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(71) Applicant: **AGFA-GEVAERT naamloze vennootschap**
Septestraat 27
B-2510 Mortsel(BE)

(72) Inventor: **Janssens, Wilhelmus**
De Egdstraat 11
B-3240 Aarschot(BE)
Inventor: **Vanmaele, Luc Jerome**
Dorpsstraat 52
B-9130 Lochristi(BE)
Inventor: **Boie, Immo**
Stöcken 13a
D-5672 Leichlingen(DE)

(54) Magenta dye-releasing compounds.

(57) In a dye diffusion transfer process the use of a photographic silver halide element incorporating a hydroquinone-type or quinone-type dye-releasing compound that is capable of releasing as a result of development and a redox-reaction a magenta azomethine dye comprising a substituted or unsubstituted anellated heterocyclic group selected from the class of the pyrazolo-azoles and imidazo-azoles.

EP 0 345 839 A1

MAGENTA DYE-RELEASING COMPOUNDS

The present invention relates to a process for the production of diffusion transfer images with non-diffusible magenta dye-releasing compounds, to such dye-releasing compounds, and to photographic elements incorporating them.

Dye diffusion transfer imaging can be carried out in a number of ways but all dye diffusion transfer imaging systems are based on the same principle of modifying the solubility of the dyes as a function of the amount of photosensitive silver halide developed.

In commonly known dye diffusion transfer processes the dye-image-producing compounds are either initially mobile in alkaline aqueous media and become immobilized during processing, or initially immobile and become mobilized during processing.

A survey of such processes has been given by Christian C. Van de Sande in Angew.Chem. Int.Ed.Engl. 22 (1983) n° 3, 191-209.

Four important categories of dye-release processes are based on the following reactions respectively:

(A) a redox-reaction controlling a solubility change;

(B) an oxidative chromogenic coupling reaction;

(C) a redox-controlled cleavage reaction;

(D) an argentolytic cleavage reaction of a dye-releasing compound with silver ions.

A dye-developer system based on redox-controlled solubility change (ref. e.g. US-A 2 983 606) was the first commercially introduced dye diffusion transfer system.

Later on redox-controlled dye-releasing compounds were introduced in commercial systems.

Oxidizable dye-releasing compounds that after oxidation release a dye moiety by hydrolysis are known, e.g., from DE-A 2,242,762, DE-A 2,406,664, DE-A 2,505,246, DE-A 2,613,005, DE-A 2,645,656 and Research Disclosure publications Nos. 15,157 (November 1976), 16,654 (April 1977) and 17,736 (January 1979). In these references dye-releasing compounds are described in which the dye moiety is linked most frequently to an oxidizable carrier moiety through a sulphonamido group. The dye released from such compounds thus contains a sulphamoyl group.

Oxidizable dye-releasing compounds that in oxidized form release a dye moiety by intramolecular displacement reaction are described, e.g. in US-A 3,443,940. The dye released from these compounds contains a sulphinate group.

It is particularly interesting in dye diffusion transfer to operate with dye-releasing compounds, the dye release of which is inversely proportional to the development of a negative-working silver halide emulsion layer so that positive dye images can be formed in an image-receiving layer.

Oxidizable dye-releasing compounds that in oxidized form are stable but in reduced state set free a dye moiety by an elimination reaction are described in DE-A 2,823,159 and DE-A 2,854,946. Compounds of this type can be used in reduced form in an unexposed silver halide emulsion material and can be called IHO-compounds, IHO being an acronym for "Inhibited Hydrolysis by Oxidation".

Reducible dye-releasing compounds that after reduction set free a dye moiety can be called IHR-compounds, IHR standing for "Increased Hydrolysis by Reduction".

Reducible quinone-type IHR-compounds, which after reduction can undergo a dye release with an intramolecular nucleophilic displacement reaction, are described in DE-A 2,809,716 wherein these compounds are called BEND-compounds, BEND standing for "Ballasted Electron-accepting Nucleophilic Displacement".

Reducible IHR-compounds, which after reduction can undergo a dye release with an elimination reaction are described in published EP-A 0,004,399 and in US-A 4,371,604.

Other classes of compounds that may release a dye after reduction are described in DE-A 3,008,588 and DE-A 3,014,669.

Particularly useful dye-releasing compounds are the redox-controlled dye-releasing compounds, which can be represented by:

BALL-REDOX-DYE

wherein :

BALL represents a moiety with ballast residue for immobilizing the dye-releasing compound in a hydrophilic colloid layer,

REDOX represents a redox-active group, i.e. a group that under the circumstances of alkaline silver halide development is oxidizable or reducible and depending on the oxidized or reduced state brings about a dye release by an elimination reaction,nucleophilic displacement reaction, hydrolysis, or cleavage reaction,

DYE represents a diffusible dye moiety or a precursor thereof.

Coloured compounds for use in a dye diffusion transfer process include e.g. triphenylmethane, xanthene, azo, azomethine, anthraquinone, alizarine, merocyanine, quinoline or cyanine dye structures. Of particularly frequent use is a mono-azo-dye group as described e.g. in US-A 3,725,062.

In conventional colour photography it is known to use colour couplers, which are capable of forming azomethine dyes derived from pyrazolo-azoles by reaction with an oxidized aromatic primary amino developing agent. For instance in the paper "J. Soc. Photogr. Sci. Technol. JPN 48 (1985) Nr. 4, pages 298-299 by T. Sato, T. Kawagishi, and N. Furutachi magenta azomethine dyes derived from pyrazolo-azoles e.g. 1H-pyrazolo[1,5-b]-1,2,4-triazole and 1H-pyrazolo[5,1-c]-1,2,4-triazole have been described. In EP-A 0,178,788 1H-pyrazolo[3,2-c]-S-triazole magenta couplers and in JA-A 83/130,339 pyrazolo-azole magenta couplers have been disclosed for use in a silver halide emulsion layer.

In dye diffusion transfer imaging there is a need for dye-releasing compounds that can yield diffusible magenta dyes having a satisfactory (wanted) absorption in the green part of the spectrum and a low (unwanted) side-absorption in the orange-red part and especially in the blue-violet part of the spectrum.

It is an object of the present invention to provide a process for the production of diffusion transfer images comprising as magenta dyes azomethine dyes having a satisfactory absorption in the green part of the spectrum whilst having particularly low unwanted side absorption.

It is another object of the present invention to provide dye-releasing compounds that are capable of releasing such magenta dyes.

It is also an object of the present invention to provide photographic elements incorporating such dye-releasing compounds.

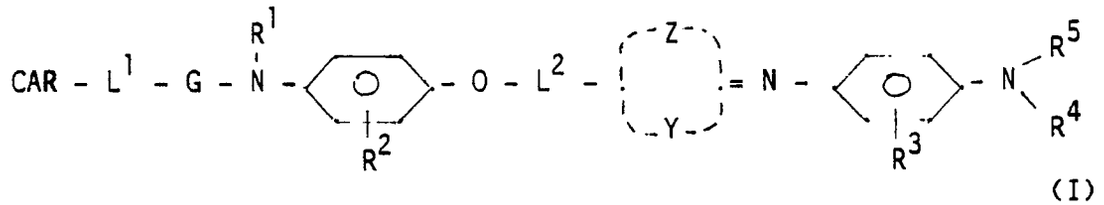
In accordance with the present invention a process for the production of diffusion transfer images is provided, which comprises the steps of:

(1) applying an alkaline aqueous processing liquid to an image-wise exposed photographic element comprising at least one photosensitive alkali-permeable hydrophilic colloid silver halide emulsion layer and in operative association therewith at least one non-diffusible dye-releasing compound that can split off a diffusible magenta azomethine dye,

(2) providing a silver halide developing agent, which is present in said photographic element at least during application of said alkaline aqueous processing liquid to effect - as a function of the development of said silver halide emulsion layer and a redox reaction - the image-wise release of said diffusible magenta azomethine dye, and

(3) allowing diffusion of said released magenta azomethine dye into an image-receiving layer held in water-permeable relationship with said silver halide emulsion layer,

characterized in that said dye-releasing compound corresponds to the following general formula I:



(I)

wherein:

CAR represents an organic carrier moiety capable of undergoing a redox reaction, which moiety may contain a ballasting group rendering said dye-releasing compound non-diffusing in a hydrophilic colloid medium in wet alkaline conditions, e.g. a hydroquinone-type or quinone-type moiety,

L' represents a chemical group cleavable or releasable from the carrier moiety as a function of a redox reaction taking place in the development of said silver halide emulsion layer under wet alkaline conditions,

G represents a bivalent organic linking group comprising at least one aromatic nucleus e.g. a phenylene nucleus or a substituted bivalent organic linking group comprising at least one aromatic nucleus,

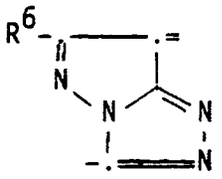
R^1 is hydrogen, an alkyl group, or an aryl group,

R^2 is hydrogen or a monovalent organic group,

L^2 represents a bivalent organic linking group comprising at least 2 carbon atoms,

Z and Y together represent the atoms necessary to complete a substituted or unsubstituted anellated heterocyclic system selected from the group of the pyrazolo-azoles and imidazo-azoles e.g. a heterocyclic system chosen fromthe following group of heterocyclic systems corresponding to the structural formulae II

to XII,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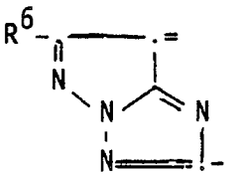
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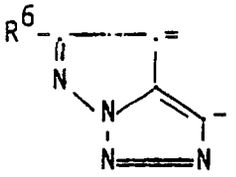
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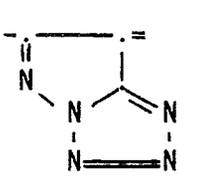
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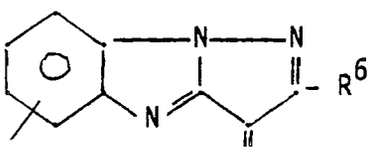
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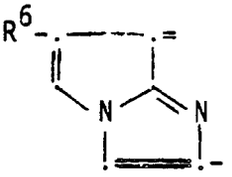
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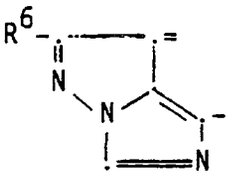
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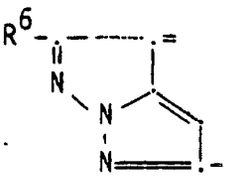
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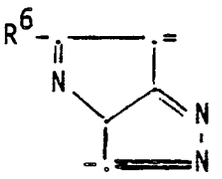
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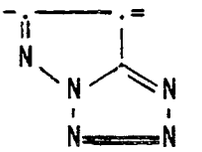
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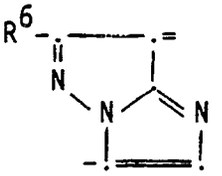

(XII)

R^3 is hydrogen, a halogen atom, an alkyl group, an alkoxy group, an acylamino group, or an aryl group, as well as a substituent in ortho-position to the group NR^4R^5, which substituent together with R^4 completes a cyclic amino group, and

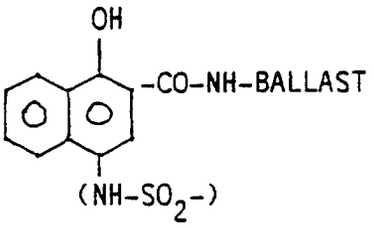
R^4 is hydrogen, a C^1-C^4 alkyl group e.g. ethyl, a substituted C^1-C^4 alkyl group e.g. 2-hydroxyethyl, 2-(methylsulphonamido)-ethyl, a substituent that together with R^3 completes a cyclic amino group, or a substituent that together with R^5 completes a cyclic amino group,

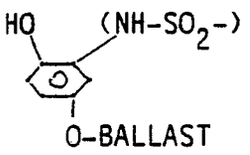
R^5 is hydrogen, a C^1-C^4 alkyl group, a substituted C^1-C^4 alkyl group, or a substituent that together with R^4 completes a cyclic amino group, and

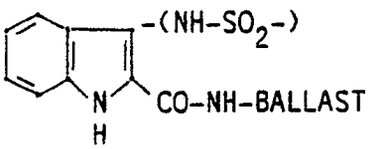
R^6 is hydrogen, a C^1-C^4 alkyl group, a substituted C^1-C^4 alkyl group, an aryl group, or a substituted aryl group.

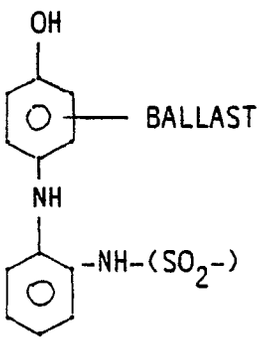
(CAR-L^1-) moieties, from which in oxidized form by a non-chromogenic reaction in alkaline medium a

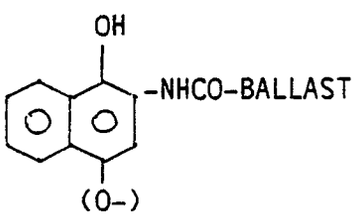
dye moiety can be split off, can be selected from e.g. the following groups including such groups in substituted form:







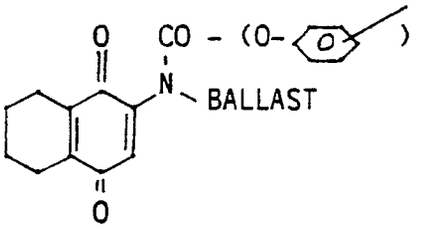


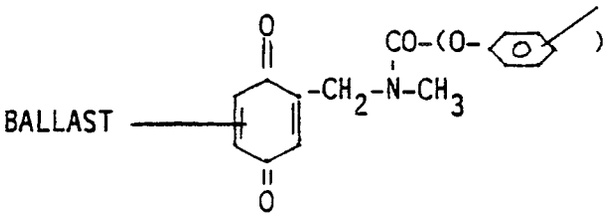


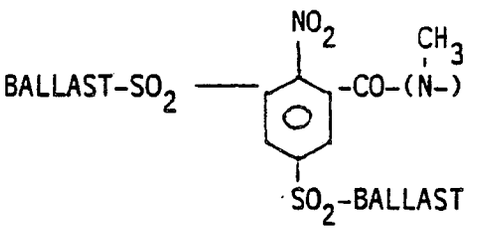
The groups within brackets are released together with the dye moiety (not represented), and remain with the dye moiety as groups promoting diffusion.

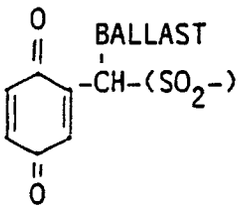
In the above-mentioned dye-releasing compounds the dye release proceeds directly proportionally to the rate of formation of the oxidation products of developing agent used in the development of silver halide. Said compounds are therefore negative-working in that they undergo dye release in correspondence with the exposed portions of a negative-working silver halide emulsion layer. For the production of positive pictures an image reversal is needed, which may be based on the use of positive-working layers containing a direct-positive silver halide emulsion or on the silver salt complex diffusion transfer process by selection of a proper layer assemblage as described e.g. in EP-A 0,003,376.

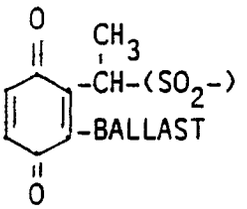
(CAR-L^1-) moieties, from which in alkaline medium a dye moiety can be set free after reduction, can be selected from the following groups including such groups in substituted form:

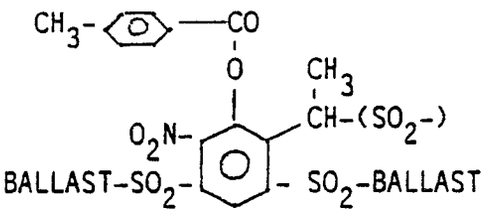


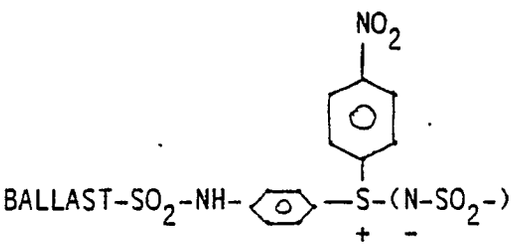






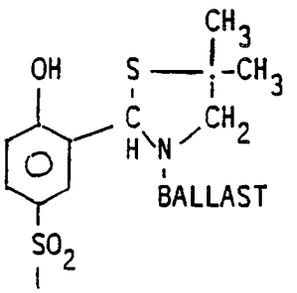


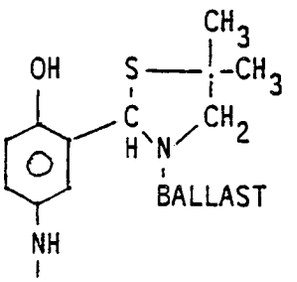




The groups within brackets are functional groups that are split off together with the dye moiety (not shown). These functional groups can be separated from the chromophoric group of the dye by a linking member having no influence on the absorption properties of the dye. The functional group, however, optionally together with said linking member, may be of importance to determine the diffusion-mobility and/or capability of the released dye to be mordanted. Useful linking members are, e.g., alkylene and arylene groups.

Examples of carriers that are capable of releasing a diffusible dye or precursor thereof by argentolysis have been described in e.g. the above-mentioned Angew. Chem. Int. Ed. Engl. 22 (1983), p. 207. Particularly useful examples thereof are the following:



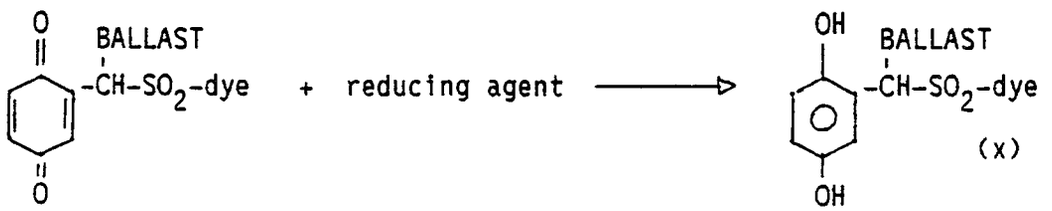


Ballast groups (BALLAST) that confer resistance to diffusion are groups that allow the compounds according to the present invention to be incorporated in non-diffusing form in the hydrophilic colloids customarily used in photographic elements. Organic groups, which generally carry straight-chain or branched-chain aliphatic groups and also isocyclic or heterocyclic or aromatic groups mostly having from 8 to 20 carbon atoms are preferred for this purpose. These groups are attached either directly or indirectly e.g. through one of the following groups : -$NHCO_2$-; -$NHSO_2$-; -NR-, in which R represents hydrogen or alkyl; -O-; -S-; or -SO_2-. The group conferring resistance to diffusion may additionally carry groups that confer solubility in water, e.g. sulpho groups or carboxy groups, and these may also be present in anionic form. Since the diffusion properties depend on the molecular size of the compound as a whole, it is sufficient in certain cases, e.g. when the molecule has a considerable size, to use one or more short-chain groups as groups conferring resistance to diffusion or to use no such group at all.

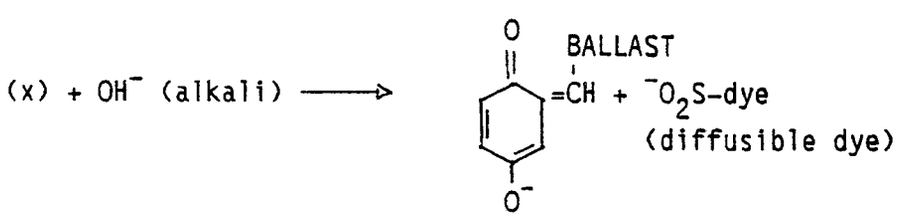
In a preferred embodiment for positive magenta dye image production with negative-working silver halide emulsions the magenta dye-releasing compounds are quinone-type IHR-compounds, from which a diffusible magenta dye moiety is released by reduction and hydrolysis.

The reaction operative in the release of a dye moiety from said quinone-type IHR-compounds proceeds in two stages (A) and (B) as illustrated by the following equations:

(A)



(B)



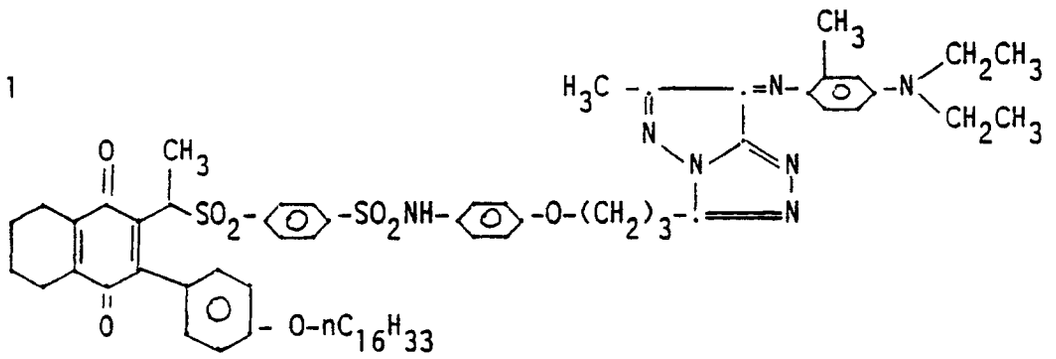
wherein:
"BALLAST" stands for a ballasting group making the compound non-diffusing in a hydrophilic colloid medium under wet alkaline conditions, such as a long-chain alkyl group e.g. n-hexadecyl. In case the compound is of such structure that it does not need a ballasting group to render it non-diffusing, "BALLAST" may stand for i.a. a lower alkyl group e.g. methyl.

The term "diffusible" as used herein stands for "having the property of diffusing effectively through colloid layers of photographic elements in alkaline liquid medium. The term "mobile" has the same meaning. The terms "non-diffusible" and immobile have the opposite meaning.

Examples of magenta dye-releasing compounds for use in the process according to the present invention are listed in the following Table 1.

TABLE 1

1



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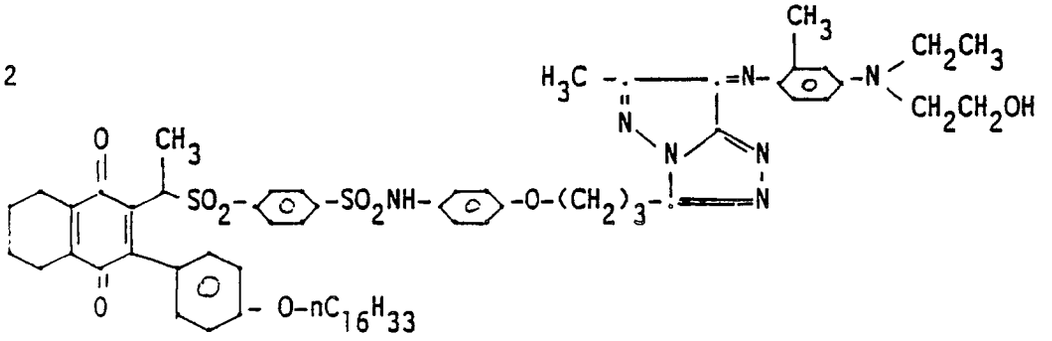

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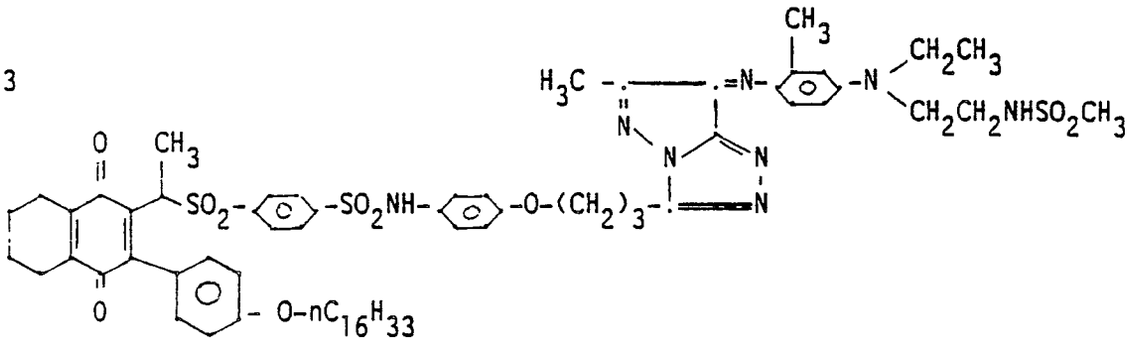

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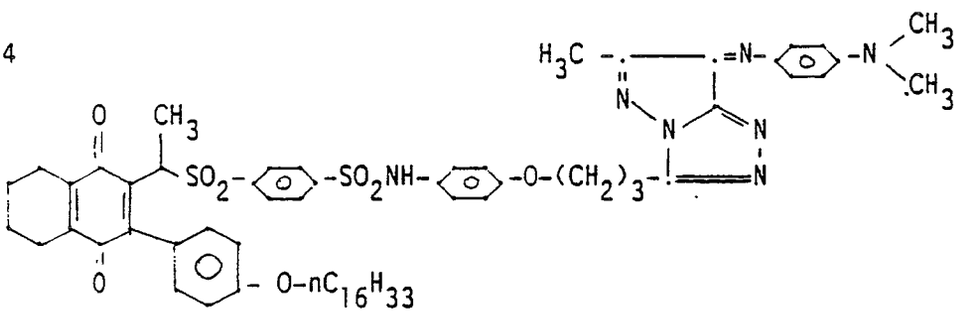

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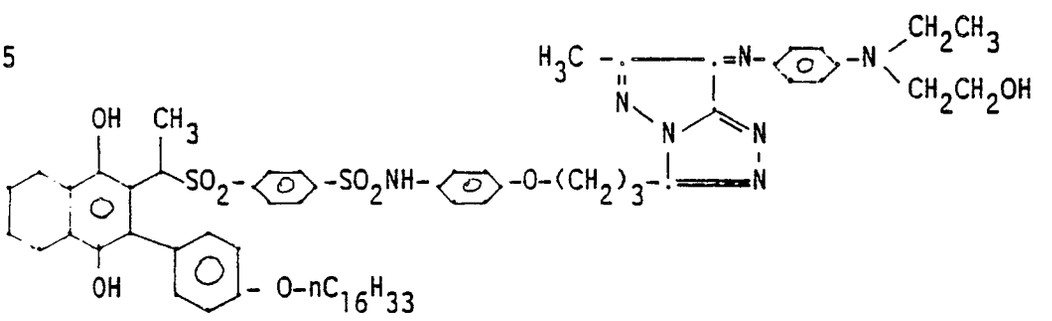

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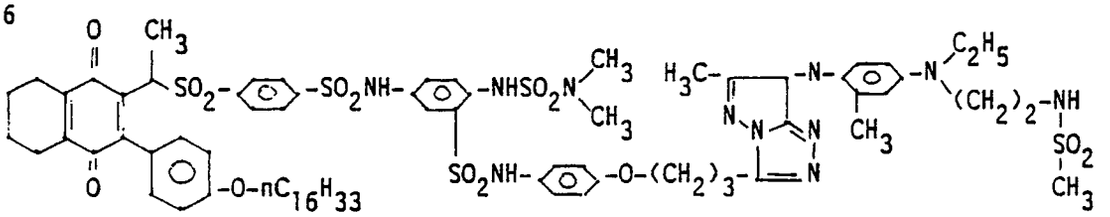

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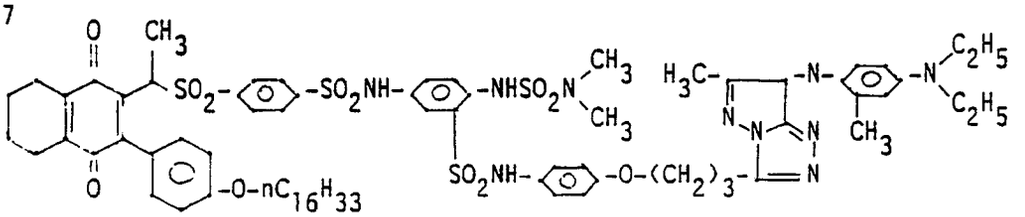

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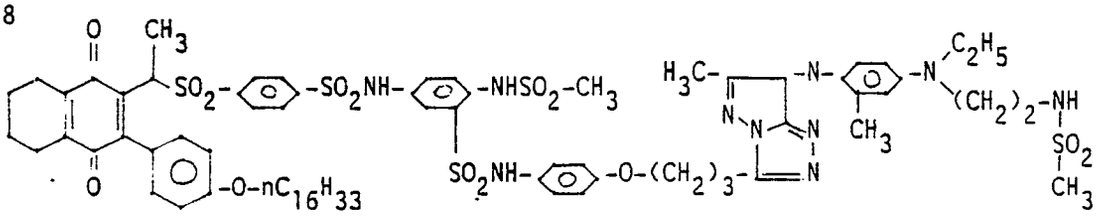

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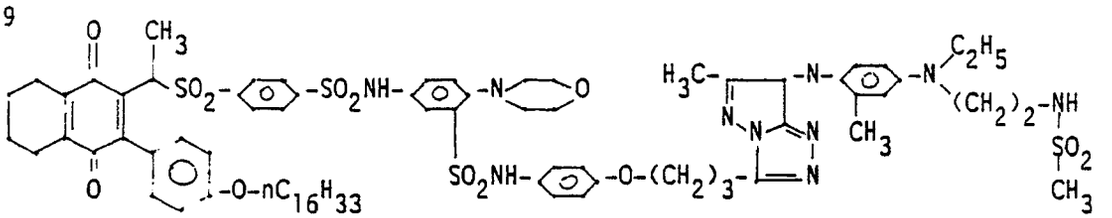

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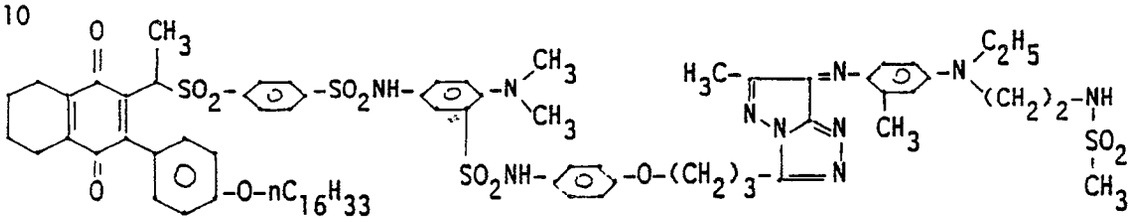

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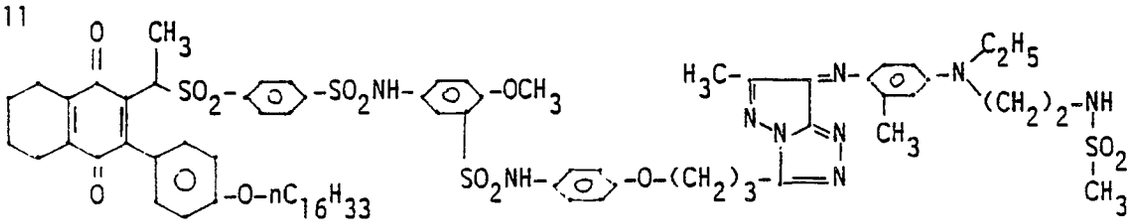
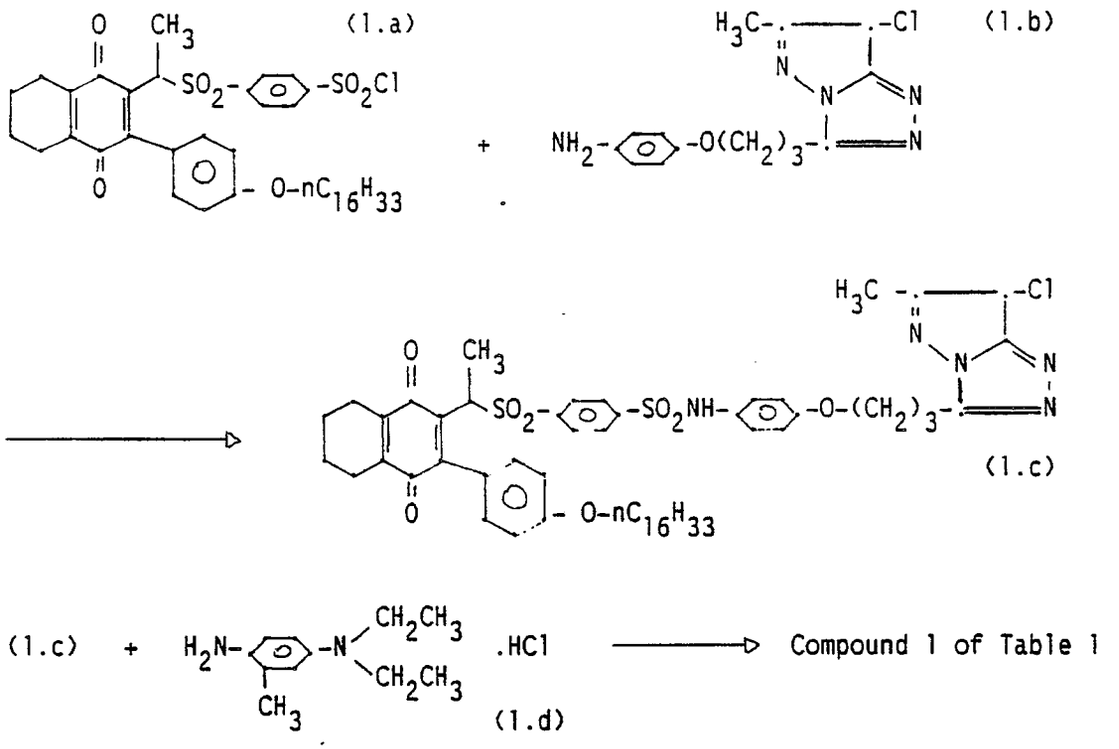


The following preparations illustrate the synthesis of dye-releasing compounds for use in accordance with the present invention. The synthesis of dye-releasing compound 1 of Table 1 is represented in the following reaction scheme and is described in Preparation 1 hereinafter.



PREPARATION 1

a) An amount of 5.5 g (18 mmol) of (1.b) is suspended in a mixture of 50 ml of dichloroethane and 10.2 ml of pyridine in a flask, which is placed in a waterbath at 80 ° C. A solution of 13.4 g of (1.a) in 50 ml of dichloroethane is added dropwise thereto. The reaction mixture is stirred for 2 h at 82 ° C and then poured out with stirring in 500 ml of water at 50 ° C. The organic phase is separated in a separatory funnel.

The dichloroethane solvent is removed by evaporation. The sticky residue is re-dissolved in acetone. The solution is poured out with thorough stirring in a mixture of 200 ml of water and 20 ml of 5N hydrochloric acid. A precipitate forms, which is stirred again in pure water. The precipitate is filtered with suction and dried under reduced pressure. Yield: 18.13 g of the intermediate product (1.c)

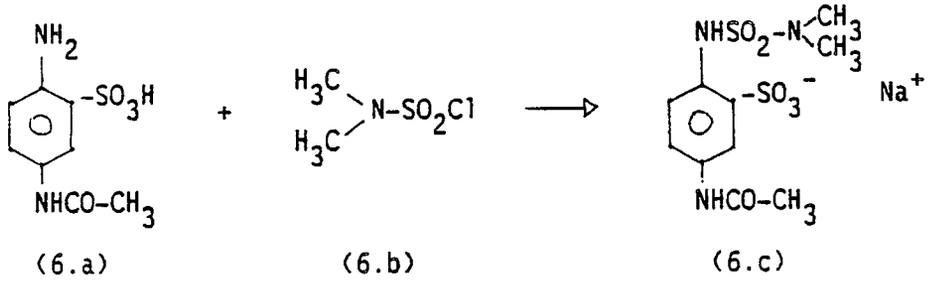
b) A solutionof 4.75 g of (1.d) in 50 ml of water is added to a solution of 20 g (19.7 mmol) of the intermediate product (1.c) in 394 ml of dimethylformamide. A volume of 9.6 ml of a solution of 8 g of potassium carbonate in 64 ml of water is added to the mixture. The remainder of the potassium carbonate solution and a solution of 32.5 g of potassium cyanoferrate (III) in 98 ml of water are added simultaneously to the mixture. An exothermic reaction takes place from 25 °C to 42 °C. The mixture is allowed to cool until room temperature is reached again. The reaction mixture is allowed to stand overnight. The purple precipitate is filtered with suction, rinsed abundantly with water, and dried under reduced pressure.
Yield 5 g (22%) of pure dye-releasing Compound 1 (after purification by column chromatography).

The dye-releasing compounds 2, 3, and 4 can be prepared as described for dye-releasing compound 1 with the only difference that instead of 2-amino-5-diethylaminotoluene hydrochloride (Compound (1.d)) the following compounds are used respectively:

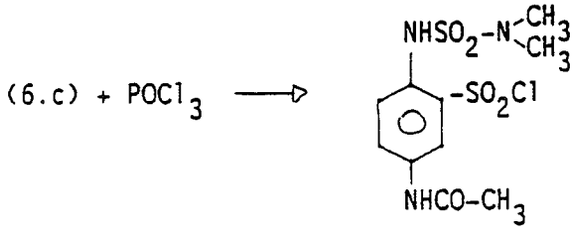
- N-ethyl-N-(Beta-hydroxy-ethyl)-m-toluidine sulphate,
- 4-amino-N-ethyl-N-(Beta-methylsulphonamido-ethyl)-m-toluidine sesquisulphate monohydrate, and
- N,N-dimethyl-p-phenylene diamine hydrochloride.

Pyrazolo-azole and imidazo-azole intermediate compounds e.g. Compound (1.b) and starting compounds needed for preparing these can be synthesized as described in DE Patent Application N° 3,610,702, which corresponds to the US Serial N° ..... .

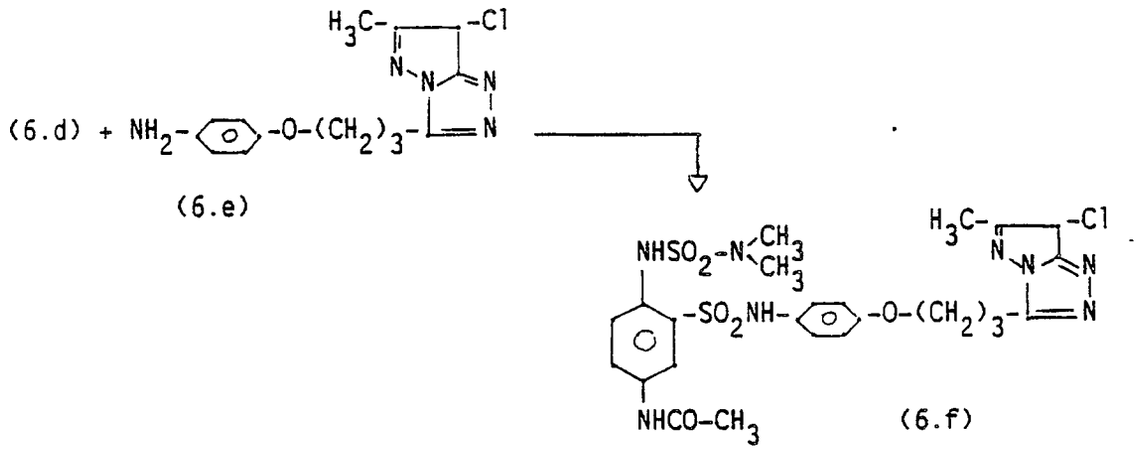
The synthesis of dye-releasing compound 6 is represented in the following reaction scheme and is described in Preparation 2 hereinafter.



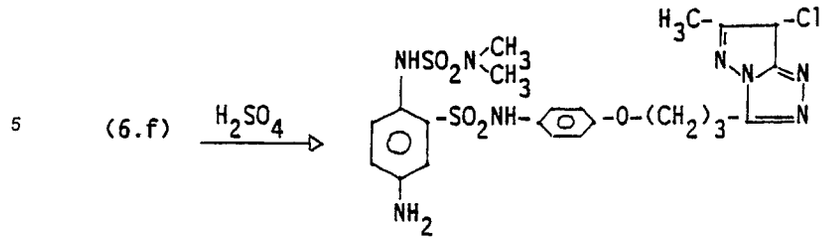
(6.a) (6.b) (6.c)



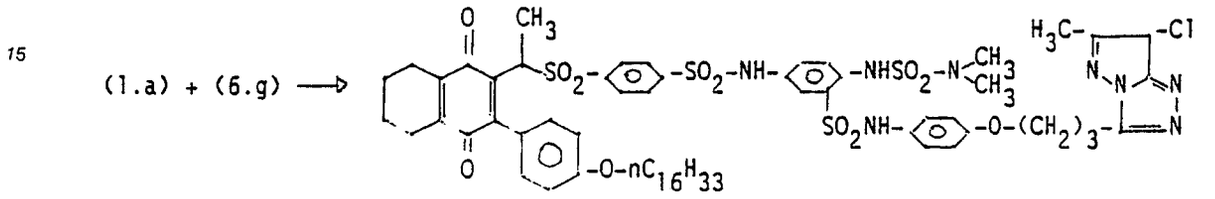
(6.d)



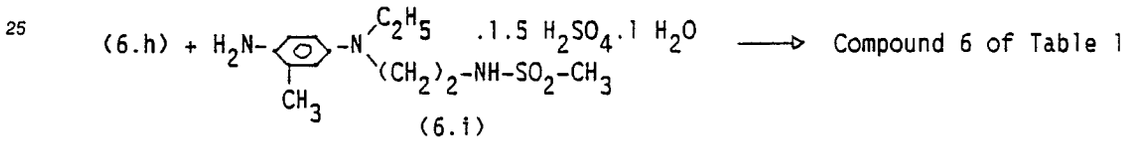
(6.e) (6.f)



(6.g)



(6.h)



(6.i)

PREPARATION 2

a) An amount of 33 g (0.14 mol) of (6.a) is added at 10-20 °C with slight cooling to 80 ml of pyridine. A volume of 38.5 ml of (6.b) is added dropwise in 30 min at 20 °C. The mixture is allowed to stand overnight at room temperature and then concentrated by evaporation. Demineralized water (100 ml) is added and the pH is adjusted to 13 by addition of 37.8 g of sodium hydroxide. A volume of 300 ml of methylene chloride is added. The resulting mixture is stirred vigorously. The reaction product is extracted 5 times with 400 ml of methylene chloride. The aqeous phase is acidified with 60 ml of 5N hydrochloric acid to pH 1. The mixture is placed in a refrigerator for 48 h. Subsequently the product is filtered and rinsed with a saturated sodium chloride solution. The product is filtered with suction and dried in a cabinet at 50 °C.
Yield : 29.93 g of (6.c).

b) An amount of 42.7 g (0.12) of (6.c) is added to 114 ml of $POCl_3$ whilst keeping the temperature below 60 °C (exothermic reaction). An amount of 22 ml of N-methylpyrrolidinone is added at a temperature not higher than 60 °C to the mixture. The temperature is then kept at 50 °C for 90 min.
The reaction mixture is added at a temperature not higher than 10 °C to a mixture of 960 ml methylene chloride, 860 ml of icewater,and 50 g of sodium acetate. The resulting organic brown phase is collected, rinsed 4 times with a saturated sodium chloride solution, dried over sodium sulphate, filtered, and concentrated by evaporation. The resulting beige reaction product is kept under nitrogen atmosphere. Yield : 36.2 g of (6.d).

c) A volume of 240 ml of acetone, 44 ml of pyridine, and 23.9 g (78.3 mmol) of (6.e) are added to 36.2 g (0.102 mol) of (6.d) at room temperature. The temperature of the reaction mixture rises to 35 °C. The reaction mixture is then heated to 50-60 °C for 90 min. The hot mixture is poured slowly into 720 ml of icewater and 52.2 ml of 12N hydrochloric acid. A beige product precipitates. The mixture is stirred for 45 min. The product is isolated and dissolved in acetone. The solution is poured into 1.5 l of hot water. The

aqueous layer is decanted from the oil layer, which is rinsed with demineralized water. The product is filtered with suction and dried under reduced pressure.
Yield : 28.1 g of (6.f).

d) A mixture of 107 ml of 2-methoxypropanol, 107 ml of demineralized water, and 5.7 ml of sulphuric acid is added to 26.8 g (43 mmol) of (6.f). The reaction mixture is heated to 100 °C for 6 h and then poured into a mixture of 900 ml of demineralized water and 89.6 g of sodium acetate. The mixture is stirred vigorously for 15 min. The product is filtered, rinsed with demineralised water, and dried under reduced pressure.
Yield : 22.8 g of (6.g).

e) An amount of 21.5 g (0.037 mol) of (6.g) is added to a mixture of 215 ml of acetone, 19 ml of pyridine, and 27.5 g of (1.a). The temperature of the reaction mixture is kept at 60 °C for 2 h. The reaction mixture is then cooled and poured slowly into a mixture of 2 l of demineralised water and 31 ml of 12N hydrochloric acid.
The yellow precipitate is filtered, rinsed with demineralised water, filtered again, and dried under reduced pressure. Yield : 44.7 g of (6.h).

f) A volume of 47.5 ml of aqueous potassium cyanoferrate(III) solution comprising 7.6 g of potassium cyanoferrate(III) and 4.3 ml of aqueous potassium carbonate solution comprising 0.64 g of potassium carbonate is added to a solution of 6 g (4.6 mmol) of (6.h) in 120 ml of dimethylformamide. (Solution A).
A volume of 5 ml of methylene chloride and enough saturated sodium hydrogen carbonate solution are added to 2.27 g of (6.i) to adjust the pH of the mixture to 8. (Solution B).
The organic layer of Solution B is slowly added to Solution A with stirring at room temperature in 40 min.
The reaction mixture is poured into 1.2 l of demineralized water with vigourous stirring. Stirring is continued for 20 min. The purple deposit is collected, rinsed with demineralized water, filtered with suction, and dried under reduced pressure. The product is purified by column chromatography (methylene chloride/methanol 98:2 by volume).
Yield : 3 g of compound 6.

Other dye-releasing compounds for use in accordance with the present invention and corresponding to the above general formula I can be prepared analogously or by techniques known in the art starting with the appropriate chemicals i.e. with the proper carrier part intermediates and the dye part intermediates that are specific for the present invention.

The compounds corresponding to the above general formula I are believed to be novel compounds and the present invention thus also includes such compounds per se.

The compounds according to the present invention are useful in a dye diffusion transfer process and for that purpose are used in operative association with a photosensitive silver halide emulsion layer, preferably of the negative-working type, i.e. of the type giving a silver image in the photo-exposed areas.

For dye image production a photographic element according to the present invention comprises a support carrying at least one photosensitive alkali-permeable hydrophilic colloid silver halide emulsion layer and in operative association therewith at least one dye-releasing compound, characterized in that said dye-releasing compound corresponds to the above general formula I.

By "operative association" is meant that the release of the diffusible magenta azomethine dye from the dye-releasing compound can proceed in dependence on and as a function of the development of the silver halide emulsion layer. The dye-releasing compound need not be present in the silver halide emulsion layer itself but may be contained in another layer that is in water-permeable relationship therewith.

According to a preferred embodiment for the production of multicolour images the present invention also provides a photographic element that comprises a support carrying (1) a red-sensitive silver halide emulsion layer having operatively associated therewith a dye-releasing compound that initially is non-diffusing in an alkali-permeable colloid medium and from which, inversely proportional to the development of the image-wise exposed silver halide by a silver halide developing agent in alkaline conditions and a redox-reaction, a cyan dye is split off in diffusible state, (2) a green-sensitive silver halide emulsion layer having operatively associated therewith a dye-releasing compound corresponding to the above general formula I, which dye-releasing compound is initially non-diffusing in an alkali-permeable colloid medium and from which, inversely proportional to the development of the image-wise exposed silver halide by a silver halide developing agent in alkaline conditions and a redox-reaction, a magenta azomethine dye is split off in diffusible state, and (3) a blue-sensitive silver halide emulsion layer having operatively associated therewith at least one dye-releasing compound that initially is non-diffusing in an alkali-permeable colloid medium and from which, inversely proportional to the development of the image-wise exposed silver halide by a silver halide developing agent in alkaline conditions and a redox-reaction, a yellow dye is split off in diffusible

state.

The magenta azomethine dyes of pyrazolo-azoles and imidazo-azoles split off in diffusible state from the dye-releasing compounds of the present invention have a very satisfactory absorption in the green part of the spectrum and at the same time low side-absorptions in the orange-red part and especially in the blue-violet part of the spectrum.

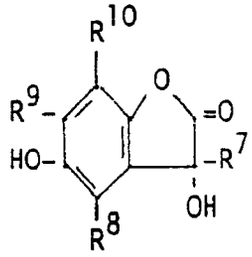
In the dye-releasing compounds for use in accordance with the present invention the dye group(s) may be associated with substituents that form a shifted dye.

Shifted dyes as described in e.g. US-A 3,260,597 include compounds, the light-absorption characteristics of which are found to be shifted hypsochromically or bathochromically when subjected to a different environment such as a change of the pK_a of the compound, or removal of a group such as a hydrolyzable acyl group linked to an atom of the chromophoric system and affecting the chromophore resonance structure. The shifted dyes can be incorporated directly in a silver halide emulsion layer or even on the exposure side thereof without substantial absorption of light used in recording. After exposure, the dye is shifted to the appropriate colour, e.g. by hydrolytic removal of said acyl group.

In the IHR mode the colour diffusion transfer process in accordance with the present invention is carried out preferably in conjunction with a mixture of reducing agents, at least one of which is a compound called electron-donor (ED-compound) and at least one of which is a compound called electron-transfer agent (ETA-compound).

The ED-compound is preferably non-diffusing. For instance, it preferably carries a ballasting group, so that it remains within the layer(s), in which it has to transfer an electron to the quinone-type compound.

Preferably, a non-diffusing ED-compound is incorporated into each silver halide emulsion layer that contains a non-diffusing IHR-quinone-type compound. Examples of suitable ED-compounds are ascorbyl palmitate and 2,5-bis-(1',1',3',3'-tetramethylbutyl)-hydroquinone. Other ED-compounds have been disclosed in US-A 4,139,379 and in published DE-A 2,947,425. Instead of an ED-compound an electron-donor precursor compound (EDP-compound) can be used in the photographic element as described e.g. in published DE-A 2,809,716 and in US-A 4,278,750. Particularly useful EDP-compounds for combination with the IHR-compounds corresponding to the above general formula I have been disclosed in EP-A 83.200.353.7 and in published DE-A 3,006,268 according to the following general formula :



wherein :

R^7 represents a carbocyclic or heterocyclic aromatic ring, each of R^8, R^9 and R^{10} (same or different) represents hydrogen, alkyl, alkenyl, aryl, alkoxy, alkylthio, amino, or

R^9 and R^{10} together represent an adjacent ring, e.g. carbocyclic ring, at least one of R^7, R^8, R^9, and R^{10} representing a ballast group having from 10 to 22 carbon atoms.

Typically useful ETA-compounds include hydroquinone compounds, aminophenol compounds, catechol compounds, phenylene diamines, and 3-pyrazolidinones such as e.g. 1,4-dimethyl-3-pyrazolidinone, 4-methyl-3-pyrazolidinone, 4,4-dimethyl-3-pyrazolidinone, 1-(2-trifluoroethyl)-4,4-dimethyl-3-pyrazolidinone, and 5-methyl-3-pyrazolidinone, and especially 1-aryl-3-pyrazolidinone compounds such as e.g. 1-phenyl-3-pyrazolidinone, 1-phenyl-4,4-dimethyl-3-pyrazolidinone, 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone, 1-m-tolyl-3-pyrazolidinone, 1-p-tolyl-3-pyrazolidinone, 1-phenyl-4-methyl-3-pyrazolidinone, 1-phenyl-5-methyl-3-pyrazolidinone, 1-phenyl-4,4-bis(hydroxymethyl)-3-pyrazolidinone, 1-(3-chlorophenyl)-4-methyl-3-pyrazolidinone, 1-(4-chlorophenyl)-4-methyl-3-pyrazolidinone, 1-(3-chlorophenyl)-3-pyrazolidinone, 1-(4-chlorophenyl)-3-pyrazolidinone, 1-(4-tolyl)-4-methyl-3-pyrazolidinone, 1-(2-tolyl)-4-methyl-3-pyrazolidinone, 1-(4-tolyl)-3-pyrazolidinone, 1-(3-tolyl)-3-pyrazolidinone, and 1-(3-tolyl)-4,4-dimethyl-3-pyrazolidinone.

A combination of different ETA-compounds such as those disclosed in US-A 3,039,869 can be employed likewise.

The above-mentioned ETA-compounds or combinations thereof can be contained in the liquid process-

ing composition or can be contained at least partially in any hydrophilic colloid layer or layers of the photographic element e.g. the photosensitive silver halide emulsion layer(s), interlayers, or in the image-receiving layer.

Among the known ETA-compounds the above-mentioned 1-aryl-3-pyrazolidinones are very appropriate representatives. However, several representatives of these 1-aryl-3-pyrazolidinones have a poor solubility in aqueous compositions or solutions. So far, ETA-compounds having a poor solubility were incorporated in the form of a dispersion into hydrophilic colloid layer compositions, the dispersion usually being made in a sand mill or a ball mill. Yet, this method of working often brought about a deterioration of certain photographic characteristics in that it caused fogging and gave rise to losses in speed, density, and gradation.

To avoid these disadvantages the above-mentioned 1-aryl-3-pyrazolidinones can be dispersed with the aid of at least one known oil-former such as an alkyl ester of phthalic acid e.g. dibutyl phthalate or a phosphoric acid ester e.g. tricresyl phosphate or any other oil-former such as those described in EP-A 0,176,628, which corresponds with the US Serial N° 06/780,585, in EP-A 86-202066.6, which corresponds with the US Serial N° 07/110,798, in US-A 4,430,422, or in the literature referred to in the above documents.

The above-mentioned 1-aryl-3-pyrazolidinone ETA-compounds can be incorporated successfully into a hydrophilic colloid layer by dissolving them in at least oil-type-solvent or oil-former, adding the resulting solution to an aqueous phase containing gelatin and a dispersing agent, passing the mixture through a homogenizing apparatus so that a dispersion of the oily solution in an aqueous medium is formed, mixing the dispersion with a hydrophilic colloid composition, and coating the resulting composition in the usual manner. The dissolution of the coupler in the oil-former may be facilitated by the use of an auxiliary low-boiling water-immiscible solvent e.g. a lower alkyl acetate, which is removed afterwards by evaporation. The auxiliary solvent can also be a water-soluble organic solvent e.g. methanol.

The selection of the specifically used ETA-compound(s) is, of course, determined by the particular electron-donor and dye-releasing compound used in the process and the processing conditions for the particular photographic element.

The concentration of ED-compound or EDP-compound in the photographic element may vary within a broad range but is in the molar range of e.g. 1:1 to 8:1 in respect of the dye-releasing compound. The ETA-compound may be present in the alkaline aqueous liquid used in the development step, but is preferably present in a non-photosensitive hydrophilic colloid layer adjacent to at least one silver halide emulsion layer.

Migration of unoxidized developing agent e.g. acting as ETA-compound, proceeds non-image-wise and has an adverse effect on colour rendition if excess unoxidized developing agent remains in the photo-exposed areas of a negative-working emulsion layer. Therefore, according to a preferred embodiment of the present invention a silver halide solvent, e.g. thiosulphate, is used to mobilize unexposed silver halide in complexed form for helping to neutralize (i.e. oxidize by physical development) such excess unoxidized developing agent in the photo-exposed areas where unaffected developing agent (ETA-compound) should no longer be available for entering into reaction with the dye-releasing compound directly or through the applied ED-compound. The use of silver halide solvents for that purpose has been described in the published EP-A 0049002.

For better colour rendition it is advantageous to intercept oxidized ETA-compound and prevent it from migrating to adjacent imaging layers where it could cause undesired oxidation of ED-compound. So-called scavengers can be used for such interception. They can be incorporated in non-diffusible state into the photographic element, e.g. in interlayers between the imaging layers. Suitable scavengers for that purpose have been described in e.g. US-A 4,205,987 and EP-A 0,029,546.

The dye-releasing compounds and optionally ED-compounds or EDP-compounds can be incorporated into the photographic element by addition to the coating composition(s) of at least one layer thereof. They can be added according to usual methods e.g. according to methods known for incorporating colour couplers into silver halide emulsion elements.

The amount of dye-releasing compound coated per m2 may vary within wide limits and depends on the maximum colour density desired.

The support of the photographic elements used according to the present invention may be of any material as long as it is dimensionally stable and does not adversely affect the photographic properties of the elements. Typical flexible sheet materials for forming the support are paper e.g. single-side or twin-side Alpha-olefin-polymer-coated paper such as polyethylene-coated paper and polypropylene-coated paper. Other flexible sheet support materials are e.g. cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, and related films or resinous materials. The support usually has a thickness of approximately 0.05 to 0.15 mm.

The image-receiving layer can form part of a separate image-receiving element or form an integral part of the silver halide emulsion element.

When after the processing of the silver halide emulsion element the image-receiving layer is to remain associated with the silver halide emulsion layer(s) of the photosensitive element, an alkali-permeable light-shielding layer, e.g. a layer containing white pigment particles is applied customarily between the image-receiving layer and the silver halide emulsion layer(s).

Any material can be employed as image-receiving layer in dye diffusion transfer photography, provided it performs the desired function of mordanting or otherwise fixing the diffused dye(s). The selection of the particular material to be used is, of course, determined by the nature of the dye(s) to be mordanted. If acid dyes are to be mordanted, the image-receiving layer can be composed of or contain basic polymeric mordants such as polymers of amino-guanidine derivatives of vinyl methyl ketone such as described in US-A 2,882,156 of Louis M.Minsk, issued April 14, 1959, and basic polymeric mordants and derivatives, e.g. poly-4-vinylpyridine, the metho-p-toluene sulphonate of 2-vinylpyridine and similar compounds described in US-A 2,484,430 of Robert H.Sprague and Leslie G.Brooker, issued October 11, 1949, and the compounds described in the published DE-A 2,200,063 filed January 11, 1971 by Agfa-Gevaert A.G. Suitable mordanting binders include e.g. guanylhydrazone derivatives of acyl styrene polymers as described in e.g. published DE-A 2,009,498 filed February 28, 1970 by Agfa-Gevaert A.G. In general, however, other binders e.g. gelatin are added to the last-mentioned mordanting binders. Effective mordanting compositions are long-chain quaternary ammonium or phosphonium compounds or ternary sulphonium compounds, e.g. those described in US-A 3,271,147 of Walter M.Bush and 3,271,148 of Keith E.Whitmore, both issued September 6, 1966, and cetyltrimethyl-ammonium bromide. In case non-polymeric phosphonium compounds are used as dye mordants it may be recommendable to prevent them from bleeding out of the image-receiving layer during storage thereof and especially during storage at increased temperature and high relative humidity. This bleeding out can be avoided by adding a stabilizer for the mordanting agent to the composition of the image-receiving layer. An appropriate stabilizer is e.g. co(n-butyl acrylate/2-acrylamido-2-methyl-propane sulphonic acid) (80/20 % parts by weight and 84/16 mol %). Certain metal salts and their hydroxides that form sparingly soluble compounds with the acid dyes can also be used as dye mordants. The dye mordants are dispersed in one of the usual hydrophilic binders for the image-receiving layer, e.g. in gelatin, polyvinyl pyrrolidone, or partly or completely hydrolysed cellulose esters.

Good results are obtained e.g. when the image-receiving layer, which preferably is permeable to an alkaline solution, is transparent and has a thickness of approximately 4 to 10 μm. Of course, the thickness can be modified depending upon the results aimed at. The image-receiving layer can also contain other additives such as ultraviolet-absorbing substances to protect the mordanted dye images from fading, brightening agents e.g. stilbenes, coumarins, triazines, oxazoles, or dye stabilizers such as the chromanols and alkyl-phenols.

The stability to light of a dye image formed in the image-receiving layer of an image receptor element is usually better, when the pH-value in the dye image remains alkaline. This applies particularly to twin sheet elements, in other words to DTR-elements operating with a separate photosensitive element and a separate image receptor element. However, in the case of monosheet elements the pH-value of the dye image in the image-receiving layer is usually lowered to avoid any further diffusion of dyes to the white image areas. In general, the pH of the layer can within a short time after imbibition be lowered from about 14 - 13 to 11 but preferably to 7 - 5. For instance, polymeric acids as disclosed in US-A 3,362,819, or solid acids or metal salts, e.g. zinc acetate, zinc sulphate, magnesium acetate, etc., as disclosed in US-A 2,584,030, can be employed successfully for that purpose. The acid for lowering the pH can be incorporated into a layer, which can be coated with an inert timing or spacer layer that times or controls the pH-reduction proportionally to the rate, at which alkali diffuses through this inert spacer layer. Examples of such timing layers include gelatin, polyvinyl alcohol, or any of the colloids disclosed in US-A 3,455,686. The timing layer can be effective in evening out the reaction rates over a wide range of temperatures. For instance, premature pH-reduction is prevented, when imbibition is effected at temperatures above room temperature, e.g. at 35° to 37°C. The thickness of the timing layer is usually comprised between approximately 2.5 and 18 μm . Especially good results are obtained when the timing layer comprises a hydrolysable polymer or a mixture of such polymers, which are hydrolysed slowly by the processing liquid. Examples of such hydrolysable polymers are e.g. polyvinyl acetate, polyamides, or cellulose esters. After formation of the dye image in the image-receiving layer of a monosheet element the pH-value can, of course, be lowered also by rinsing with water.

An alkaline aqueous processing liquid employed in the production of dye images according to the present invention may be a conventional aqueous solution of an alkaline substance e.g. sodium hydroxide, sodium carbonate or an amine such as diethylamine. Preferably this alkaline aqueous processing liquid has

a pH above 11.

According to one embodiment the alkaline aqueous processing liquid contains the diffusible developing agent that effects the reduction of the silver halide, e.g. ascorbic acid or a 3-pyrazolidinone developing agent such as 1-phenyl-4-methyl-3-pyrazolidinone.

The alkaline aqueous processing liquid used in accordance with the process of the invention may also contain a desensitizing agent such as methylene blue, a nitro-substituted heterocyclic compound, or a 4,4′-bispyridinium salt, to ensure that the photographic element is not further exposed after its removal from the camera for processing.

For in-camera-processing the alkaline aqueous processing liquid preferably also contains a viscosity-increasing compound such as a high-molecular-weight polymer, e.g. a water-soluble ether inert to alkaline solutions such as hydroxyethylcellulose or alkali metal salts of carboxymethylcellulose e.g. sodium carboxymethylcellulose. A concentration of viscosity-increasing compound of approximately 1 to 5 % by weight of the alkaline aqueous processing liquid is preferred. It imparts a viscosity of about 100 mPa.s to about 200,000 mPa.s.

Although the common purpose in known dye diffusion transfer systems is to produce dye images in a receiving layer or sheet by means of dye(s) released from the photosensitive element, a residual image of dye-releasing compound in the photosensitive element may be of practical interest for forming a so-called "retained image". This terminology is used, e.g. in Research Disclosure (No. 17362) of September 1978 and a dye diffusion process relating thereto has been exemplified in Research Disclosure (No. 22711) of March 1983.

Processing can proceed in a tray developing unit as is contained, e.g., in an ordinary silver complex diffusion transfer (DTR) apparatus, in which contact between the image-wise exposed photosensitive element and a separate dye image-receiving element is effected after sufficient absorption of processing liquid by these elements has taken place. A suitable apparatus for this purpose is the COPYPROOF CP 42 DTR-developing apparatus. COPYPROOF is a trade mark of Agfa-Gevaert N.V., Antwerp, Belgium.

In case the photosensitive layer(s) and the image-receiving layer are integrated in one single element, the alkaline aqueous processing liquid can be applied from at least one rupturable container, which may itself form part of said element, or by spraying.

Examples of rupturable containers that can be employed are those disclosed in US-A 2,543,181 of Edwin H.Land, issued February 27, 1951, 2,643,886 of Ulrich L. di Ghilini, issued June 30, 1953, 2,653,732 of Edwin H.Land, issued September 29, 1953, 2,723,051 of William J.McCune Jr., issued November 8, 1955, 3,056,492 and 3,056,491, both of John E.Campbell, issued October 2, 1962, and 3,152,515 of Edwin H.Land, issued October 13, 1964. In general, such containers comprise a rectangular sheet of fluid-and air-impervious material folded longitudinally upon itself to form two walls that are sealed to one another along their longitudinal and end margins to form a cavity in which processing liquid is contained.

In the above described dye diffusion transfer processing the development temperature normally is room temperature, i.e. approximately 20 °C, but according to a particular embodiment the dye-releasing compounds according to the present invention can be used in a so-called photothermographic dye diffusion transfer method, e.g. of the type described in EP-A 0,120,306 and DE-A 3,215,485.

According to this particular embodiment the image formation comprises image-wise exposing a light-sensitive element and heating it in the presence of a small amount of water, said element comprising a support and provided thereon light-sensitive silver halide in a binder, a reducing agent capable of reducing the light-sensitive silver halide, and at least one of the dye-releasing compounds according to the present invention.

According to an embodiment of said method a photographic element is used which contains a combination of silver halide and silver benzotriazolate, a developing agent, a said dye-releasing compound, and a base precursor releasing a base upon heating as described in e.g. GB-A 998,949. The image-wise exposed photographic element is wet with water as the sole processing liquid and placed in contact with an image-receiving element. The thus formed sandwich is subjected to heat, so that development of the exposed silver halide and transfer of image-wise released dye can take place.

According to another embodiment the heat-induced development of the exposed silver halide proceeds in the presence of a thermal solvent.

Examples of thermal solvents and their use have been described in Research Disclosure publications, October 1976, item 15 027, November 1976, item 15 108 and June 1978 item 17 029, in DE-OS 3 529 930 and 3 529 934 and in EP-A 119,615 and 112,512.

Thermal solvents are solid at room temperature (20 °C) but play the role of a good solvent for water-soluble compounds in molten form by their relatively strong dipole moment.

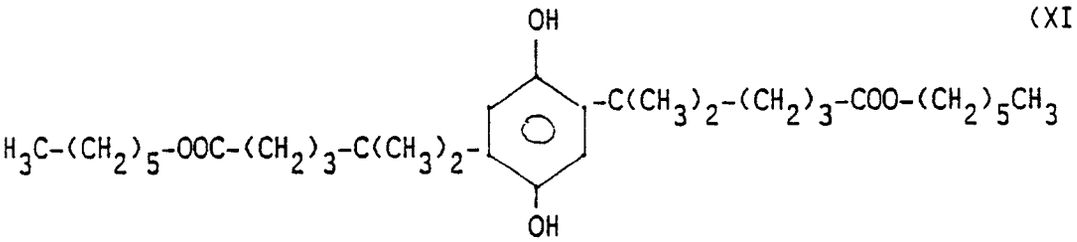
The following example illustrates the present invention.

EXAMPLE

A number of photographic elements were prepared as follows. Strips of subbed polyethylene terephthalate support having a thickness of 0.1 mm were coated with the following layers in the given order:

1) an alkali-permeable photosensitive silver halide hydrophilic colloid emulsion layer containing:

gelatin	2.0 g
AgCl expressed as $AgNO_3$	0.6 g
magenta dye-releasing compound as defined in Table 2	0.36 mmol/m2
ED-compound corresponding to structural formula XIII	0.3 g



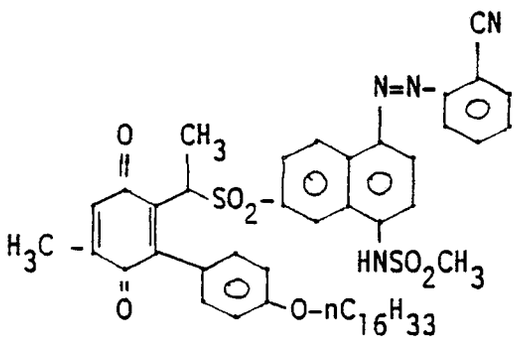
(XIII)

2) protective layer containing:

gelatin	2.5 g
1-phenyl-4-methyl-pyrazolidin-3-one	0.250 g

The resulting strips of photographic element were identical except for the composition of the magenta dye-releasing compound as defined in Table 2 hereinafter.

For comparison with the magenta dye-releasing compounds 1, 2, 3, and 6 of the present invention the following magenta dye-releasing compound (called Comparison hereinafter) disclosed in US-A 4,496,645 and corresponding to the following structural formula was entered in the test:



Each strip was exposed image-wise, placed in contact with a COPYCOLOR CCP image-receiving element, and together fed through a CP 38 diffusion transfer processing apparatus containing in its tray a COPYCOLOR CC 292 bath. COPYCOLOR and CP 38 are trade marks of Agfa-Gevaert N.V., Antwerp, Belgium. The contact time was 60 s.

The peak absorption (Lambda max) and the maximum density (D max) of the magenta dye images obtained as well as the densities of the side-absorptions obtained were measured by means of a MACBETH Densitometer RD 919 in Status A.

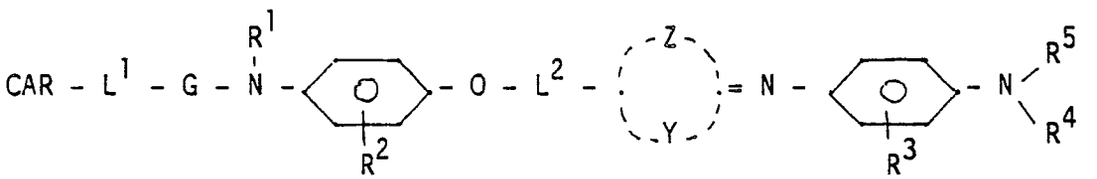
TABLE 2

Magenta dye-releasing compd.	Lambda max in nm	D max	Density measured through		
			blue filter	green filter	red filter
Comparison	535	1.88	0.58	1.48	0.25
1	538	1.97	0.28	1.48	0.18
2	550	1.48	0.28	1.48	0.22
3	552	1.81	0.28	1.48	0.22
6	542	1.92	0.31	1.48	0.20

The results listed in Table 2 show that the absorption in the green part of the spectrum of the magenta dyes obtained according to the present invention is very satisfactory and comparable with that of the magenta dye obtained from the known Comparison compound. It is, however, striking that the density values obtained by measurement through a blue filter and through a red filter, which values are indicative of the unwanted side-absorption in the blue-violet part and in the orange-red part of the spectrum, are considerably lower in the case of the magenta dyes obtained according to the present invention than in the case of the magenta dye obtained from the known Comparison compound.

Claims

1. Process for the production of diffusion transfer images comprising the steps of:
(1) applying an alkaline aqueous processing liquid to an image-wise exposed photographic element comprising at least one photosensitive alkali-permeable hydrophilic colloid silver halide emulsion layer and in operative association therewith at least one non-diffusible dye-releasing compound that can split off a diffusible magenta azomethine dye,
(2) providing a silver halide developing agent, which is present in said photographic element at least during application of said alkaline aqueous processing liquid to effect - as a function of the development of said silver halide emulsion layer and a redox reaction -the image-wise release of said diffusible magenta azomethine dye, and
(3) allowing diffusion of said released magenta azomethine dye into an image-receiving layer held in water-permeable relationship with said silver halide emulsion layer,
characterized in that said dye-releasing compound corresponds to the following general formula I:

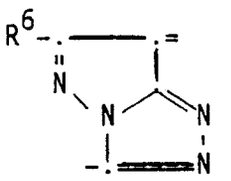


(I)

wherein:
CAR represents an organic carrier moiety capable of undergoing a redox reaction, which moiety may contain a ballasting group rendering said dye-releasing compound non-diffusing in a hydrophilic colloid medium in wet alkaline conditions,
L^1 represents a chemical group cleavable or releasable from the carrier moiety as a function of a redox reaction taking place in the development of said silver halide emulsion layer under wet alkaline conditions,
G represents a bivalent organic linking group comprising at least one aromatic nucleus or a substituted bivalent organic linking group comprising at least one aromatic nucleus,
R^1 is hydrogen, an alkyl group, or an aryl group,
R^2 is hydrogen or a monovalent organic group,
L^2 represents a bivalent organic linking group comprising at least 2 carbon atoms,

Z and Y together represent the atoms necessary to complete a substituted or unsubstituted anellated heterocyclic system selected from the group of the pyrazolo-azoles and imidazo-azoles
R^3 is hydrogen, a halogen atom, an alkyl group, an alkoxy group, an acylamino group, or an aryl group, as well as a substituent in ortho-position to the group NR^4R^5, which substituent together with R^4 completes a cyclic amino group, and
R^4 is hydrogen, a C^1-C^4 alkyl group, a substituted C^1-C^4 alkyl group, a substituent that together with R^3 completes a cyclic amino group, or a substituent that together with R^5 completes a cyclic amino group,
R^5 is hydrogen, a C^1-C^4 alkyl group, a substituted C^1-C^4 alkyl group, or a substituent that together with R^4 completes a cyclic amino group, and
R^6 is hydrogen, a C^1-C^4 alkyl group, a substituted C^1-C^4 alkyl group, an aryl group, or a substituted aryl group.

2. A process according to claim 1, characterized in that said substituted or unsubstituted anellated heterocyclic system is chosen from the following group of heterocyclic systems corresponding to the structural formulae II to XII,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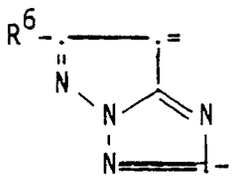
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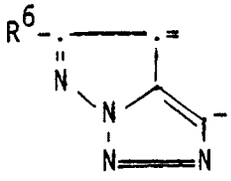
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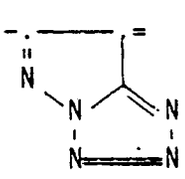
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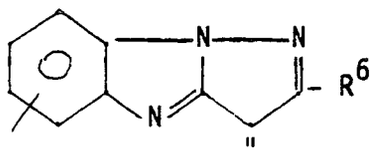
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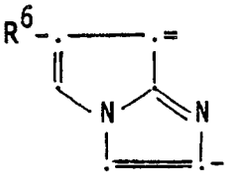
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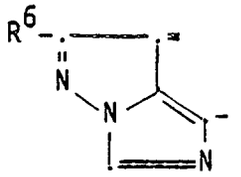
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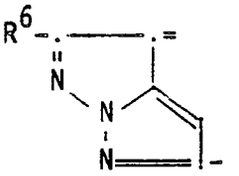
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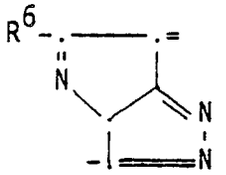
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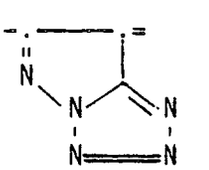
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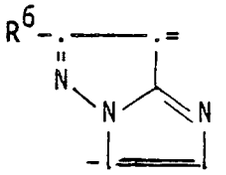
(XII)

3. A process according to claim 1 or 2, characterized in that said dye-releasing compound is a quinone-type IHR-compound.

4. Photographic element comprising a support carrying at least one photosensitive alkali-permeable hydrophilic colloid silver halide emulsion layer and in operative association therewith at least one dye-releasing compound, characterized in that said dye-releasing compound corresponds to the general formula I set out in claim 1.

5. A photographic element according to claim 4, characterized in that it comprises a support carrying:
- a red-sensitive silver halide emulsion layer having operatively associated therewith a dye-releasing compound that initially is non-diffusing in an alkali-permeable colloid medium and from which, inversely proportional to the development of the image-wise exposed silver halide by a silver halide developing agent in alkaline conditions and a redox-reaction, a cyan dye is split off in diffusible state,
- a green-sensitive silver halide emulsion layer having operatively associated therewith a dye-releasing compound, which dye-releasing compound is initially non-diffusing in an alkali-permeable colloid medium and from which, inversely proportional to the development of the image-wise exposed silver halide by a silver halide developing agent in alkaline conditions and a redox-reaction, a magenta azomethine dye is split off in diffusible state, and
- a blue-sensitive silver halide emulsion layer having operatively associated therewith at least one dye-releasing compound that initially is non-diffusing in an alkali-permeable colloid medium and from which, inversely proportional to the development of the image-wise exposed silver halide by a silver halide developing agent in alkaline conditions and a redox-reaction, a yellow dye is split off in diffusible state,
the dye-releasing compound that splits off a magenta azomethine dye corresponding to the general formula I set out in claim 1.

6. A photographic element according to claim 4 or 5, characterized in that Z and Y in the formula of said dye-releasing compound together represent the atoms necessary to complete a heterocyclic system chosen from the group of heterocyclic systems corresponding to the structural formulae II to XII set out in claim 2.

7. A photographic element according to any of claims 4 to 6, characterized in that said silver halide emulsion layer is of the negative-working type.

8. Compound corresponding to the general formula I set out in claim 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 20 1201

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.4)
Y	EP-A-0 012 908 (AGFA-GEVAERT) * Page 9, line 20 - page 10, line 8; claims *	1-7	G 03 C 5/54 C 09 B 55/00
Y	GB-A-2 061 537 (KODAK) * Page 8, lines 4-23; claims *	1,2,4-6	
Y	US-A-3 698 897 (T.E. GOMPF et al.) * Column 4, lines 33-44; column 5, lines 20-45; claims *	1-7	
A	US-A-4 183 753 (B.D. BAIGRIE)		
A	PATENT ABSTRACTS OF JAPAN, vol.9, no. 109 (P-355)[1832], 14th May 1985; & JP-A-59 231 539 (KONISHIROKU SHASHIN KOGYO K.K.) 26-12-1984 * Abstract *		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

G 03 C 5
G 03 C 7

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-08-1989	PHILOSOPH L.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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