate of release of -S-R_1-R_2. The TIME group can contain added substituents, such as added photographically useful groups which can remain attached to the timing group and be released independently. The TIME groups can contain a ballast group.

The following R_2 groups are examples of useful water solubilizing groups

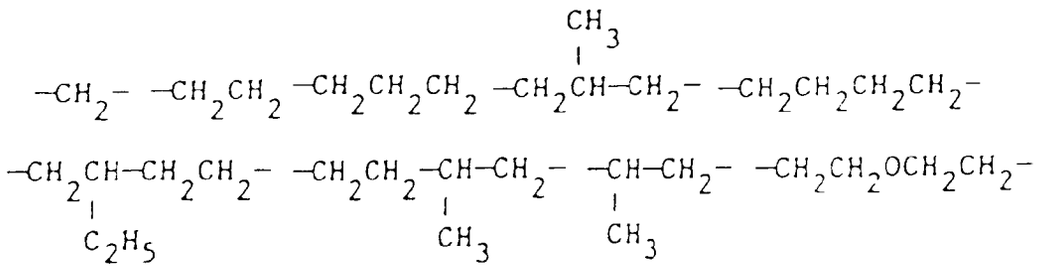


wherein

R_5 is H or alkyl of 1 to 4 carbons,

R_6 is alkyl of 1 to 4 carbons and wherein at least one of R_5 and R_6 is alkyl, and the total carbon atoms in R_5 and R_6 is no more than 8.

The following are examples of useful R_1 groups:

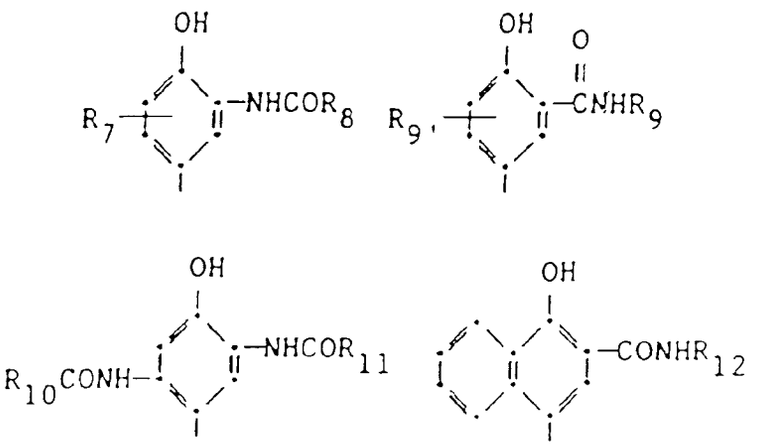


The following is a listing of patents and publications which describe representative COUP groups useful in the invention. In these structures the unsatisfied bonds in each of the COUP groups show the point of attachment to TIME or, should no TIME group be present, then to the bleach accelerator moiety; the vertical unsatisfied bond in TIME shows the point of attachment to COUP and the horziontal unsatisfied bond in TIME shows the point of attachment of the bleach accelerator moiety.

I. COUP's

A. Useful couplers which form cyan dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as: U.S. Patent Nos. 2,772,162; 2,895,826; 3,002,836; 3,034,892; 2,474,293; 2,423,730; 2,367,531; 3,041,236; and 4,666,999.

Preferably such couplers are phenols and naphthols which form cyan dyes on reaction with oxidized color developing agents and have the releasable bleach accelerator moiety attached at the coupling position, that is the carbon atom in the 4-position of the coupler moiety. Structures of preferred cyan-dye-forming coupler moieties are:



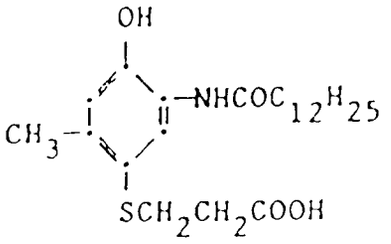
wherein

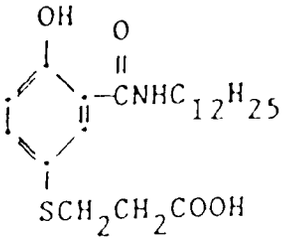
R_8, R_9, R_{10}, R_{11} and R_{12} individually represent ballast groups;

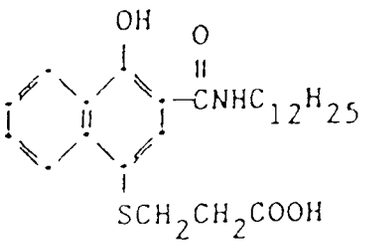
R_7 and R_9, individually represent at least one halogen atom, such as chloro or fluoro; alkyl, such as alkyl containing 1 to 4 carbon atoms, for example methyl, ethyl, propyl or butyl; or alkoxy, such as alkoxy containing

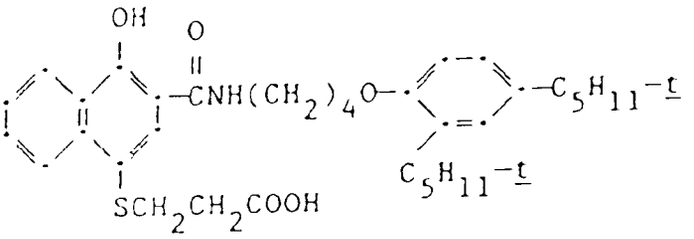
1 to 4 carbon atoms, for example methoxy, ethoxy, propoxy and butoxy.

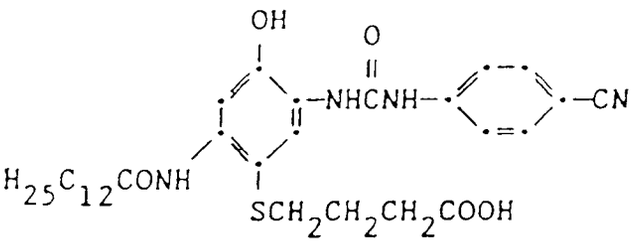
Examples of such cyan dye-forming couplers are:

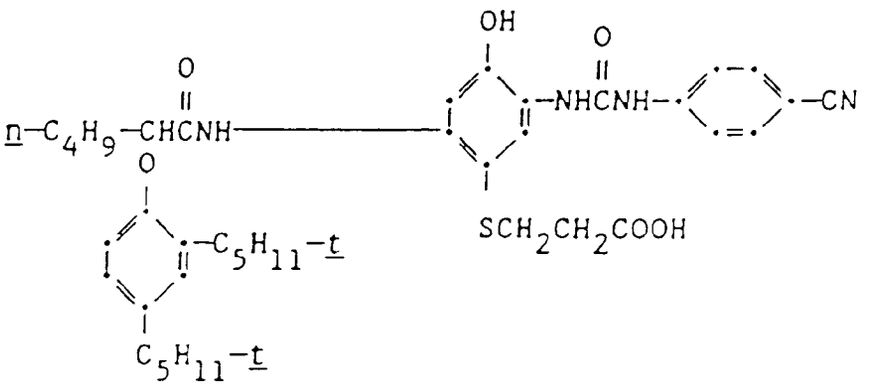


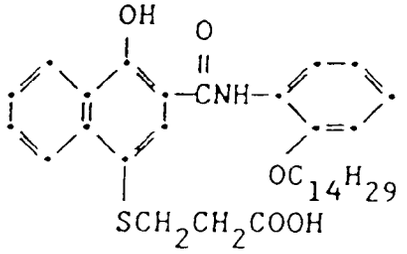


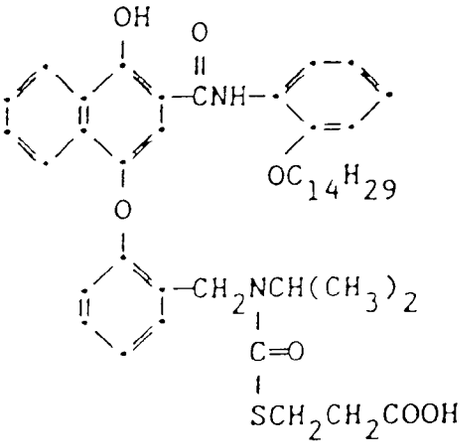


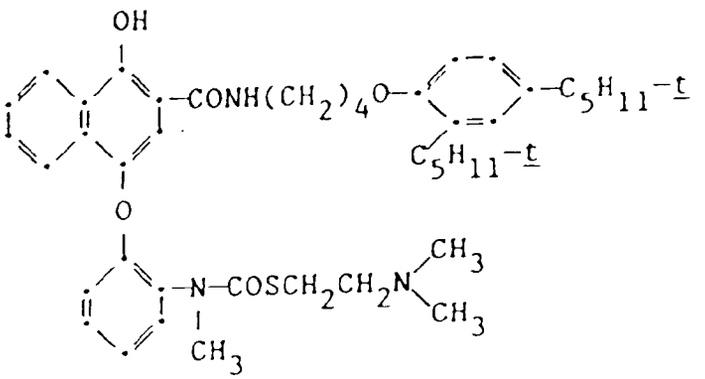


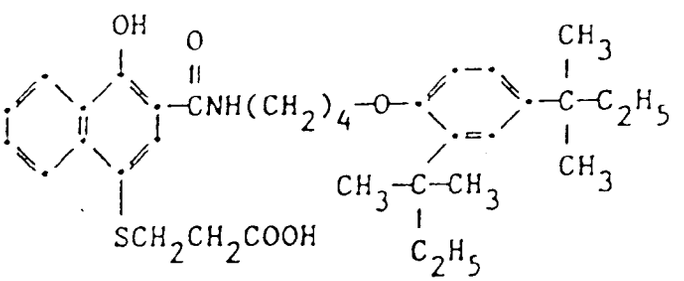


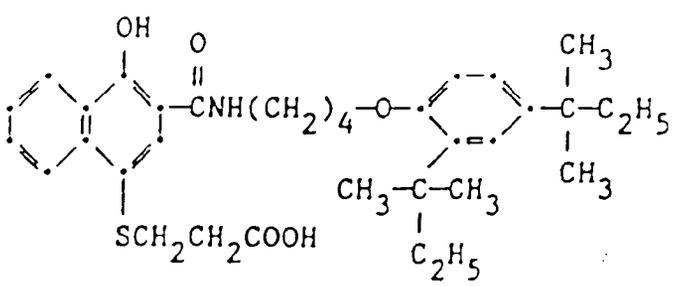






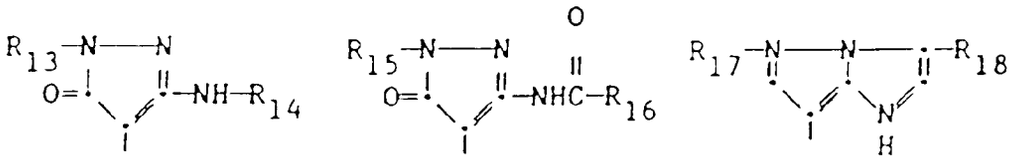






B. Examples of couplers which form magenta dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as: U.S. Patent Nos. 2,600,788; 2,369,489; 2,343,703; 2,311,082; 3,152,896; 3,519,429; 3,062,653; and 2,908,573.

Preferably such magenta dye-forming couplers are pyrazolones and pyrazolotriazoles which form magenta dyes upon reaction with oxidized color developing agents. Structures of preferred magenta dye-forming couplers are:

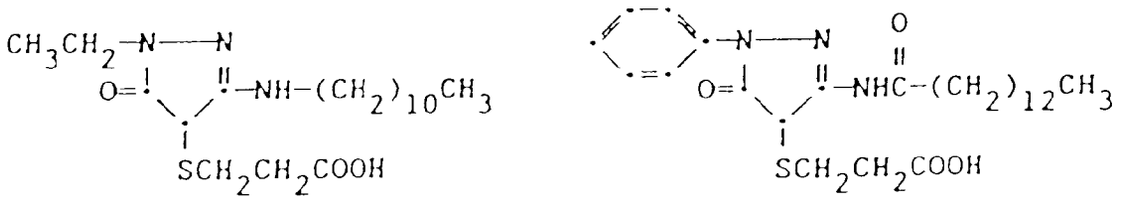


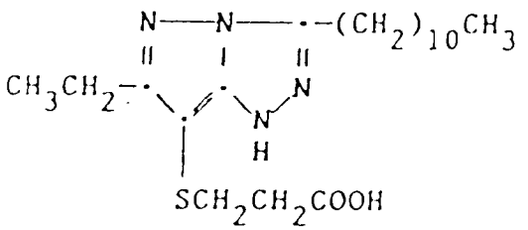
wherein

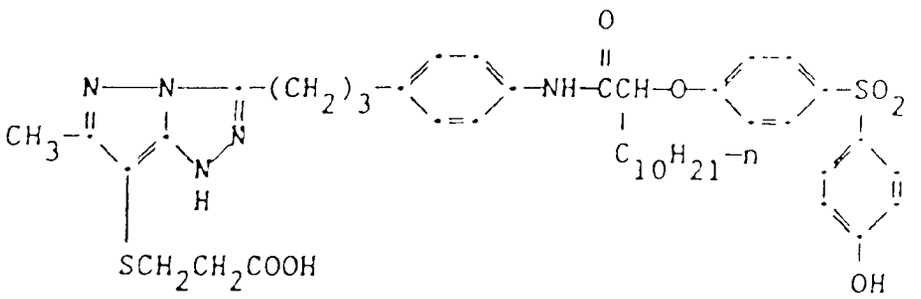
R_{14}, R_{16} and R_{17} are individually aryl, alkyl, such as alkyl containing 1 to 30 carbon atoms; and

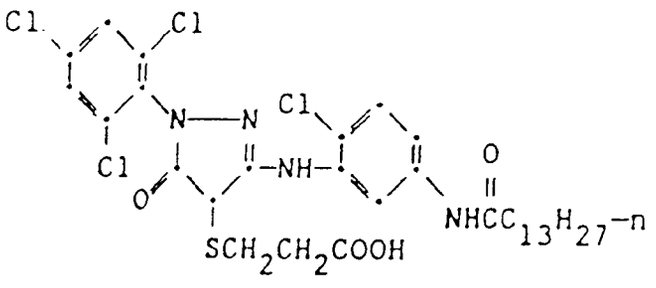
R_{13}, R_{15} and R_{18} are individually ballast groups, or are phenyl or substituted phenyl, such as 2,4,6-trihalophenyl, for example 2,4,6-trichlorophenyl.

Examples of such magenta dye-forming couplers are:





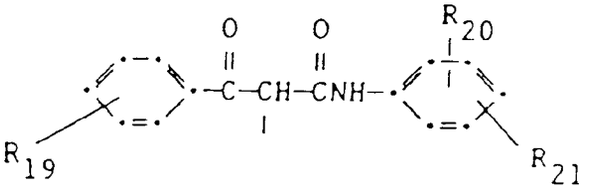


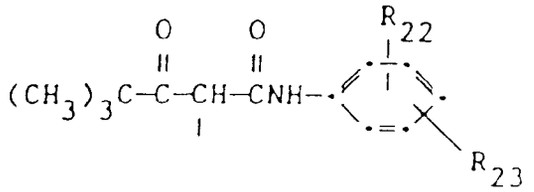


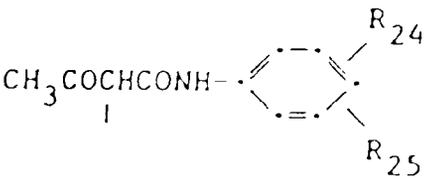
C. Couplers which form yellow dyes upon reaction with oxidized color developing agents are described in such representative patents as: U.S. Patent Nos. 2,875,057; 2,407,210; 3,265,506; 2,298,443; 3,048,194; and 3,447,928.

Preferably such yellow dye-forming couplers are acylamides, for example, benzoylacetanilides and pivalylacetanilides.

Examples of such yellow dye-forming couplers are:





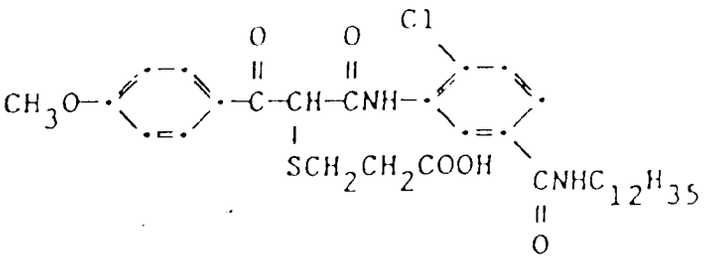


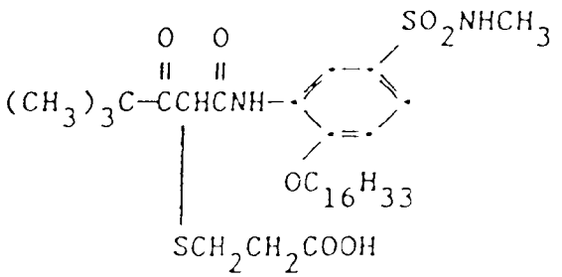
wherein

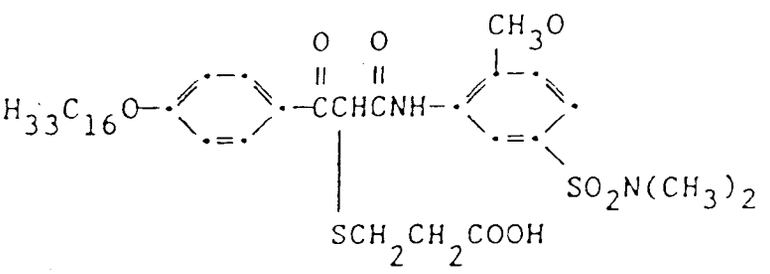
R_{21}, R_{23} and R_{25} are individually ballast groups; and

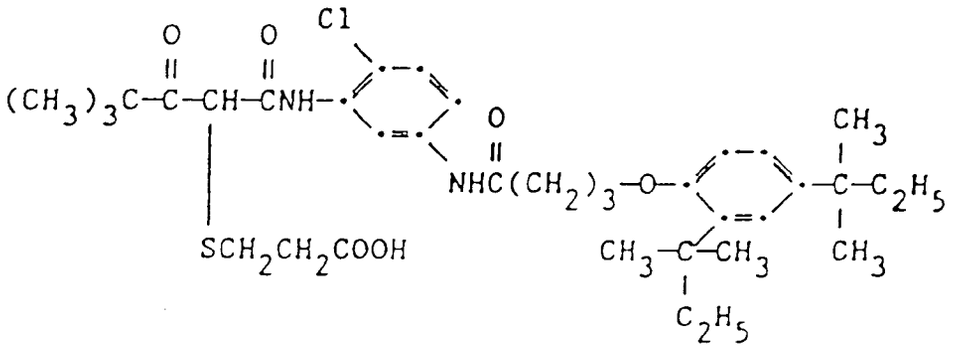
R_{19}, R_{20}, R_{22} and R_{24} are individually hydrogen or one or more haqlogen, such as chlorine and fluoride; alkyl, such as alkyl containing 1 to 4 carbon atoms, for example methyl, ethyl, propyl and butyl; alkoxy, such as alkoxy containing 1 to 20 carbon atoms; or a ballast group.

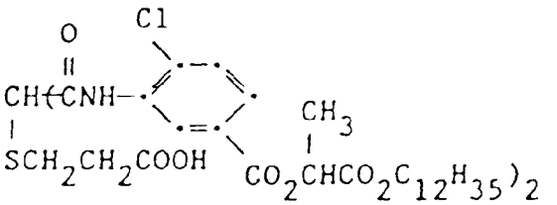
Examples of such yellow dye-forming couplers are:

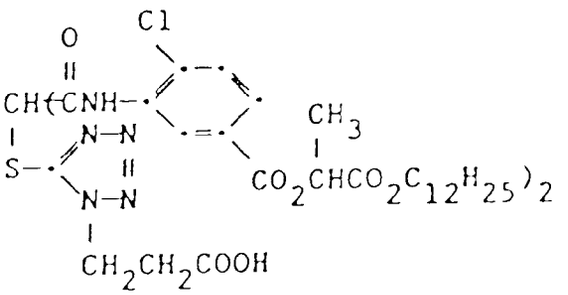


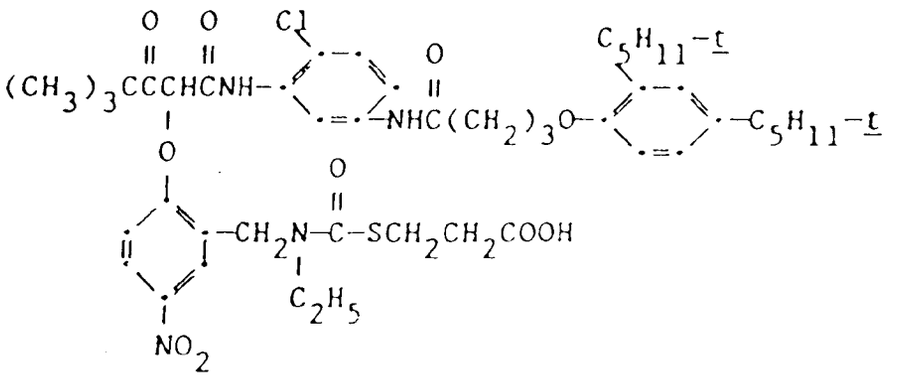






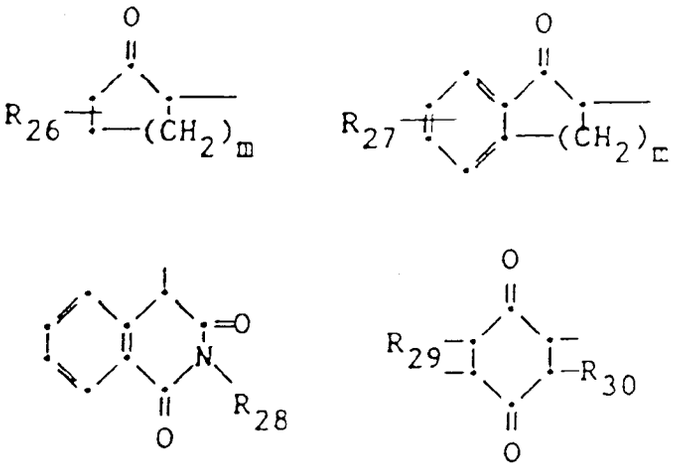






D. Couplers which form colorless products or form products which do not significantly absorb electromagnetic radiation within the visible range of the spectrum are described in such representative patents as: U.K. Patent No. 861,138; U.S. Patent Nos. 3,632,345; 3,928,041; 3,958,993; and 3,961,959. Preferably such couplers are cyclic carbonyl containing compounds which form colorless products on reaction with oxidized color developing agents.

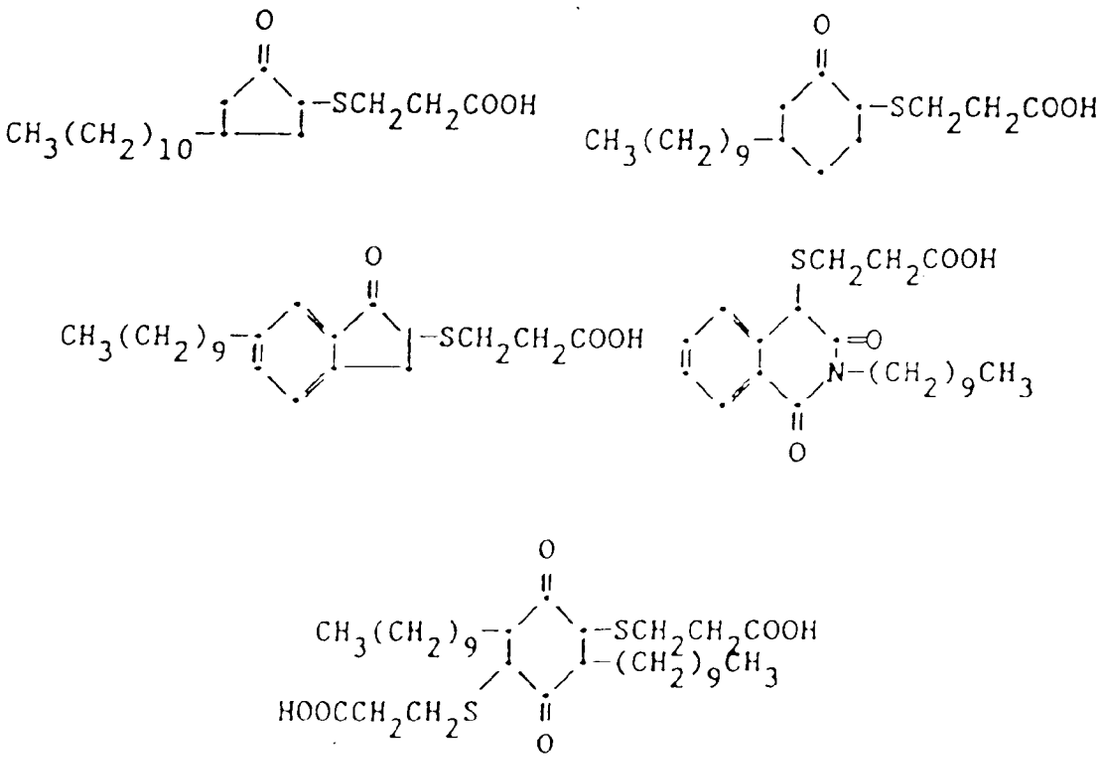
Structures of representative couplers which form colorless products are:



wherein

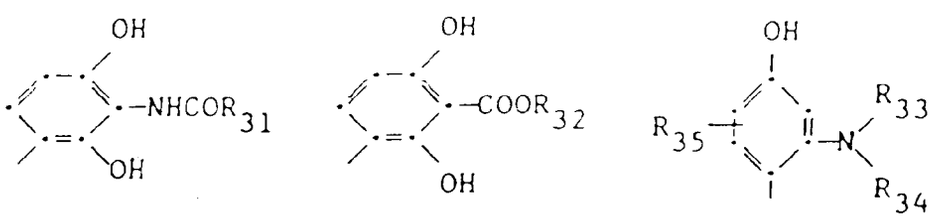
R_{26}, R_{27}, R_{28}, R_{29} and R_{30} are individually ballast groups; m is 1 or 2.

Examples of such couplers capable of forming a colorless or nearly colorless product are:



E. Couplers which form black dyes upon reaction with oxidized color developing agents are described in such representative patents as: U.S. Patent Nos. 1,939,231; 2,181,944; 2,333,106; 4,429,035; 4,439,518; 4,254,213; 4,387,158; 4,126,461 and 4,200,466.

Preferably such couplers are resorcinols or m-aminophenols which form black products on reaction with oxidized color developing agents. Structures of preferred couplers capble of forming a black dye are :



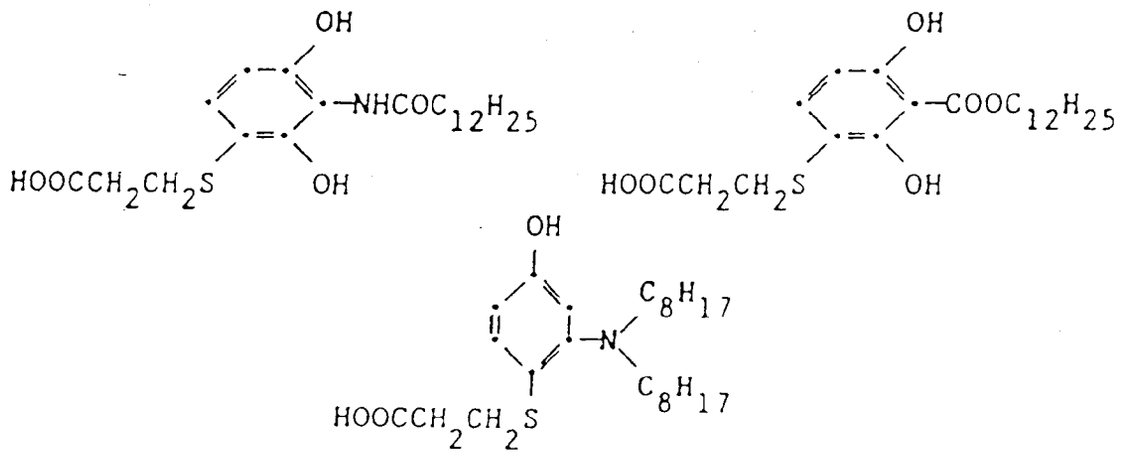
wherein

R_{31} and R_{32} are individually alkyl, such as alkyl containing 3 to 20 carbon atoms, phenyl or phenyl substituted with hydroxy, halo, such as chloro or bromo, amino, alkyl, such as alkyl containing 1 to 20 carbon atoms, or alkoxy, such as alkoxy containing 1 to 20 carbon atoms; and

R_{33} and R_{34} are individually hydrogen, alkyl such as alkyl containing 1 to 20 carbon atoms, alkenyl, such as alkenyl containing 1 to 20 carbon atoms, or aryl, such as aryl containing 6 to 20 carbon atoms; and,

R_{35} is one or more halogen, such as chlorine or bromine, alkyl, such as alkyl containing 1 to 20 carbon atoms, alkoxy, such as alkoxy containing 1 to 20 carbon atoms, or other monovalant organic groups that do not adversely affect the dye formation or release of the bleach accelerator moiety.

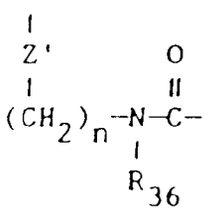
Examples of such couplers capable of forming a black dye are:



II. TIME's

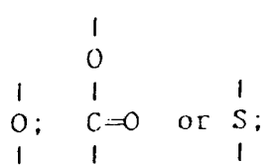
TIME groups which are useful enable relase of the bleach accelerator moiety at the appropriate time during processing, that is at the time which enables accelerated bleaching of the photographic element. Examples of such TIME groups are:

A. Acyclic TIME groups:



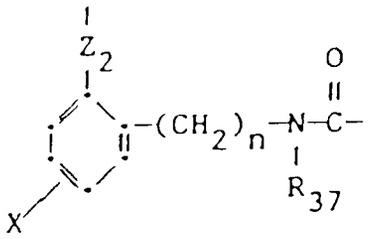
wherein

n is 1 to 4; Z' is



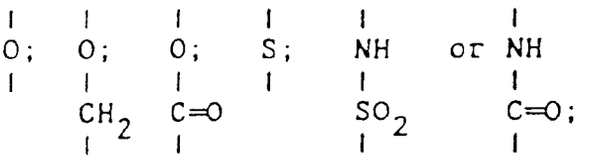
R_{36} is hydrogen, alkyl, such as alkyl containing 1 to 20 carbon atoms; or aryl, such as aryl containing 6 to 20 carbon atoms, preferably unsubstituted phenyl or substituted phenyl.

B. Aromatic TIME groups:



wherein

n is 0 or 1; Z_2 is



R_{37} is hydrogen, alkyl, such as alkyl containing 1 to 20 carbon atoms; or aryl, such a aryl containing 6 to 20 carbon atoms, for example, phenyl;

X is hydrogen; cyano; fluoro; chloro; bromo; iodo; nitro; alkyl, such as alkyl containing 1 to 20 carbon atoms; preferably methyl, ethyl, propyl or butyl; or aryl, such as aryl containing 6 to 20 carbon atoms, preferably unsubstituted phenyl or substituted phenyl.

The bleach accelerator releasing coupler can be used in combination with a colorless coupler or a colored coupler and added to a silver halide emulsion together with an image dye-forming coupler, or alternatively in the form of an independent emulsion in an auxiliary layer, such as an intermediate layer and/or an undercoat layer. The bleach accelerator releasing compounds are useful alone or in combinations with two or more bleach accelerator releasing compounds.

The bleach accelerator releasing couplers can be incorporated in photographic elements 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 nondiffusible; that is, they should be of such molecular size and configuration that they will not significantly diffuse or wander from the layer which they are coated.

Photographic elements in which the photographic couplers used in 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 coupler compounds can be incorporated in the silver halide emulsion layer or in another 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 coupler compounds, such as development inhibitor releasing (DIR) couplers, color forming couplers and colored masking couplers. These other photographic coupler compounds can form dyes of the same or different color and hue as the bleach accelerator releasing compounds. Additionally, the silver halide emulsion layer can contain addenda conventionally contained in such layers.

A typical multilayer, multicolor photographic element used in this invention 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 the bleach accelerator releasing compound. Each silver halide emulsion unit can be composed of one or more layers and the various units and layers can arranged in different locations with respect to one another. Typical arrangements are described in U.S. Patent Nos. 3,227,554; 3,620,747; 3,843,369; and U.K. Patent No. 923,045. The coupler compounds can be incorporated in or associated with one or more layers or units of the element. The layer(s) and unit(s) affected by the bleach accelerator moiety can be controlled by incorporating in appropriate locations in the element scavenger layer(s) which will confine the action of the bleach accelerator moiety to the desired layer(s) or unit(s).

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 emulsion can be negative-working or a direct-positive emulsion. They can form latent images predominantly on the surface of the silver halide grains or predominantly in the interior of the silver halide grains. They can be chemically and spectrally sensitized. The emulsions typically will be gelatin emulsions although other hydrophillic colloids can be used in accordance with usual practice. Tabular grain photographic silver halide emulsions, described in, for example, *Research Disclosure*, January 1983, Item No. 22534 and U.S. Patent 4,434,226 are particularly useful.

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, flexible support is employed, such as a polymeric film or paper support. Paper supports can be acetylated or caoted with baryta and/or an α-olefin polymer, particularly a polymer of an α-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

If the coupler moiety is a dye-forming coupler, it can react with oxidized developing agent in the same or an adjacent layer to form a dye of the same or different color or hue as that obtained from the primary coupler. If the coupler moiety is a competing coupler, it can react with oxidized color developing agent in the same or an adjacent layer to reduce dye density.

The optimum concentration range of bleach accelerator releasing compound will depend upon such factors as the desired image, the location of the bleach accelerator releasing compound, processing conditions, the particular bleach composition, the particular layers of the photographic element, processing steps and the particular bleach accelerator moiety. A typical concentration of bleach accelerator releasing compound in a photographic element is within the range of about 50 to about 500 mg/sq meter.

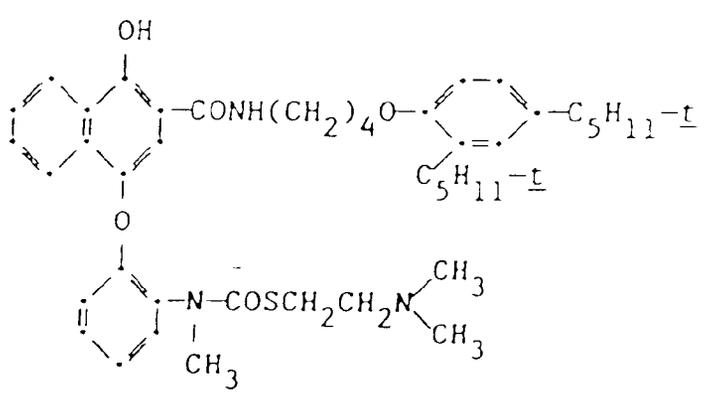
A particularly useful photographic element is a dye-forming photographic element having a layer format known to be useful in forming a multicolor image by a subtractive color process. Any or all of the respective color records can be in the form of a double or triple layer structure.

The process of forming a dye image in a photographic element as described comprises conventional color processing involving a bleaching step. The bleaching step is preferably conducted separately from fixing. The bleaching composition comprises known bleaching agents. Examples of typical processes are described in *Research Disclosure*, December 1978, Item No. 17643 and in "Modern Photographic Processing", by Grant Haist, Vol. 2, pages 569-587, John Wiley and Sons, N.Y., 1979. Processing of a dye-forming photographic element according to the invention typically comprises a color development step, a bleaching step and a fixing step. The bleaching step and fixing step can be combined into one step if desired. Other processing steps which are also useful in this process include a pre-hardening step, a neutralization step, a first development step (black-and-white development), a stabilizing step, and water washing step. Processing steps are typically carried out at a temperature within the range of 18°C to 60°C.

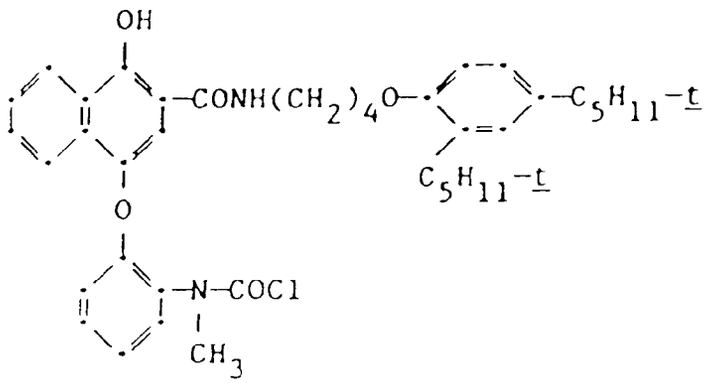
The bleach accelerator releasing compounds are prepared by organic synthesis procedures known in the organic compound synthesis art. For example, the coupler moiety can be reacted with the bleach accelerator moiety in an appropriate solvent. The following are representative preparations of bleach accelerator releasing couplers:

Synthesis Example A

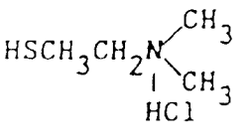
This relates to the synthesis of the following bleach accelerator releasing coupler:



To a solution of 5.6 g (8 mmol) of the coupler moiety:



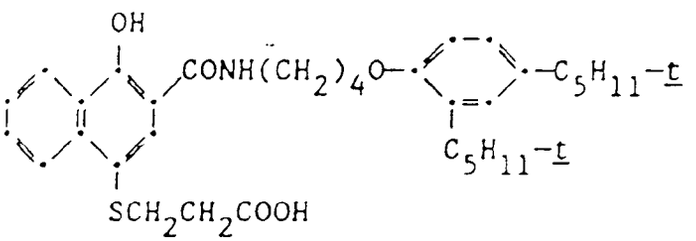
(prepared by procedures described in U.S. Patent 4,248,962) is added 1.1 g (8 mmol) of 2-dimethylamino-ethanethiol hydrochloride represented by the formula:



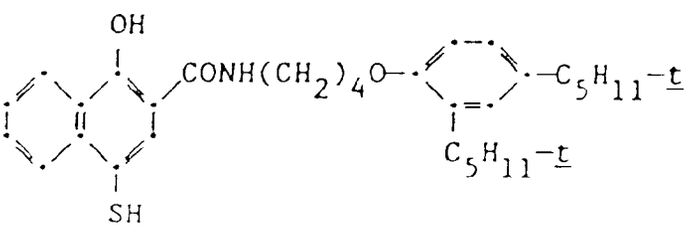
in 25 ml of dry pyridine. The mixture is stirred overnight and then drowned in water. The resulting product is then extracted and purified. The desired product can be isolated by ethyl acetate extraction, triturated with ligroin and dried to obtain the desired bleach accelerator releasing coupler having a melting point of 130-131°C, and which is identified by spectral and elemental analysis.

Synethesis Example B

This relates to the synthesis of the bleach accelerator releasing coupler:



To a solution of 5 g (9.9 mmol) of the coupler moiety:

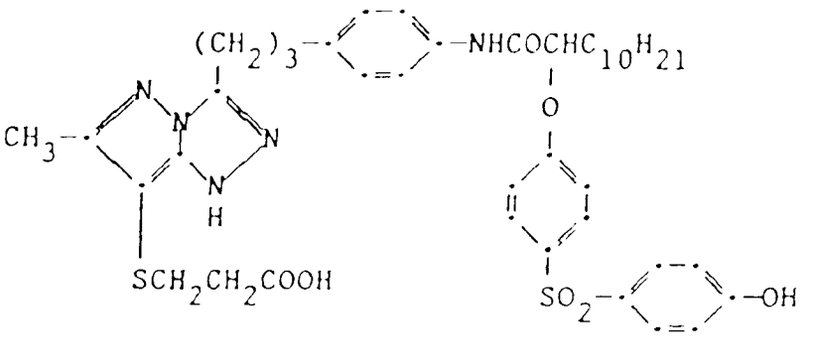


in 75 ml of tetrahydrofuran, stirred under nitrogen, in added 1.4 g (9.9 mmol) of tetramethylguanidine and then 1.1 ml (9.9 mmol) of ethyl acrylate. After 30 minutes 50 ml of methanol and 10 ml of 1.25 N sodium hydroxide solution are added and the resulting composition stirred for 15 minutes. The mixture is then drowned in ice-cold dilute hydrochloric acid. The desired product is extracted and purified. For example, the desired product

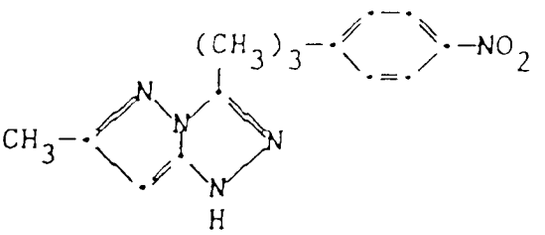
is extracted with diethyl ether to obtain, after crystallization, the desired bleach accelerator releasing coupler which is a colorless solid having a melting point of 139°C to 141°C. The product is also identified by elemental and spectral analysis.

Synthesis Example C

This relates to the synthesis of the bleach accelerator releasing coupler:

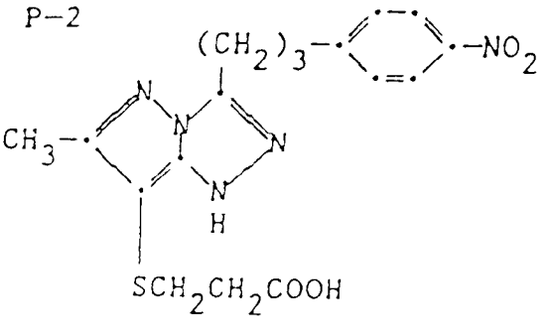


To a stirred solution of 20 g (70 mmol) of the compound



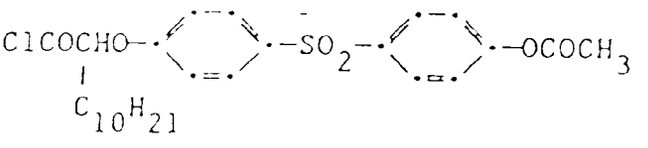
and 7.4 g (70 mmol) 3-mercaptopropionic acid ($HSCH_2CH_2COOH$) in 75 ml of dimethylformamide is added, dropwise, 3.85 ml of bromine in 25 ml of dimethylformamide. After stirring overnight the mixture is drowned in water. A single product, designed as P-2:

P-2



is isolated by filtration. Next, 11.8 g of zinc is added to a solution of 5.6 g (13.7 mmol) of P-2 in 200 ml of glacial acetic acid and stirred 30 minutes before filtration. Then 6.9 g (13.7 mmol) of the compound, designated as P-3:

P-3



is added to the filtrate, stirred for 1 hour and the mixture poured into water. The resulting product isolated by extraction, is then dissolved in methanol/tetrahydrofuran (equal parts by volume), then hydrolyzed with 50% sodium hydroxide solution, and acidified with cold excess dilute hydrochloric acid. The desired bleach accelerator releasing coupler is then extracted and purified by silica gel chromatography. This bleach accelerator releasing coupler has a melting point of 120-122°C and is identified by elemental analysis indicating one water of hydration is present.

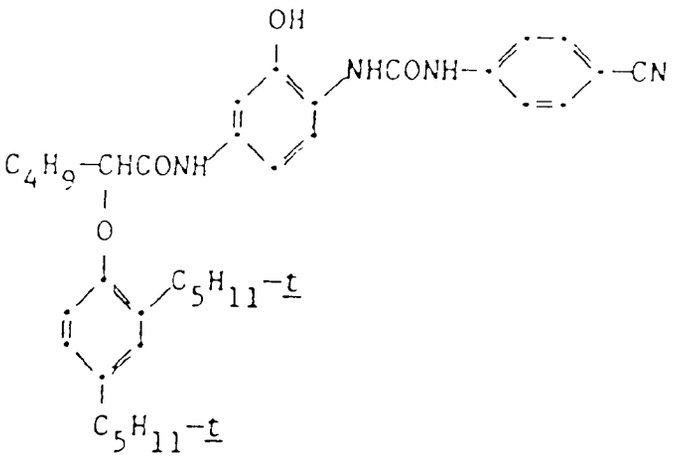
The following examples further illustrate the invention:

Example 1

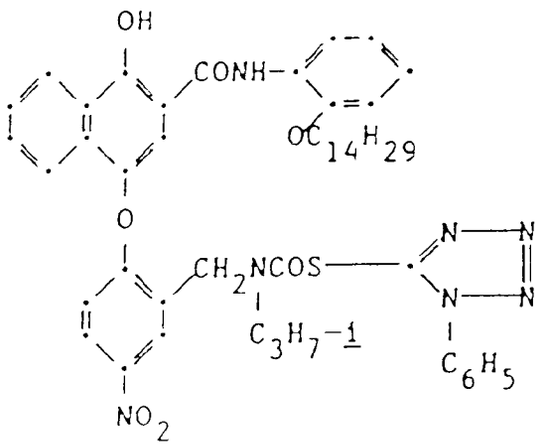
This illustrates a multilayer color photographic element comprising a bleach accelerator releasing coupler.

A multilayer color photographic element, designated herein as Sample a, was prepared by coating the following layers on a cellulose triacetate film support in the designated order (levels coated are given in mg/m^2 with silver halide stated as silver level):

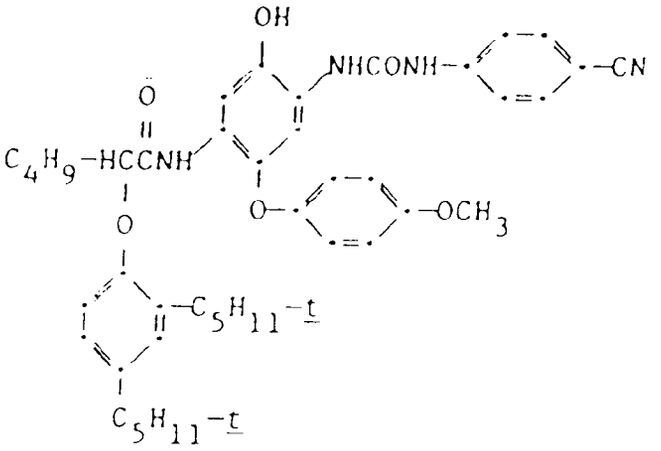
Layer 1: (bottom layer) Slow Cyan Layer - Slow, red-sensitized silver bromoiodide tabular grain gelatino emulsion (1615 mg/m^2), gelatin (2153 mg/m^2). This layer also comprises a cyan image dye-forming coupler, designated as C-1 (603 mg/m^2):



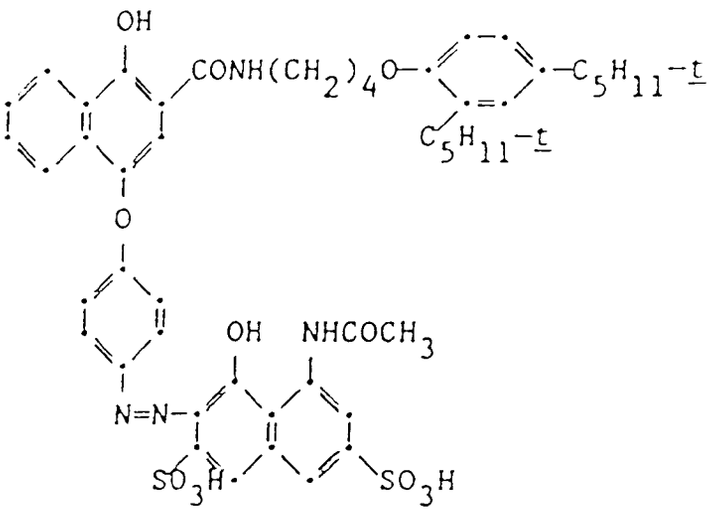
and a colored coupler (65 mg/m^2), designated as C-3 and described below, as well as a development inhibitor releasing coupler, designated as D-1 (43 mg/m^2):



Layer 2: Fast Cyan Layer - Fast red-sensitized silver bromoiodide tabular-grain gelatino emulsion, prepared as described in U.S. Patent 4,434,226 of Wilgus. This layer also comprises gelatin (1615 mg/m^2) and a cyan image dye-forming coupler, designated as C-2 (194 mg/m^2):

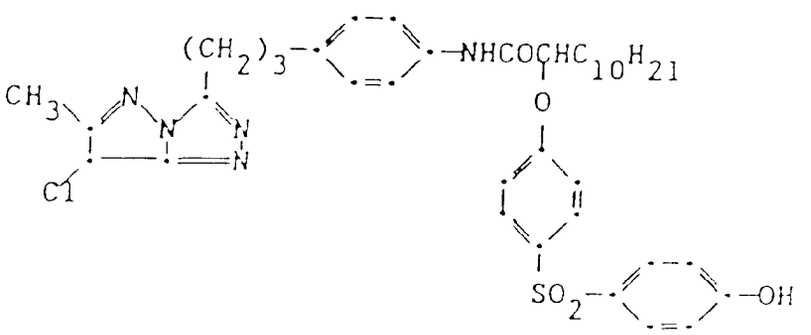


and a colored coupler, designated as C-3 (16 mg/m^2):

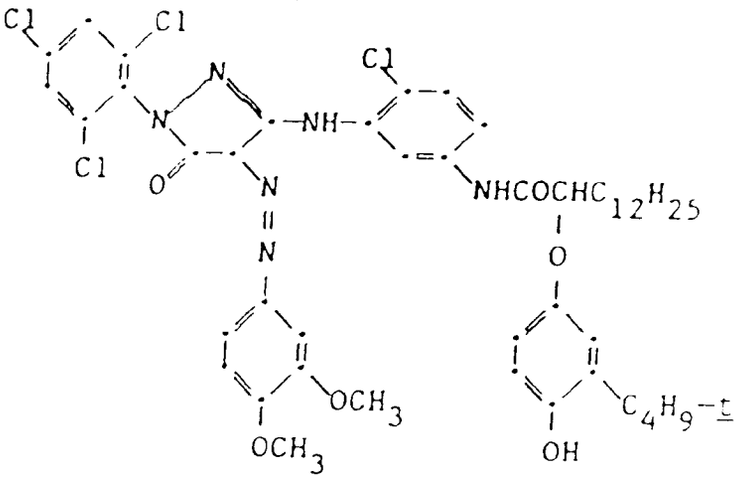


Layer 3: Interlayer - Gelatin (1292 mg/m^2)

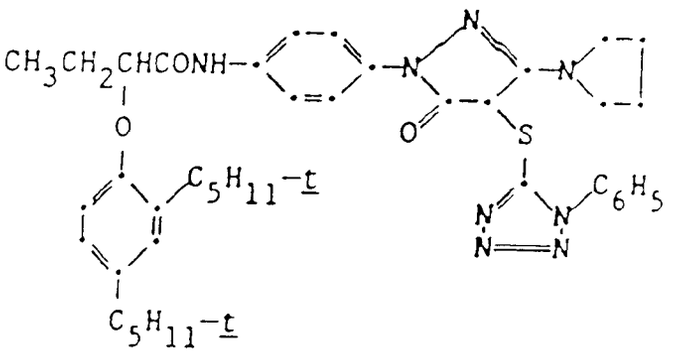
Layer 4: Slow Magenta Layer - Green sensitized silver bromoiodide tabular-grain gelatino emulsion, prepared as described in U.S. Patent 4,434,226 of Wilgus. This layer also comprises a magenta image dye-forming coupler, designated as coupler M-1:



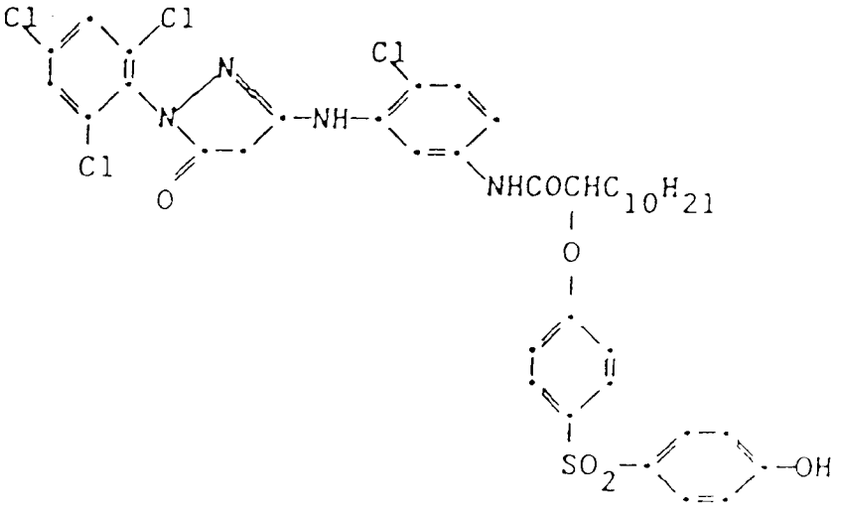
and a colored coupler, designated as M-3:



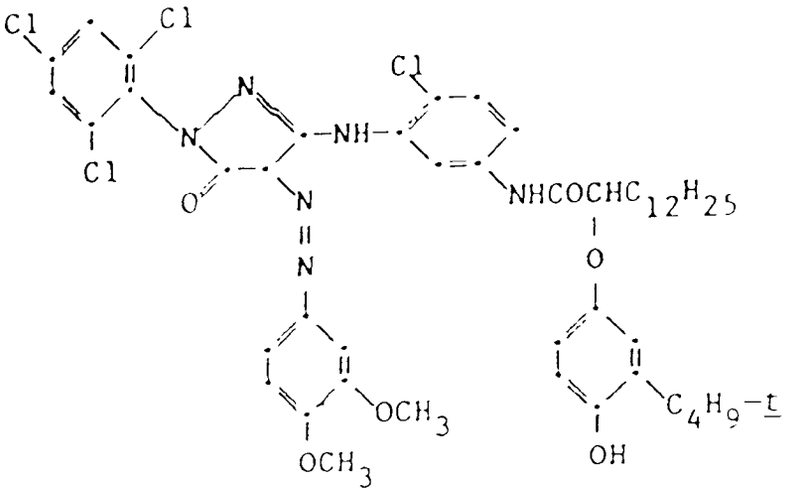
as well as a development inhibitor releasing coupler, designated as DIR coupler D-2:



Layer 5: Fast Magenta Layer - Fast green-sensitized layer bromoiodide tabular-grain gelatino emulsion prepared as described in U.S. Patent 4,434,226 of Wilgus. This layer also comprises a magenta image dye-forming coupler, designated as coupler M-2:

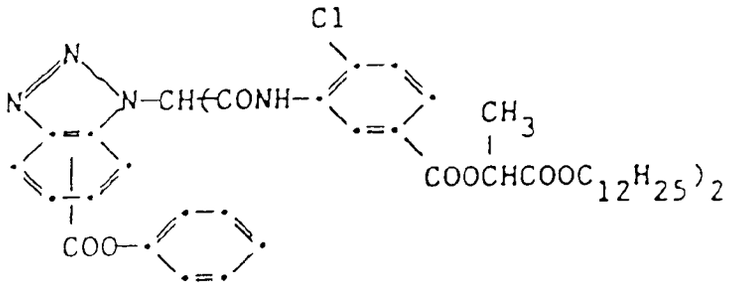


and a colored coupler, designated as M-3:



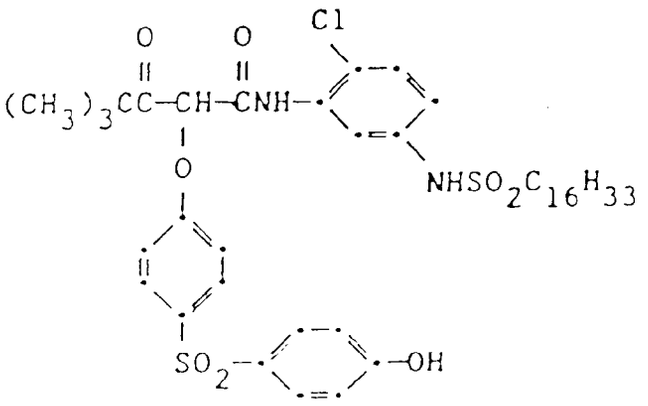
Layer 6: Interlayer - Gelatin

Layer 7: Slow Yellow Layer - Blue-sensitized silver bromoiodide tabular-grain gelatino emulsion (3 to 6 mol % iodide) prepared as described in U.S. Patent 4,434,226 of Wilgus. This layer also comprises yellow image dye-forming coupler Y-1 and a development inhibitor releasing coupler (DIR coupler):



and a gelatin hardener.

Layer 8: Fast Yellow Layer - Fast, blue-sensitized silver bromoiodide gelatino emulsion as described in U.S. Patent 3,320,069 of Illingsworth, and optimally sensitized with sulfur and gold. This layer also contains a yellow image-dye-forming coupler designated as coupler Y-1:



Layer 9: Protective Overcoat - Blend of U.V. absorbers and gelatin

Samples b, d, f, and h were prepared in the same manner as for Sample a except that coupler C-2 in Layer 2 was replaced by the amounts indicated in Table 1 of comparison coupler C-4, and bleach accelerator releasing couplers designated as BARC-1, -2, or -3, respectively. Further, Samples c, e, g and i were similarly pre-

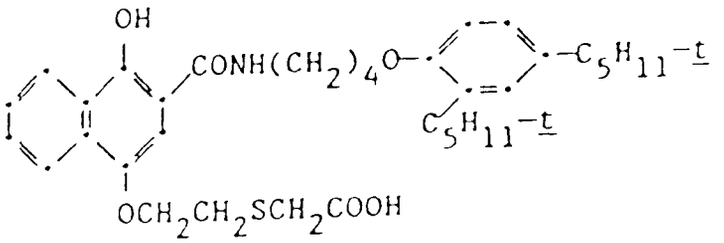
pared by replacing half of coupler C-1 in Layer 1 of Sample a by the indicated amounts of comparison coupler C-4 and BAR couplers 1, 2, or 3, respectively. These samples were each given a white light exposure through a graduated density step tablet and processed for 3.25 minutes in a color developer of the type described in the British Journal of Photography Annual, 1979, pp. 204-206. From plots of density to red light vs. log exposure the D-min, D-max, and relative photographic speed ΔS (in log E units at D = fog + 0.1) were determined as reported in Table A. The residual silver remaining after the bleach step was determined by x-ray fluorescence measurement and the average for the two highest exposure steps is given in Table A.

TABLE A

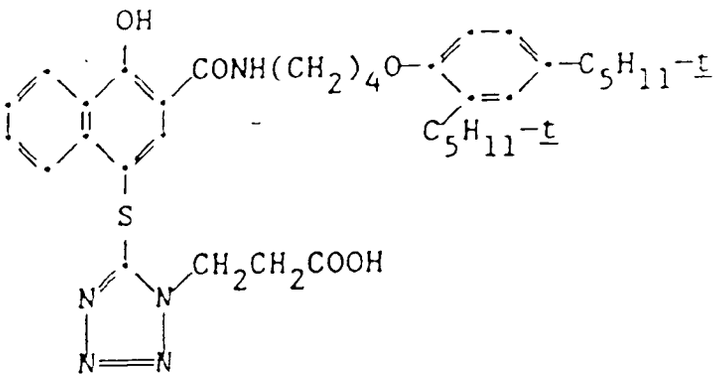
Example	Sample	Added Coupler	Amt. mg/m^2	Layer	D-min	D-max	ΔS	mg Ag/m^2	% Ag Removed
1a (control)	a	—	—	—	.29	1.79	0	94	0
1b (comparison)	b	C-4	164	2	.35	1.80	+.10	75	20
1c (comparison)	c	C-4	307	1	.48	2.34	0	79	16
1d (comparison)	d	BARC-1	174	2	.24	1.66	-.27	59	37
1e (comparison)	e	BARC-1	326	1	.38	1.86	0	56	40
1f	f	BARC-2	208	2	.28	1.46	-.50	13	86
1g	g	BARC-2	390	1	.28	1.73	-.04	0	100
1h	h	BARC-3	156	2	.32	1.85	-.02	0	100
1i	i	BARC-3	292	1	.46	2.34	-.04	0	100

The data in Table A show that addition of BARC-1, -2, or -3 to cyan layers of the multilayer element improves the removal of silver which otherwise would be retained causing color reproduction problems. When added to the fast layer at relatively high levels BARC-1 and -2 give substantial speed losses while for BARC-3 such loss is minimal. All except BARC-2 when added to the slow layer increase the minimum density.

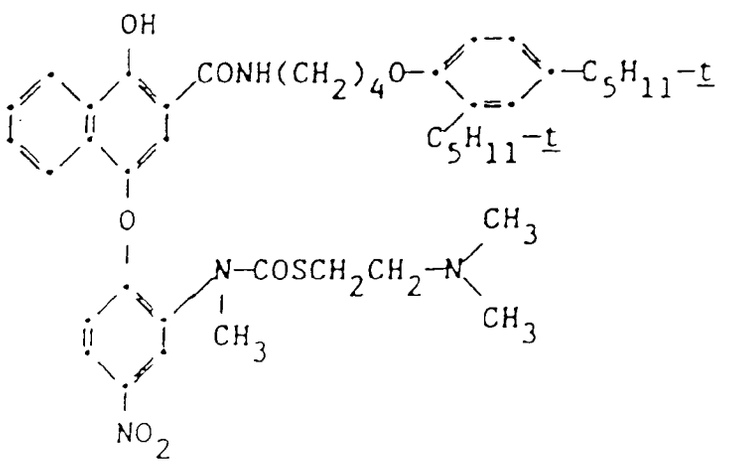
Comparison C-4 herein is:



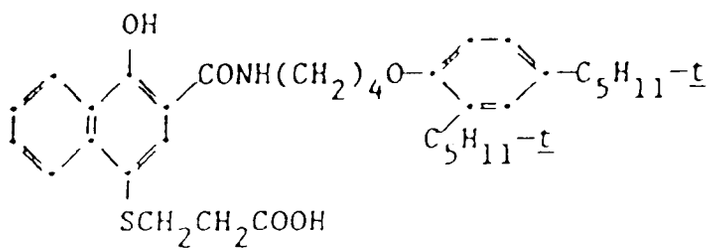
BARC-1 herein is:



BARC-2 herein is:



BARC-3 herein is:



Example 2

Multilayer incorporated coupler photographic elements were prepared in the same manner as for Sample a of Example 1, with coated amounts given in mg/m². Control Sample j was coated as follows on the film support:

Layer 1; (bottom layer)	Slow Cyan Layer — Comprising a red-sensitized silver bromoiodide tabular-grain emulsion blend (1615), gelatin (2153), cyan image coupler C-1 (603), colored coupler C-3 (32), and DIR coupler D-1 (32).
Layer 2:	Fast Cyan Layer — Comprising a fast red-sensitized silver bromoiodide tabular-grain emulsion (1076), gelatin (1615), cyan image coupler C-2 (151), and colored coupler C-3 (48).
Layer 3:	Interlayer — Comprising gelatin (1292).
Layer 4	Slow Magenta Layer — Comprising a green-sensitized silver bromoiodide tabular-grain emulsion blend (1292), gelatin (1615), magenta image coupler M-1 (646), colored coupler M-3 (43), and DIR coupler D-2 (13).
Layer 5:	Fast Magenta Layer — Comprising a fast green-sensitized silver bromoiodide tabular-grain emulsion (969), gelatin (1292), magenta image coupler M-2 (108), and coloured coupler M-3 (46).
Layers 6 through 9	were the same as for Sample a, Example 1.
Sample k was prepared as for Sample j but with the following changes in the magenta layers:	
Layer 4:	Coupler M-1 (484), coupler D-2 (32), and added bleach accelerator releasing coupler designated as BARC-4 (108).
Layer 5:	Coupler M-2 (54) and added BARC-4 (54).
Sample l was prepared as for Sample j but with the following changes in the cyan layers:	
Layer 1:	Coupler C-1 (517) and added BARC-3 (86).
Layer 2:	Coupler C-2 (75) and added BARC-3 (60).

Sample m was prepared as for Sample j but adding bleach accelerator releasing couplers to both cyan and magenta layers 1, 2, 4 and 5 according to the changes indicated in preparing Samples k and l.

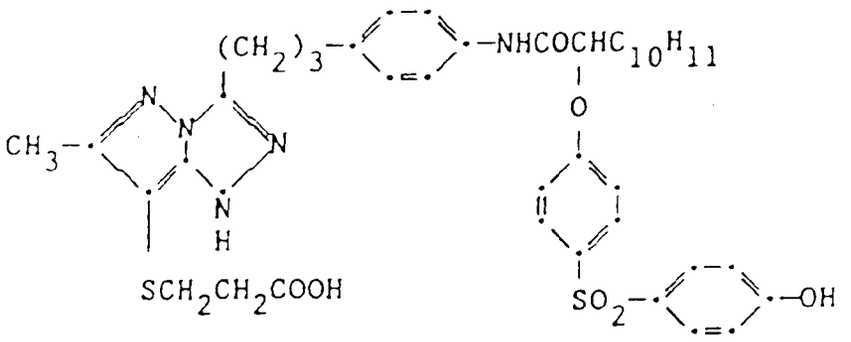
Photographic results after exposure and processing as in Example 1 are shown in Table B, where R, G, and W indicate samples were given red, green, or white light exposures, respectively.

TABLE B

Residual Ag in mg/m^2 (and % silver Removed)

Sample	BAR Compd.	G	R	W
j	— (control)	34(0)	77(0)	85(0)
k	magenta layers	7(80)	60(22)	21(75)
l	cyan layers	3(91)	5(94)	8(91)
m	magenta and cyan layers	8(76)	7(91)	6(93)

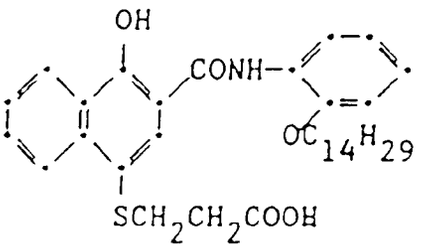
BARC-4 herein is:



The following examples can be carried out according to Example 1 with the exception that the bleach accelerator releasing coupler is replaced by the bleach accelerator releasing coupler designated in the following examples:

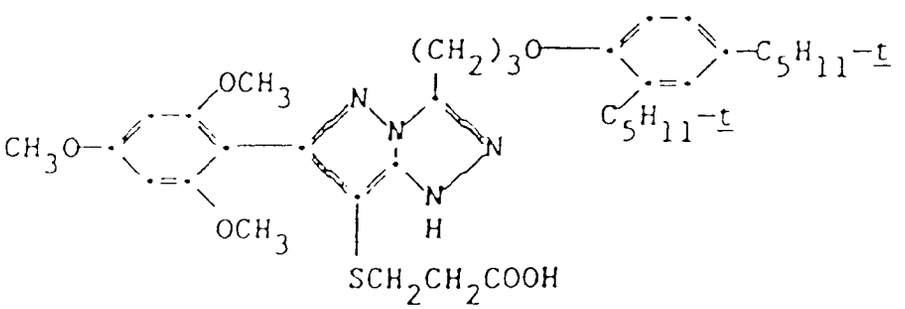
Example 3

BARC-5 herein is:



Example 4

BARC-6 herein is:



Claims

1. Use of a coupler comprising a coupler moiety having a releasable bleach accelerator moiety represented by the formula:

$$-(TIME)_n-S-R_1-R_2$$

wherein

TIME is a timing group;

n is 0 or 1;

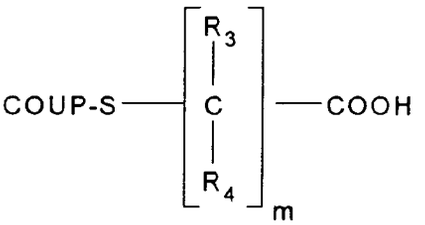
R_1 is a linking group consisting of alkylene comprising 1 to 8 carbon atoms; and,

R_2 is a water solubilizing group,

as a bleach accelerator releasing coupler in a photographic element comprising a support, a photographic silver halide emulsion layer and the bleach accelerator releasing coupler incorporated in the emulsion layer or a layer adjacent thereto.

2. Use as in claim 1 wherein said water solubilizing group is a carboxy group.

3. Use as in claim 1 wherein the bleach accelerator releasing coupler is represented by the formula:

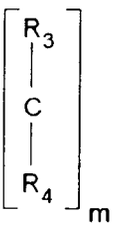


wherein

COUP is a coupler moiety;

m is 1 to 8;

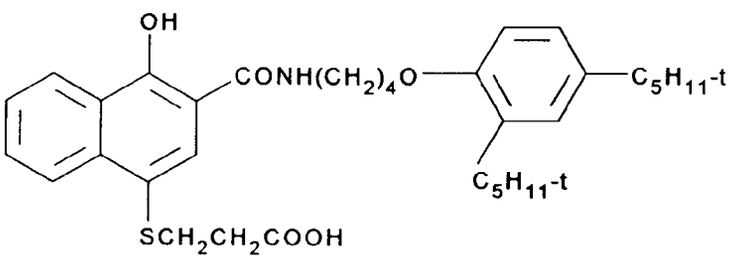
R_3 and R_4 are individually hydrogen or alkyl containing 1 to 4 carbon atoms; and wherein the total number of carbon atoms in



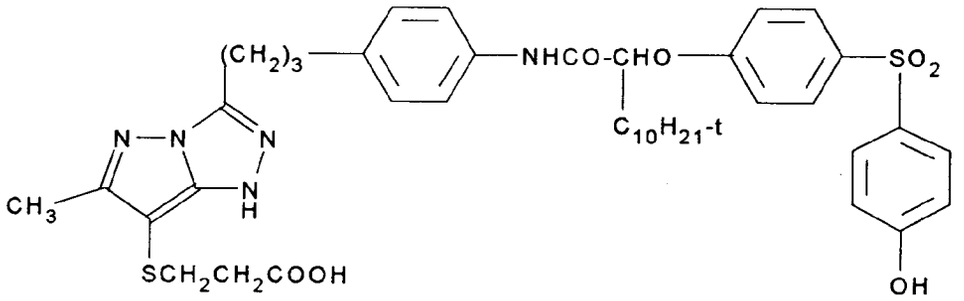
is 1 to 8.

4. Use as in claim 1 wherein said $-S-R_1-R_2-$ group is $-S-CH_2CH_2-COOH$ and n is 0.

5. Use as in claim 3 wherein said bleach accelerator releasing coupler is a compound of the formula:



6. Use as in claim 3 wherein said bleach accelerator releasing coupler is a compound of the formula:



7. A photographic element comprising a support, a photographic silver halide tabular grain emulsion layer and a bleach accelerator releasing coupler as defined in any of claims 1-6 in the emulsion layer or a layer adjacent thereto.

Patentansprüche

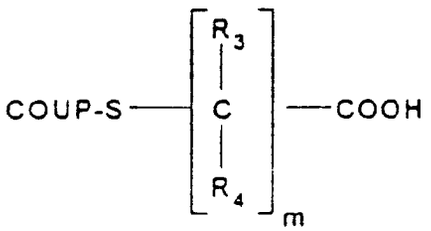
1. Verwendung eines Kupplers mit einem Kupplerrest mit einem freisetzbaren Bleichbeschleunigerrest der Formel:

$$-(TIME)_n-S-R_1-R_2$$

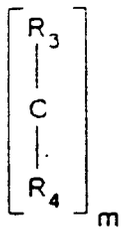
worin bedeuten:
TIME eine Zeitgebergruppe;
n gleich 0 oder 1;
R_1 eine verbindende Gruppe, bestehend aus Alkylen mit 1 bis 8 Kohlenstoffatomen; und
R_2 eine wasserlöslich machende Gruppe,
als einen einen Bleichbeschleuniger freisetzenden Kuppler in einem photographischen Element mit einem Träger, einer photographischen Silberhalogenidemulsionsschicht und dem einen Bleichbeschleuniger freisetzenden Kuppler in der Emulsionsschicht oder einer hierzu benachbarten Schicht.

2. Verwendung nach Anspruch 1, wobei die wasserlöslich machende Gruppe eine Carboxygruppe ist.

3. Verwendung nach Anspruch 1, wobei der den Bleichbeschleuniger freisetzende Kuppler durch die folgende Formel wiedergegeben wird:



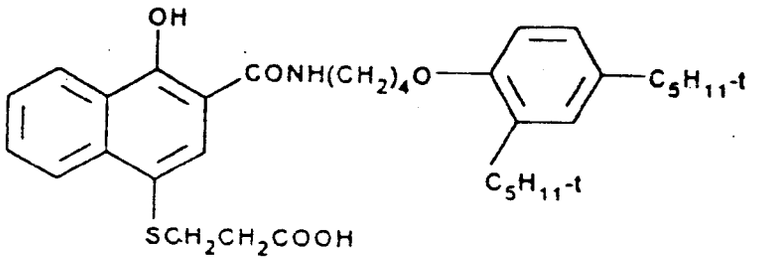
worin bedeuten:
COUP einen Kupplerrest;
m gleich 1 bis 8;
R_3 und R_4 einzeln Wasserstoff oder Alkyl mit 1 bis 4 Kohlenstoffatomen, wobei die Gesamtanzahl von Kohlenstoffatomen in dem Rest



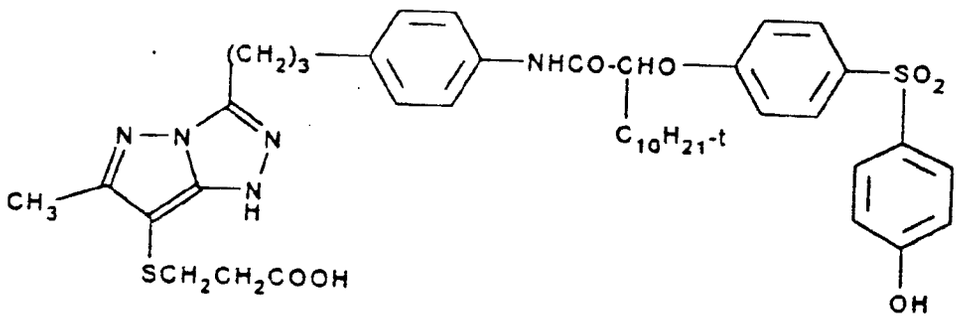
bei 1 bis 8 liegt.

4. Verwendung nach Anspruch 1, wobei die Gruppe -S-R_1-R_2 entspricht -S-CH_2CH_2-COOH und worin n gleich 0 ist.

5. Verwendung nach Anspruch 3, wobei der einen Bleichbeschleuniger freisetzende Kuppler eine Verbindung der folgenden Formel ist:



6. Verwendung nach Anspruch 3, wobei der einen Bleichbeschleuniger freisetzende Kuppler eine Verbindung der folgenden Formel ist:



7. Photographisches Element mit einem Träger, einer photographischen Emulsionsschicht mit tafelförmigen Silberhalogenidkörnern sowie einem einen Bleichbeschleuniger freisetzenden Kuppler nach einem der Ansprüche 1 bis 6 in der Emulsionsschicht oder einer hierzu benachbarten Schicht.

Revendications

1. Utilisation d'un coupleur ayant un groupe accélérateur de blanchiment séparable représenté par la formule :

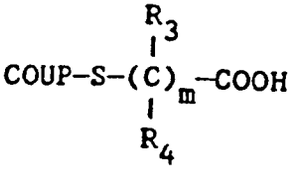
$$-(TIME)_n-S-R_1-R_2$$

où

TIME est un groupe retardateur ;
n est 0 ou 1 ;
R_1 est un groupe alkylène de 1 à 8 atomes de carbone ; et
R_2 est un groupe solubilisant dans l'eau, comme coupleur libérant un accélérateur de blanchiment dans un produit photographique comprenant un support, une couche d'émulsion photographique aux halogénures d'argent et un coupleur libérant un accélérateur de blanchiment incorporé dans la couche d'émulsion ou dans une couche adjacente.

2. Utilisation selon la revendication 1, dans laquelle le groupe solubilisant dans l'eau est un groupe carboxy.

3. Utilisation selon la revendication 1, dans laquelle le coupleur libérant un accélérateur de blanchiment a la formule :



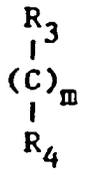
où

COUP est un radical de coupleur ;

m est un nombre de 1 à 8 ;

R_3 et R_4 représentent individuellement l'hydrogène ou un groupe alkyle de 1 à 4 atomes de carbone ;

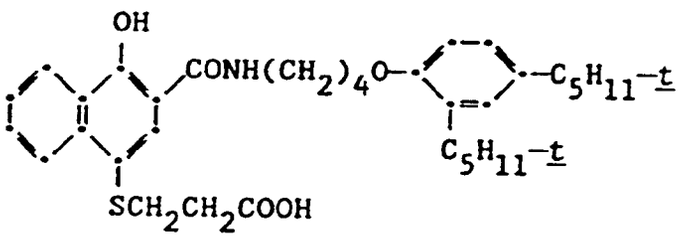
et où le nombre total d'atomes de carbone dans



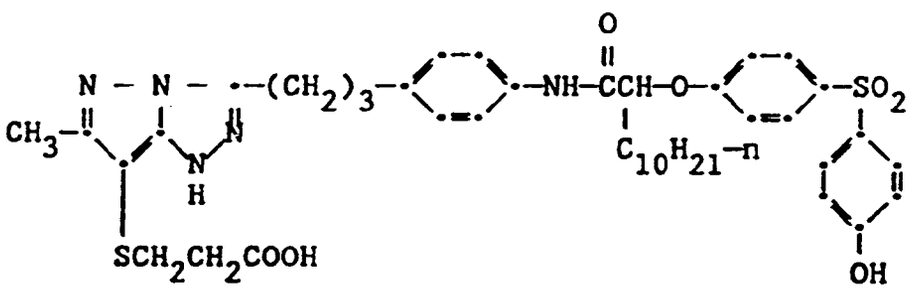
est de 1 à 8.

4. Utilisation selon la revendication 1, où -S-R_1-R_2 est -S-CH_2CH_2COOH et n est 0.

5. Utilisation selon la revendication 3, où le coupleur libérant un accélérateur de blanchiment est un composé de formule :



6. Utilisation selon la revendication 3, où le coupleur libérant un accélérateur de blanchiment est un composé de formule



7. Produit photographique comprenant un support, une couche d'émulsion photographique à grains tabulaires d'halogénure d'argent et un coupleur libérant un accélérateur de blanchiment tel que défini dans l'une quelconque des revendications 1 à 6 dans la couche d'émulsion ou bien dans une couche adjacente à la couche d'émulsion.