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

(11) EP 0 754 968 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
22.01.1997 Bulletin 1997/04

(51) Int. Cl.[6]: **G03C 1/485**

(21) Application number: **95201965.1**

(22) Date of filing: **17.07.1995**

(84) Designated Contracting States:
BE DE FR GB NL

(71) Applicant: **AGFA-GEVAERT**
naamloze vennootschap
B-2640 Mortsel (BE)

(72) Inventors:
- **Viaene, Kris**
  B-2640 Mortsel (BE)
- **Dewanckele, Jean-Pierre**
  B-2640 Mortsel (BE)
- **Loccufier, Johan**
  B-2640 Mortsel (BE)
- **Andriessen, Hieronymus**
  B-2640 Mortsel (BE)

(54) Photographic directpositive material containing thioalkyleneamine compounds

(57) Photographic direct positive material comprising a support and as hydrophilic layers one or more radiation sensitive emulsion layers containing internal latent image-forming silver halide grains and one or more protective antistress layers characterized in that at least one of the hydrophilic layers further contains at least one compound corresponding to one of the general formulae (I) to (III)

$$R^1\text{-}X\text{-}[(LINK_1\text{-}Y)_n\text{-}LINK_2\text{-}Z]_p\text{-}LINK_3\text{-}X\text{-}R^1 \quad (I)$$

$$[R^1\text{-}X\text{-}(LINK_1\text{-}Y)_n\text{-}LINK_2\text{-}Z]_2\text{-}LINK_3 \quad (II)$$

$$[R^1\text{-}X\text{-}(LINK_1\text{-}Y)_n\text{-}LINK_2]_2\text{-}Z \quad (III)$$

wherein

X, Y and Z each independently represents S, O or NR^2;
R^1 and R^2 each independently represents a member selected from the group consisting of hydrogen, alkyl or substituted alkyl, or the necessary atoms to form a ring together with the N-atom to which they are attached if X represents NR^2;
$LINK_1$, $LINK_2$ and $LINK_3$ each independently represent a divalent linking group;
n is an integer having a value of 0 or 1 and
p is an integer having a value from 1 to 10.

EP 0 754 968 A1

Description

1. Field of the invention.

The present invention relates to direct positive black-and-white photographic materials. More particularly it relates to direct positive materials containing boosters of a particular type.

2. Background of the invention.

Photographic black-and white materials producing a density upon development which is directly related to the radiation received on exposure are termed negative working. From such a negative image a positive image resembling the originally recorded scene can be produced by copying it on another negative working material. Direct positive images are understood in photography to be formed without intervention of a negative image by development of photographic emulsion layers containing specially designed so-called direct positive emulsions.

In this method of photographic imaging the application of two main types of emulsions can be distinguished, the first one being externally fogged emulsions, usually containing an electron acceptor, the second one being unfogged internal latent image-forming emulsions, which are positive-working by fogging development, preferably in the presence of a so-called nucleating agent.

Surface-fogged emulsions are disclosed, e.g., in Kendall US-P 2,541,472, Schouwenaars GB 723,019, Illingsworth US-P 3,501,307,Berriman US-P 3,367,778 and Research Disclosure, Vol 134, June 1975, Item 13452.

Internal latent image-forming silver halide grains are disclosed in, e.g., Ives US-P 2,563,785, Evans US-P 3,761,276, Knott US-P 2,456,953 and Jouy US-P 3,511,662. Further patents include Davey US-P 2,592,250, which describes internal sensitive emulsions prepared by conversion, Porter US-P 3,206,313, which discloses direct positive emulsions of a particular core-shell type, Milton US-P 3,761,266, illustrating direct positive emulsions rich in chloride, Gilman US-P 3,761,267, Atwell US-P 4,035,185, and Daubendiek US-P 4,504,570, which discloses direct positive emulsions of the internal latent image-forming type containing tabular grains.

As is well known in the art direct-positive silver halide emulsions exhibit various disadvantages as compared to negative working emulsions. The high level of sensitivity which can be routinely attained with negative emulsions cannot easily be reached with direct positive emulsions. It is not easy to reconciliate the various demands of high maximum density, good contrast, low minimum density and sufficient speed. The term "speed" can apply to the intrinsic blue or near-ultraviolet sensitivity or to the sensitivity in a defined spectral region. The spectral sensitivity depends on the intrinsic sensitivity and the efficiency of the spectral sensitizer used. The intrinsic sensitivity can be influenced by emulsion parameters, by coating parameters, by external factors, by `developer parameters, and by the presence or absence of particular ingredients in the coated layer or in the developer. As already indicated the best known emulsion parameter influencing sensitivity is the average grain size. To a certain limit increasing the average grain size enhances sensitivity simply by increasing the probability of photon absorption. A further important emulsion factor is the optimization of chemical ripening which should create sensitivity specks on the grain surface acting as efficient traps for photoelectrons generated during exposure and thus giving rise to a concentrated developable latent image. As external factors the pH and the pAg at which the coating is performed, the humidity of the environment, the presence of a halogen acceptor and mechanical pressure should be mentioned.

Further on, the obtained sensitivity can be influenced by the presence in the developer of so-called development accelerators, e.g., polyoxyalkylene development accelerators and thioether-polyoxyalkylene development accelerators as has been described in, e.g., US-P 4,292,400. Nevertheless polyalkylene development accelerators have been better known for their activities in negative materials as in direct-positive materials fogging may occur and, as a result thereof, loss in maximum density and speed.

And last but not least the "positive-working" developing solution preferably is a high alkaline solution with "hydroquinone-metol" or "hydroquinone-phenidone" as developing agents, having a pH value of at least 11.0 in order to activate the fogging agent, also called "nucleating agent".

A suitable agent added to the developer having a further activating function is an aminoalcohol as, e.g., N-methylaminoethanol. Disadvantages related to the measures summarised hereinbefore are the oxidation-sensitivity of the developer, the offensive fish-like odor, the thereby caused sludge and the difficulty in making concentrated developer solutions.

3. Objects of the invention.

It is an object of the present invention to provide a photographic direct positive material, working by means of internal `image-forming silver halide emulsion grains, with excellent sensitometric characteristics after processing, being a high maximum density, a low minimum density, a good contrast and sensitivity, making use of a classical negative-working developer which is less sensitive to air-oxidation and which doesn't have an unagreable smell due to the presence

of aminoalcohols.

Other objects will become apparent from the description given hereinafter.

4. Summary of the invention.

The objects of the present invention are realised by providing a photographic direct positive material comprising a support and as hydrophilic layers one or more radiation sensitive emulsion layers containing internal latent image-forming silver halide grains and one or more protective antistress layers characterized in that at least one of the hydrophilic layers further contains at least one compound corresponding to one of the general formulae (I) to (III)

$$R^1\text{-}X\text{-}[(LINK_1\text{-}Y)_n\text{-}LINK_2\text{-}Z]_p\text{-}LINK_3\text{-}X\text{-}R^1 \quad (I)$$

$$[R^1\text{-}X\text{-}(LINK_1\text{-}Y)_n\text{-}LINK_2\text{-}Z]_2LINK_3 \quad (II)$$

$$[R^1\text{-}X\text{-}(LINK_1\text{-}Y)_n\text{-}LINK_2]_2\text{-}Z \quad (III)$$

wherein

X, Y and Z each independently represents S, O or NR^2;
R^1 and R^2 each independently represents a member selected from the group consisting of hydrogen, alkyl or substituted alkyl, or the necessary atoms to form a ring together with the N-atom to which they are attached if X represents NR^2;
$LINK_1$, $LINK_2$ and $LINK_3$ each independently represent a divalent linking group;
n is an integer having a value of 0 or 1 and
p is an integer having a value from 1 to 10.

According to a further aspect of this invention the described direct positive material is meant to be processed in a surface developer (a) in the presence of a nucleating agent or (b) with light flashing of the photographic element. However procedure (a) constitutes the preferred embodiment. More preferably an arylhydrazide, and most preferably a p-sulphonamidophenylhydrazide nucleating agent is used, which is preferably incorporated in an emulsion layer too.

Said surface developer is free from aminoalcohols and is offered to the customer as a concentrated developer with a pH ready-for-use of not higher than 11.0.

5. Detailed description of the invention.

In order to promote the formation of a direct positive image the photographic materials of the present invention can be image-wise exposed and then subjected to uniform flash lighting during processing. Preferably however the direct positive image is formed with the aid of a so-called nucleating agent (or development nucleator) which triggers development. This nucleating agent can be present in the developing solution but most preferably it is present in the photographic material itself. The nucleating agent is preferably incorporated in the emulsion layer(s), but can also be present in the undercoat layer between the support and the emulsion layer(s). When used in the silver halide emulsion layer(s) the development nucleators are present in a preferred concentration from 10^{-5} mole to 10^{-1} mole per mole of silver halide.

According to this invention it has been found unexpectedly that thioether-polyoxyalkylene amine development accelerators act as sensitivity or speed-boosters in direct-positive materials comprising a support and as hydrophilic layers one or more radiation sensitive emulsion layers containing internal latent image-forming silver halide grains and one or more protective antistress layers.

Preferably said "speed-boosters" correspond to one of the formulae (I) to (III), wherein, $LINK_2$ represents $-(C_2H_4\text{-}O)_m\text{-}C_2H_4-$ as a divalent linking group, and wherein m is an integer having a value from 1 to 20.

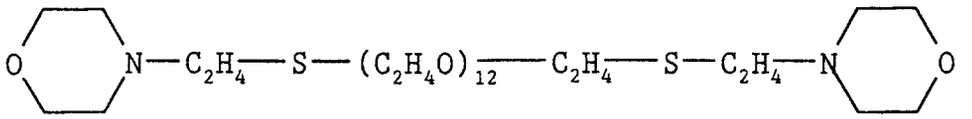
In another preferred embodiment $LINK_2$ represents $-(CH_2\text{-}CH(R)O)_m\text{-}C_2H_4-$ as a divalent linking group, wherein R represents a substituted or unsubstituted alkyl group and wherein m represents an integer having a value from 1 to 20.

Preferably $LINK_1$ and $LINK_2$ in the formulae (I) to (III) are divalent groups comprising a limited number of atoms, in order to get the silver-ion complexing atoms X, Y and Z in 1,4- or 1,5-position.

Specific examples of such speed boosters are:

$$(H_5C_2)_2\text{-}N\text{-}C_2H_4\text{-}S\text{-}(C_2H_4\text{-}O)_{12}\text{-}S\text{-}C_2H_4\text{-}N\text{-}C_2H_5 \quad (C\text{-}1)$$

$$(H_5C_2)_2\text{-}N\text{-}C_2H_4\text{-}S\text{-}(C_2H_4\text{-}O)_{12}\text{-}S\text{-}C_2H_4\text{-}S\text{-}C_2H_4\text{-}N\text{-}C_2H_5 \quad (C\text{-}2)$$



(C-3)

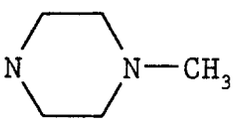
C_2H_5-NH-C_2H_4-S-$(C_2H_4$-O$)_{12}$-C_2H_4-S-C_2H_4-NH-C_2H_5 (C-4)

$(R_1R_2$-N-C_2H_4-O-C_2H_4-O-C_2H_4-$)_2$S (C-5)

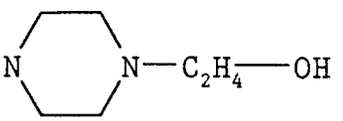
wherein

R_1	R_2	
C_2H_5	C_2H_5	(C-5a)
C_4H_9	C_4H_9	(C-5b)
CH_3	C_4H_9	(C-5c)

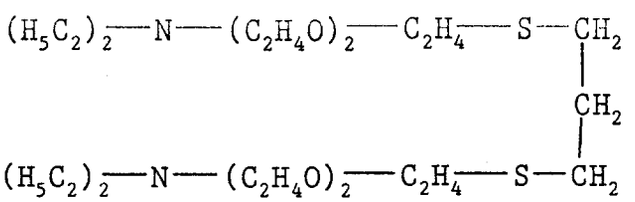
or wherein NR_1R_2 is replaced by



(C-5d)



(C-5e)

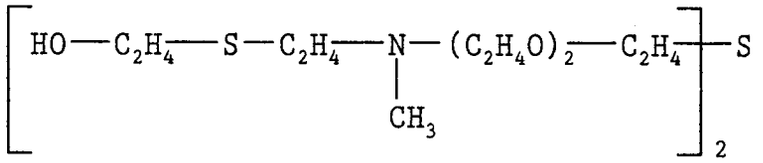


(C-6)

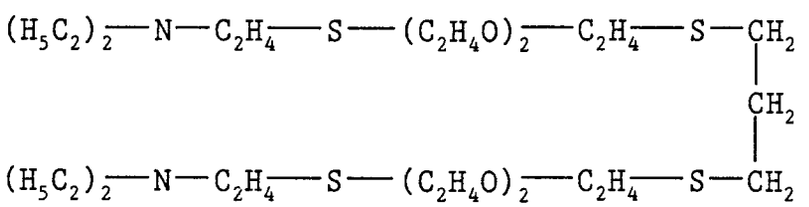
(C_4H_9-NH-C_2H_4-O-C_2H_4-O-C_2H_4-$)_2$S (C-7)

(H_5C_2)-N(CH_3)-$(C_2H_4$-O$)_2$-C_2H_4-$)_2$S (C-8)

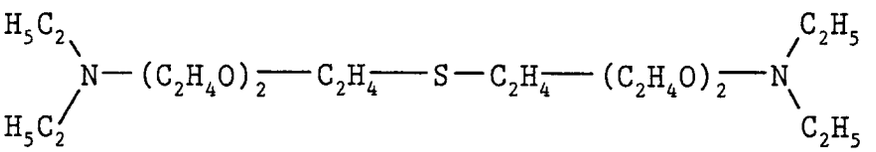
$((H_5C_2)_2$-N-C_2H_4-S-$(C_2H_4$-O$)_2$-C_2H_4-$)_2$S (C-9)



(C-10)



(C-11)



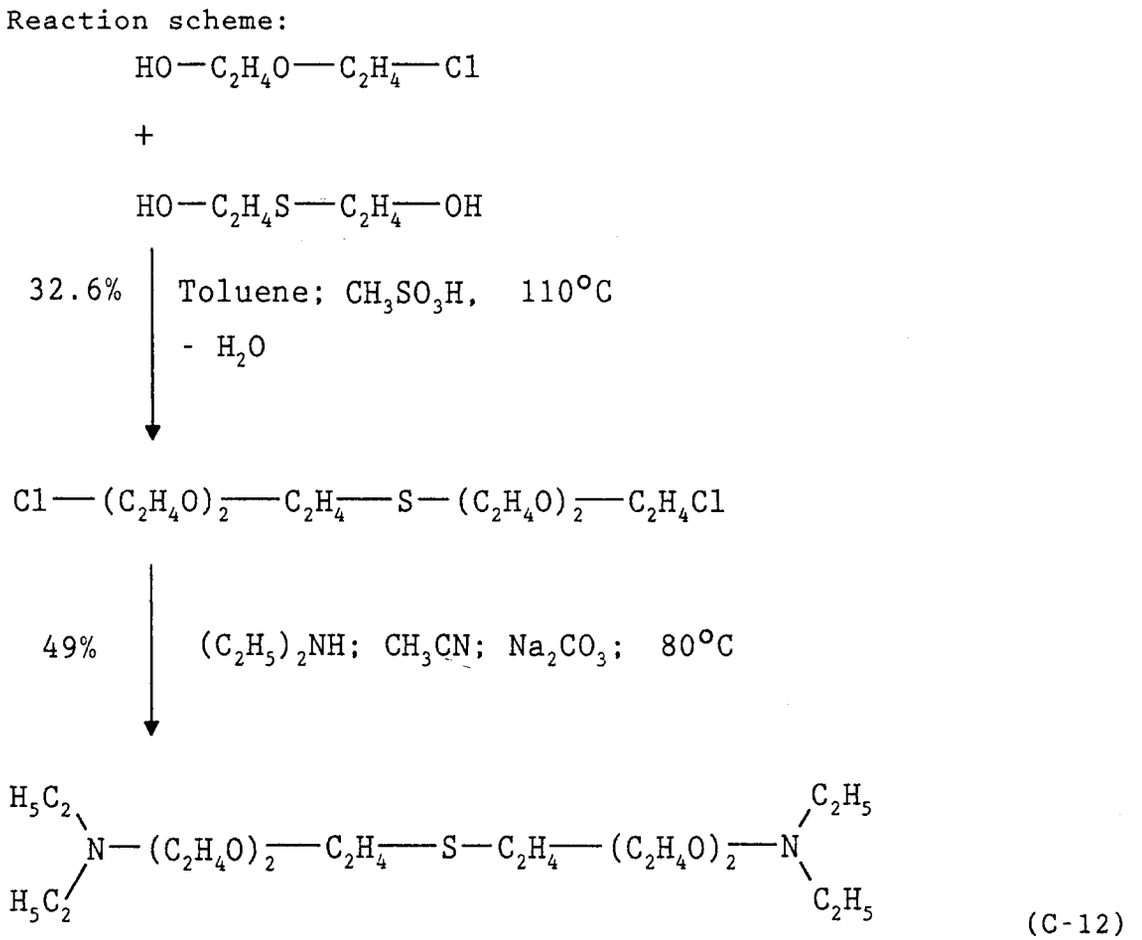
(C-12)

Hereinafter the synthesis is given for some relevant products for use in the material according to this invention.

Synthesis of compound (C-3)

Therefor we refer to US-P 4,292,400, wherein the synthesis of compound (C-3) is given.

Synthesis of compound (C-12)



(C-12)

Synthesis of compound (C-13):

Cl—$(C_2H_4O)_2$—C_2H_4—S—C_2H_4—$(C_2H_4O)_2$—Cl (C-13)

A mixture of 2,2'-dithioethanol (68.3 g; corresponding with 0.56 mole); 2-(2-chloroethoxy)ethanol (212 g; 1.7 mole) and methanesulphonic acid (2.7 g; 0.028 mol) was refluxed in toluene for 6 hours while stirring. The water molecules liberated during condensation are separated by means of a Dean-Starck apparatus. After cooling the reaction mixture was washed three times with an amount of 100 ml of water and dried on 50 g of sodium sulphate. The solvent was vapourised and the residue was purified by means of column chromatography. The yield was 61.3 grams or 32.6 %. The structure of the colourless oily product was confirmed by means of NMR-spectroscopy.

Synthesis of compound (C-12)

The dichloride, compound (C-13), (13.4 g; 0.04 mole) and the diethylamine (26.3 g; 0.36 mole) were dissolved in 200 ml of acetonitrile. Sodium carbonate was added thereto in an amount of 38.2 g (0.36 mole). This suspension was boiling for 16 hours and the reaction mixture was filtrated and the solvent vapourised under reduced pressure. The residue was dissolved in 100 ml of methylene chloride and the solution obtained was washed with 50 ml of a solution of HCl 5 N. The aqueous phase was washed thereafter again with 50 ml of methylene chloride and the pH value of the solution was increased to a value of about 13 with a NaOH solution 10 N. The resulting two phases were extracted separately by means of methylene chloride in three steps, using 50 ml of methylene chloride for each step. The organic phase was dried on sodium sulphate and concentrated by vapourising the solvent after filtration. The oil obtained was purified by means of column chromatography (silica, eluens methylene chloride:ammonia:methanol 80:3:17). The yield was 8 grams or 49 %. The structure of the colourless oily product was confirmed by means of NMR-spectroscopy.

Synthesis of compound (C-9):

This compound was synthesised by the reaction of compound (C-13) and 2-diethylaminoethanethiol in an analogous way as has been described for compound (C-3) (see US-P 4,292,400).

Synthesis of compound (C-10):

This compound was synthesised by the reaction of compound (C-13) and 2-(methylaminoethylthioxo)ethanol in an analogous way as has been described for compound (C-12).

As set forth hereinbefore at least one of the hydrophilic layers of the direct-positive material according to this invention contains a compound corresponding to the general formulae (I),(II) or (III) or more particular to the formulae given hereinbefore, but in a preferred embodiment said compound is added to the protective antistress layer(s).

Further according to this invention the photographic direct positive material according to this invention contains a nucleating agent.

A first class of suitable development nucleators for use in combination with the sensitivity boosters according to the present invention are the hydrazide-type compounds corresponding to the following general formula N-1 :

$$R^1\text{-NH-NH-CO-}R^2 \qquad \text{(N-1)}$$

wherein :
each of R^1 and R^2 independently represent hydrogen, an alkyl group, a substituted alkyl group, an aryl group, or a substituted aryl group.

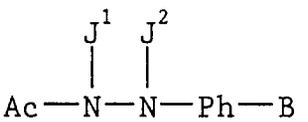
Development nucleators for use in accordance with the present invention are aryl hydrazides e.g. 1-formyl-2-phenyl-hydrazide, 1-p-acetamidophenyl-2-acetyl-hydrazide, and 1-[2-(2,4-di-tert-pentyl-phenoxy)-propionamidophenyl]- 2-formyl-hydrazide.

Another class of suitable hydrazide-type development nucleators are hydrazides comprising a heterocyclic nitrogen-containing nucleus or a substituted heterocyclic nitrogen-containing nucleus, e.g., a thiohydantoin nucleus and a mercaptotetrazolyl nucleus.

Another class of hydrazide-type development nucleators for use in accordance with the present invention, which comprise a heterocyclic nitrogen-containing nucleus are the hydrazines carrying a pyrazolidin-3-one-1-yl-phenyl group or a substituted pyrazolidin-3-one-1-yl-phenyl group.

An interesting class of development nucleators corresponding to general formula N-1 are the aryl hydrazides containing water-solubilizing polyhydroxy moieties.

Another class of aromatic hydrazide nucleating agents are those in which the aromatic nucleus is substituted with one or more groups to restrict mobility and, preferably promote adsorption of the hydrazide derivative to the silver halide grain surface, Preferred hydrazides of this kind are represented by following general formula (N-2) :

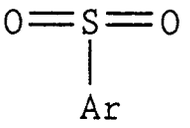


(N-2)

wherein

Ac is an acyl group,
J^1 is hydrogen and J^2 is a sulphinic acid radical or vice versa,
Ph is a phenylene or substituted phenylene group, and
B is a moiety capable of restricting mobility, such as a ballasting or an adsorption promoting moiety.

Hydrazides of this type are, e.g., disclosed by Hess US 4,478,928. A type of sulphinic acid radical is represented by the following :



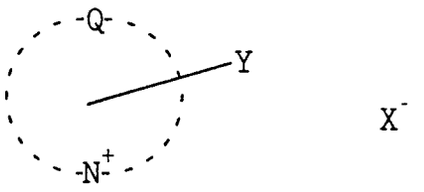
wherein Ar is an aryl group or substituted aryl group, preferably phenyl or naphthyl.

A still further class of aromatic hydrazide nucleating agents are acylhydrazinophenylthioureas as disclosed by Leone US 4,030,925 and US 4,276,364. other variants are described by von König US 4,139,387 and Adachi GB 2,012,443.

Still another class of nucleating agents of the hydrazide type consists of N-(acylhydrazinophenyl)thioamide compounds as disclosed in Leone US 4,080,207. Further preferred compounds are triazolo-substituted phenyl hydrazide nucleating agents as described by Sidhu US 4,278,748. Comparable nucleating agents having a somewhat broader range of adsorption promoting groups are disclosed in GB 2,011,391.

Other useful hydrazine and hydrazide nucleating agents have been disclosed in e.g. Research Disclosure Item 23510 Vol. 235, Nov. 10, 1983 and in US 4,269,929, US 4,243,739, US 4,272,614. Recently new hydrazine and hydrazide derivatives or new combinations with other useful ingredients have been disclosed in e.g. EP 0 254 195, US 4,915,354, DE 3 829 078, EP 0 311 009, US 4,816,373, US 4,686,167, EP 0 351 077, US 4,833,064, US 4,937,160, US 4,912,016, US 4,950,578, US 4,975,354, US 4,988,604, EP 0 399 460, US 4,971,890, US 4,994,365, EP 0 420 005, EP 0 398 355, US 4,971,888, US 4,960,672, EP 0 393 711, EP 0 393 720, EP 0 393 721, and Japanese Unexamined Patent Publications 63-306438, 63-234245, 63-234244, 01-105941, 01-179982, 01-201650, 01-235943, 01-296238, 01-090439, 01-055549. These hydrazine and hydrazide compounds can likewise be used in the present invention.

A further general class of suitable development nucleators consists of reactive N-substituted cycloammonium quaternary salts corresponding to the following general formula (N-3):



(N-3)

wherein Q represents the necessary atoms to close an heterocyclic 5- or 6-membered ring or ring system, and R^4 and Y can represent several kinds of substituents depending on the specific chemical class.

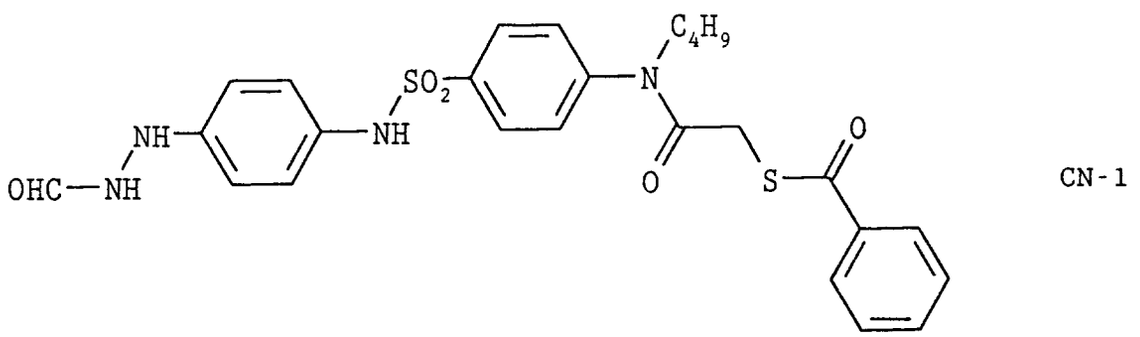
Useful classes of N-substituted cycloammonium derivatives are disclosed in e.g. US 3,615,615, US 3,759,901, US 3,734,738, US 3,719,494, US 4,115,122, US 4,471,044 and Research Disclosure, Vol. 232, August 1983, Item 23213. Recent disclosures on N-substituted cycloammonium derivatives include e.g. Japanese Unexamined Patent Publications 01-61638, 01-217338, 01-217339, 01-20024 and 01-179142.

Other classes of suitable development nucleators are, e.g., sulphur compounds e.g. thiourea dioxide, phosphonium salts e.g. tetra(hydroxymethyl)phosphonium chloride, hydroxylamine, bis-(p-aminoethyl)-sulphide and water-soluble salts thereof, reductic acid and derivatives thereof, e.g., 4,4,5,5-tetramethyl-reductic acid, kojic acid, ascorbic acid, 2-hydroxy-1,3-cyclohexanedione, 2-acetoxy- 1,2-di(2-pyridyl)-ethanone, 2-hydroxy-1,2-di(2-pyridyl)-ethanone.

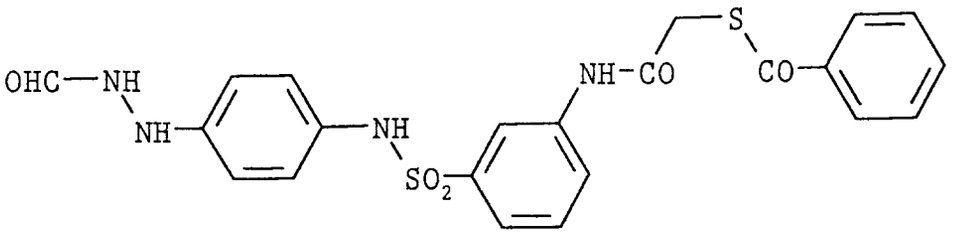
The most preferred classes of development nucleators have been described in EP-A-0 634 693, with p-sulphonamidophenylhydrazide derivatives being the most preferred compounds, having a protected silverion complexing function.

Said development nucleator is not able to react with nor adsorb on the surface of the silver halide emulsion crystals prior to development, but contains a group protected against reaction with as well as against adsorption to silver halide and which is transformed during development into a nucleating derivative with an enhanced reactivity for the surface of the silver halide crystals.

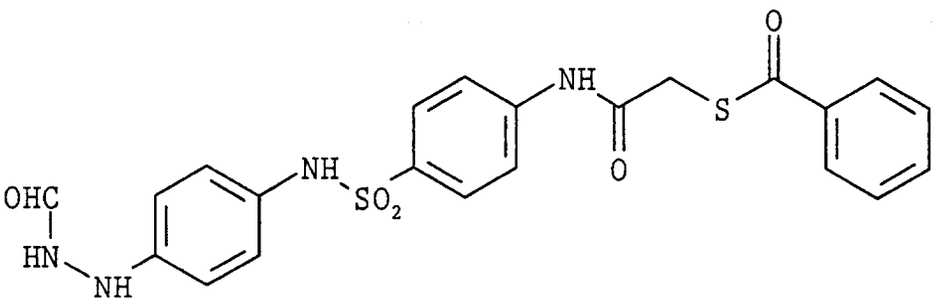
Specific examples thereof are the compounds CN-1, CN-2 and CN-3, according to the formulae:



CN-1



CN-2



CN-3

Mixtures of at least two of the above-mentioned development nucleators can be used advantageously.

Prior to the coating of the composition that will form the photographic layer comprising at least one development nucleator, the development nucleator(s) can be dissolved in an organic solvent, e.g., N-methyl-pyrrolidone, and added to said composition.

Alternatively the development nucleator(s) can be added in dispersed form to the hydrophilic colloid composition that will form said emulsion layer. In this case this dispersion can be prepared by dissolving these nucleators first in at least one water-immiscible, oil-type solvent or oil-former, adding the resulting solution to an aqueous phase containing a hydrophilic colloid preferably 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 e.g. a gelatin silver halide emulsion, and coating the resulting composition in the usual manner to produce a system in which particles of development nucleator(s), surrounded by an oily membrane, are distributed throughout the gel matrix. The dissolution of the development nucleator(s) in the oil-former may be facilitated by the use of an auxiliary low-boiling water-immiscible solvent, e.g. ethylacetate, which is removed afterwards by evaporation.

Preferred latent image-forming silver halide emulsions are so-called core-shell emulsions consisting of a core and at least one shell with the same or different halide compositions. Both shell and core can mutually independently be composed of silver bromide, silver chloride, silver chlorobromide, silver chloroiodide, silver bromoiodide and silver chlorobromoiodide. The emulsions can show a coarse, medium or fine average grain size and be bounded by (100), (111), (110) crystal planes or combinations thereof. Also high aspect ratio tabular core-shell emulsion grains can be contemplated gas disclosed in US 4,504,570. The core-shell emulsions contain internal sensitization sites which can be of various nature and which form an internal latent image upon exposure.

A first type of core-shell emulsions contains internal physical sensitization sites formed by crystallographic irregularities in the phase bounderies between a core and a shell of distinctly different halide composition, e.g., a silver bromide core and a silver bromoiodide shell with a relative high iodide percentage.

Another simple method for applying internal sensitization sites consists of incorporating a polyvalent metal ion dopant in the core grains during their formation. This metal dopant can be placed in the reaction vessel prior to precipitation or it can be added to one or more of the solutions taking part in the precipitation in order to divide it homogenously over the whole core or over the whole shell, or in well-defined locations as a band of dopant. Preferred polyvalent metal dopants are the metals of group VIII of the Periodic System, e.g., Iridium, as disclosed in US-P 3,367,778, Ruthenium as disclosed in, e.g., EP-S 0 336 425 and 0 336 426, in EP-A 0 617 323 and in US-P 4,643,965 or Rhodium. They are preferably used in the form of a soluble salt or coordination complex, The usual concentration range is comprised between 10^{-8} and 10^{-4} mole per mole of silver halide.

The most common method of creating internal sensitization sites consists of interrupting the precipitation after completion of the core and apply chemical sensitization or even fogging to this core, after which process the precipita-

tion of the shell is resumed. The usual chemical ripening agents containing middle-chalcogen elements like sulphur, selenium and tellurium can be used as has been disclosed, e.g., in US 3,761,276. Preferably these agents are combined with compounds containing noble metal atoms, e.g., gold. Contrast can be controlled by optimizing the ratio of middle-chalcogen amount to gold sensitizer amount as is described in US 4,035,185.

The choice of the halide composition of the shell portion will depend on the requirements of the specific photographic application. In order to achieve fast developability emulsion shells with a high chloride content are best suited. On the contrary when high sensitivity is most important bromide or iodobromide grain shells are to be preferred. The shell portion of the grain must contain a sufficient percentage of the total silver halide in order to restricts access of a surface developer to the internal sensitization centers. The surface of the finished core-shell emulsion grains can be chemically sensitized or not. For obtaining good reveral speed and maximum density a moderate degree of surface sensitization using conventional techniques can be applied. This degree of chemical sensitization is limited to that which will realize an optimal balance between internal and surface sensitivity, the internal sensitization usually remaining predominant.

It is specifically contemplated that in order to control sensitometric characteristics two or more internal latent image-forming emulsions can be blended before coating and thus be applied in the same emulsion layer. Alternatively several different emulsions can be used each in a different emulsion layer arranged in a pack. However in a most preferred embodiment of the present invention simply one emulsion layer is coated containing one direct positive emulsion or a blend of several direct positive emulsions.

The internal latent image-forming emulsions can, if desired, be spectrally sensitized according to the exposure source to be used depending on the specific photographic application. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes and complex merocyanine dyes as described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. The process of spectral sensitization can take place at any stage of the emulsion preparation but most commonly spectral sensitization is undertaken subsequent to the completion of surface chemical sensitization, if any.

Preferred orthochromatic spectral sensitizing dyes have been presented in EP 0 473 209.

In conventional silver halide photography, both negative or direct positive working, so-called stabilizers or anti-foggants are well known ingredients which can be incorporated in photographic materials and/or in photographic developing solutions. Their principal function consists in minimizing the obtained fog level on developing exposed photographic materials and/or to reduce the rise of development fog after prolonged storage of the photographic material compared to the fog level of a freshly coated material. Numerous chemical classes of stabilizers are disclosed in photographic scientific and patent literature. Suitable examples are, e.g., the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, imidazoles, nitroimidazoles, benzimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, indazoles, nitroindazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione , oxazoline-thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JP-A 75-39537, and GB 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-P 4,727,017, and other compounds such as benzenethiosulphonic acid, toluenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide. A review of useful compounds is published in Research Disclosure N° 17643 (1978), Chapter VI. Several patent publications disclose particularly useful classes of antifoggants or stabilizers in connection with direct positive materials in order to counteract their specific disadvantages. So JP-A 62-229134 describes benzotriazoles in backing layers of materials containing core-shell type direct positive emulsions in order to improve processing stability. The addition of several kinds of mercapto-substituted N-containing heterocyclic compounds to direct positive emulsions of the internal sensitivity type are disclosed in JP-A's 63-029752, 01-197742, 63-040148 and 63-040148. In JP-A 57-096331 the addition after physical maturation to direct positive emulsions of specific mercaptotriazoles in order to improve raw stock stability is described. Stauffer US-P 2,497,917 recognized that certain antifoggants when used in internal latent image-forming direct positive elements not only reduce the minimum density but also increase maximum density. Members of this special class of antifoggants are known to be effective whether incorporated in the photographic element itself or in a developing solution. Further applications of maximum density enhancing antifoggants are illustrated in Evans US 3,761,276 cited above. Hoyen US 4,572,892 discloses a black-and-white direct positive photographic element comprising one or more emulsion layers containing internal latent image-forming silver halide grains and further a maximum density enhancing 1,2,3-triazole antifoggant (preferably a benzotriazole derivative) which has to be incorporated in an undercoat layer between the emulsion layer(s); in the preferred embodiment a nucleating agent is present, e.g., an arylhydrazide derivative. An improved direct positive sensitometry is claimed together with an extended overexposure margin before rereversal occurs. However the practice of this procedure exhibits the technological and economical disadvantage of the requirement for an extra undercoat layer. Further the solubility

in water of benzotriazole derivatives is rather limited so that for the incorporation of higher amounts the use of organic solvents which are ecologically disadvantageous are needed.

The 1-(2-sulphonatobenzoyl)-benzotriazole derivatives represented by formula (I) and used in accordance with the present invention form a subclass of a class of so-called masked stabilizers which was disclosed in US-P 5,236,815. The term "masked stabilizer" refers to the fact that these compounds are easily decomposed (or "demasked") to form the free stabilizer molecule under the alkaline pH conditions commonly occuring during the development step. Examples of usefull masked stabilizers (MS) are set forth in US-P 5,254,443.

Thanks to their higher solubily as compared to the corresponding free stabilizers the masked benzotriazoles can simply be added as aqueous solutions to the coating solution. The concentration of the masked benzotriazoles in the emulsion layer is preferably comprised between 10^{-4} and $5x10^{-2}$ mole per mole of silver halide.

The binder of the photographic element, especially when the binder used is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type, e.g. 1,3-vinylsulphonyl-2-pro-panol, chromium salts, e.g., chromium acetate and chromium alum, aldehydes, e.g., formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds, e.g., dimethylolurea and methyloldimethylhydantoin, dioxan derivatives, e.g., 2,3-dihydroxy-dioxan, active vinyl compounds, e.g., 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds, e.g., 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids, e.g., mucochloric acid and mucophenoxychloric acid, These hardeners can be used alone or in combination. The binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US 4,063,952.

The photographic element of the present invention may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides, e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycolalkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes, e.g., as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion. Preferred surface-active agents are compounds containing perfluorinated alkyl groups.

The photographic element of the present invention may further comprise various other additives such as, e.g., compounds improving the dimensional stability of the photographic element, antistatic agents, spacing agents, light absorbing dyes, e.g., antihalation dyes, filter dyes or acutance dyes, lubricants, opacifying compounds, e.g. titanium dioxide, and plasticizers.

Antistatic agents can be used in one or more of the layers on the emulsion side or in a backing layer.

Suitable additives for improving the dimensional stability of the photographic element are, e.g., dispersions of a water-insoluble or hardly soluble synthetic polymer, e.g. polymers of alkyl(meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

Spacing agents can be present of which, in general, the average particle size is comprised between 0.2 and 10 μm. Suitable spacing agents can be made, e.g., of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US 4,614,708. Spacing agents can also serve as matting agents. Other common matting agents consist of silica particles of which different size classes can be used.

In the direct positive material of the present invention non-light sensitive hydrophilic colloid layers can be present, e.g., a protective layer and one or more backing layers.

The support of the photographic material may be opaque or transparent, e.g., a paper support or resin support. When a paper support is used preference is given to one coated at one or both sides with an Alpha-olefin polymer, e.g., a polyethylene layer which optionally contains an anti-halation dye or pigment. It is also possible to use an organic resin support, e.g., cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinylchloride film or poly-Alpha-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.07 and 0.35 mm. These organic resin supports are preferably coated with a subbing layer which can contain water insoluble particles such as silica or titanium dioxide.

The photographic direct positive materials of the present invention can be exposed in any convenient way according to their particular application, e.g., by daylight or by artificial light like tungsten light, xenon, metal-halogen lamps, quartz-halogen lamps, by laser sources or invisible radiation like ultraviolet, X-rays and infrared.

The processing of the photographic materials of the present invention proceeds in a surface developer composed according to specifications dependent on the particular use of the material.

The developing solution preferably contains one or more developing agents, sulphite ions, bromide ions and polyalkyleneoxides. Preferred developing agents are, e.g. hydroquinone and derivatives, 3-pyrazolidinone derivatives like 1-phenyl-5-pyrazolidinone ("Phenidone") and analogues mostly in combination with hydroquinone(s), aminophenols, hydroxylamin, hydrazine derivatives, and ascorbic acid and analogues. Other adjuvants well known to those skilled in the art may be added to the developer liquid of the present invention. A survey of conventional developer addenda is given by Grant Haist in "Modern Photographic Processing" - John Wiley ans Sons - New York (1979) p. 220-224. Examples of such addenda include complexing agents for calcium and magnesium ions, present in hard water, e.g., ethylene diamine tetraacetic acid and analogues compounds. Further can be present anti-foaming agents, surface-active agents, biocides, thickening agents like polystyrene sulphonate and antioxidants like benzoate and cyclodextrine. The developing liquid can contain so-called anti-sludge agents in order to reduce dirt streaks on developed photographic material. The alkaline pH value of the developing solution is preferably established by means of conventional buffering agents like phosphate buffers, carbonate buffers and borax buffers. The pH can be additionally adjusted to the desired value by means of an alkali hydroxide, e.g., sodium or potassium hydroxide and is, according to the developing method of the direct-positive materials of this invention, not higher than 11.0. Finally the solution can contain hardening agents including latent hardeners.

As aminoalcohols are preferably absent, a fish-like odor is not present, sludge is prevented and the concentration of the developer can be enhanced.

As a consequence it is remarkable that a classical negative-working developer is used in the developing method of the materials according to this invention.

For processing preferably an automatically operating apparatus is used provided with a system for automatic replenishment of the processing solutions.

The development step can be followed by a washing step, fixing in a fixing solution and another washing or stabilization step. Finally the photographic material is dried.

The photographic direct positive materials of the present invention can be used in various types of photographic elements such as, e.g., in photographic elements for graphic arts, for general amateur and professional photography, for cinematographic recording and duplicating, for radiographic recording and duplicating purposes, and in diffusion transfer reversal photographic elements. A preferred application however is micrographic recording, e.g., in a microfilm for computer output.

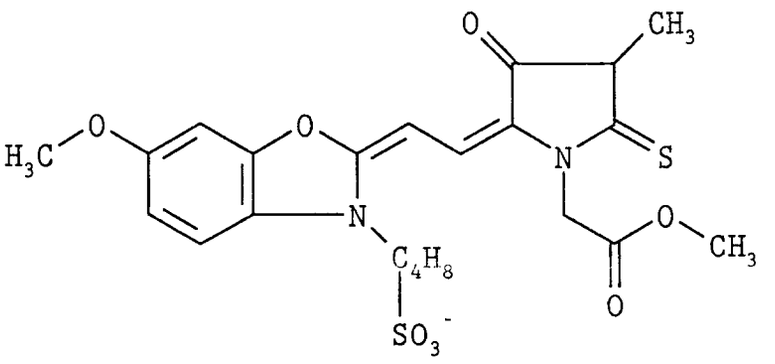
The following examples illustrate the invention without however limiting it thereto.

EXAMPLES

Example 1

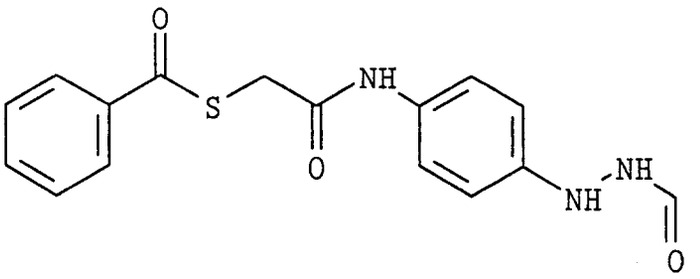
A cubic silver bromide core-shell emulsion showing a final average grain size of 0.33 µm was prepared by simultaneous addition of equimolar solutions of silver nitrate and potassium bromide to a stirred aqueous gelatin solution. The precipitation of the core was carried out at 60 °C and at a pAg of 7.01. After addition of 50 % of the total silver the core grains were chemically sensitized by means of 25.8×10^{-3} mmole of sodium thiosulphate, 16.3×10^{-3} mmole of aurochloric acid and 27.5×10^{-3} mmole of p-toluenesulphonic acid sodium salt, all expressed per mole of silver halide. Then the grains were further grown under the same precipitation conditions until the final average grain size was reached. The gelatin / silver ratio was brought to 0.5 by the addition of extra gelatin and the core-shell emulsion was surface sensitized by means of 1.62×10^{-3} mmole of p-toluenesulphonic acid sodium salt, 13.8×10^{-3} mmole of sodium thiosulphate, 2.48×10^{-3} of aurochloric acid and 26.8×10^{-3} of ammoniumthiocyanate, all expressed per mole of silver halide.

To the finished emulsion was added 2.0 mmole/mole of $AgNO_3$ of spectral sensitizing dye SD-1



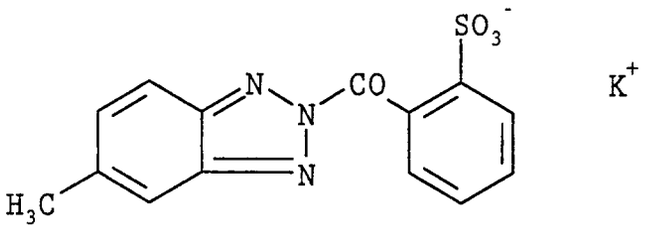
SD-1

and 6.6 mmole/mole of $AgNO_3$ of nucleating agent, according to the formula CN-4



CN-4

An amount of 0.9×10^{-4} mmole/100 g of $AgNO_3$ of masked methylbenzotriazole, according to the formula MS



MS

was added.

Each emulsion sample was coated on a transparent support at a coverage of 4.0 g/m^2, expressed as $AgNO_3$.

Use was made of the slide hopper coating technique for simultaneous application of the emulsion layer and the antistress layer.

The composition of said protective antistress layer per 50 m^2 was as follows:

-an ammoniumperfluorocarbonate compound represented by the formula $F_{15}C_7COONH_4$	1 ml
-MOBILCER Q (trademarketed product from MOBIL OIL)	40 ml
-gelatin (Rouselot t 13311)	90 g
$(C_2H_5)(C_4H_9)CH\text{-}CH_2\text{-}CH_2\text{-}CH(CH_2\text{-}CH\text{-}(CH_3)_2)(OSO_3H)$	25 ml
$\text{-}C_8H_{17}\text{-}CH{=}CH\text{-}C_7\text{-}CO\text{-}N(CH_3)\text{-}CH_2\text{-}CH_2\text{-}SO_3H$	5 ml

- polystyrene sulphonic acid as a polymeric thickener: amount in order as to reach a viscosity of 16-20 mPas

- di-(vinyl-sulphonyl)-methane was added as a hardener just before coating in an amount of 94 mg/m^2.
- demineralised water added in an amount just as to reach a total weight of 1787 g.

Total amounts of gelatin per square meter in the emulsion layer and in the protective antistress layer were 2.18 and 1.80 g respectively.

Protective antistress coating No, 1 (comparative) was prepared without the addition of a booster to the composition given hereinbefore.

To the protective antistress coatings Nos. 2-4 (invention) amounts of respectively 40, 70 and 100 mg/m^2 of a booster, the formula of which has been given hereinafter, were added to the composition given hereinbefore.

Further to the protective antistress coatings Nos. 5-6 (invention) amounts of respectively 70 and 100 mg/m^2 of a booster, having the formula given hereinafter were added to the composition given hereinbefore.

Then the coatings were exposed through a continuous wedge on a EG&G sensitometer using a 10^{-5} s flashlight and developed at 35 °C in developer G3231C, trade marked product from Agfa-Gevaert, diluted four times before use. The said developer working as a classical negative-working developer doesn't contain an aminoalcohol and has a pH value before use of 10.90: hydroquinone and hydroxymethylmethylphenidone are the developing agents used therein.

After development during 30 s at 34°C the coatings were treated in a conventional fixing bath and finally washed and dried. The direct positive sensitometric characteristics were evaluated and represented in Table 1.

Herein the relative sensitivities are expressed as relative log Et values measured at a density D=1.10+Dmin : as this invention is related with direct-positive materials a lower figure means a higher sensitivity.

Further gradations are measured between densities D=0.10+Dmin and D=1.1+Dmin .

TABLE 1

Coating No.	Booster Amt.(mg/m^2)	Dmin	Dmax	Sensitivity	Gradation
1 (comp.)	—	0.03	0.03	—	—
2 (inv.)	40	0.05	1.53	1.62	1.30
3 (inv.)	70	0.05	1.73	1.45	1.56
4 (inv.)	100	0.07	1.92	1.36	1.65
5 (inv.)	70	0.06	1.97	1.31	1.69
6 (inv.)	100	0.08	1.98	1.24	1.86

Table 1 illustrates the better direct positive sensitometry for the materials prepared according to this invention: a higher sensitivity and a higher gradation are attained when using the boosters according to this invention added to the protective antistress layer of the direct-positive material. No direct-positive image is obtained without its presence as is clearly illustrated by the comparative coating No. 1.

Claims

1. Photographic direct positive material comprising a support and as hydrophilic layers one or more radiation sensitive emulsion layers containing internal latent image-forming silver halide grains and one or more protective antistress layers characterized in that at least one of the hydrophilic layers further contains at least one compound corresponding to one of the general formulae (I) to (III)

$$R^1\text{-}X\text{-}[(LINK_1\text{-}Y)_n\text{-}LINK_2\text{-}Z]_p\text{-}LINK_3\text{-}X\text{-}R^1 \quad (I)$$

$$[R^1\text{-}X\text{-}(LINK_1\text{-}Y)_n\text{-}LINK_2\text{-}Z]_2\text{-}LINK_3 \quad (II)$$

$$[R^1\text{-}X\text{-}(LINK_1\text{-}Y)_n\text{-}LINK_2]_2\text{-}Z \quad (III)$$

wherein

X, Y and Z each independently represents S, O or NR^2;
R^1 and R^2 each independently represents a member selected from the group consisting of hydrogen, alkyl or

substituted alkyl, or the necessary atoms to form a ring together with the N-atom to which they are attached if X represents NR^2;

$LINK_1$, $LINK_2$ and $LINK_3$ each independently represent a divalent linking group;

n is an integer having a value of 0 or 1 and

p is an integer having a value from 1 to 10.

2. Photographic direct positive material according to claim 1, wherein in the formulae (I) to (III) $LINK_1$ and $LINK_2$ are divalent groups comprising a limited number of atoms, in order to get the silver-ion complexing atoms X, Y and Z in 1,4- or 1,5- position.

3. Photographic direct positive material according to claim 1, wherein in the formulae (I) to (III) $LINK_2$ is represented by a $-(C_2H_4-O)_m-C_2H_4-$ divalent linking group and wherein m represents an integer having a value from 1 to 20.

4. Photographic direct positive material according to claim 1, wherein in the formulae (I) to (III) $LINK_2$ is represented by a $-(CH_2-CH(R)O)_m-C_2H_4-$ divalent linking group, wherein R represents a substituted or unsubstituted alkyl group and wherein m represents an integer having a value from 1 to 20.

5. Photographic direct positive material according to any of claims 1 to 4, wherein said compound(s) is(are) added to the protective antistress layer(s).

6. Photographic direct positive material according to any of claims 1 to 5, wherein said material further contains a nucleating agent.

7. Photographic direct positive material according to claim 6 wherein said nucleating agent is a p-sulphonamido-phenylhydrazide derivative.

8. Photographic direct positive material according to any of claims 1 to 7, wherein said internal latent image forming silver halide grains are core-shell grains.

9. Photographic direct positive material according to claim 8, wherein the core of said core-shell grains is chemically ripened.

10. Photographic direct positive material according to any of claims 1 to 9, wherein said internal latent image-forming silver halide grains are internally doped with a polyvalent metal dopant, chosen from the metals of group VIII of the Periodic Table.

11. Photographic direct positive material according to claim 1, wherein said compounds according to general formula (I) to (III) are present in a concentration comprised between 10^{-4} and $5x10^{-2}$ mole per mole silver halide.

12. Method of developing an imagewise exposed photographic direct positive material according to any of claims 1 to 11, (a) in the presence of a nucleating agent, or (b) with light flashing of said material during processing.

13. Method of developing an imagewise exposed photographic direct positive material according to claim 12, wherein the pH of the developer ready-for-use is not more than 11.0 and wherein no aminoalcohol(s) is(are) present.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 1965

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.6)
X,Y	EP-A-0 249 239 (FUJI PHOTO FILM CO LTD) * page 7 - page 28 * * compounds 1-4, 6-10, 12-17,19, 21, 23-25, 31-34, 37, 46-48,51, 57-63, 65-67, 73,89,90, 94-101 * page 32, line 41 - line 45 * ---	1-13	G03C1/485
X,Y	EP-A-0 318 987 (FUJI PHOTO FILM CO LTD) * compounds A-9 to A-11, A-13 and A-14 on p.20 * * page 5, line 55 - page 6, line 10; claims * ---	1-13	
X,Y	EP-A-0 650 086 (KODAK LTD./EASTMAN KODAK CO.) * page 5, line 21 - line 55 * * page 8, line 15 - line 16 * -----	1-13	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 February 1996	Buscha, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)