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(54) **Photographic direct positive material containing a particular stabilizer**

(57) A photographic direct positive material is provided, comprising a support and one or more radiation sensitive emulsion layers containing internal latent image-forming silver halide grains characterized in that a hydrophilic non-light-sensitive interlayer adjacent to said emulsion layer(s) and coated between said emulsion layer(s) and the support comprises a nucleation inhibitor releaser which is characterised by a half-life of from 1 to 180 seconds, said half-life being defined as the time necessary to convert $(1-1/e)^{th}$ of the inhibitor releaser to its inhibitor in the developing step of the exposed material at a developer temperature of 36°C.

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Description

1. Field of the invention.

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

2. Background of the invention.

10 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 original 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.

15 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.

20 Surface-fogged emulsions are disclosed e.g. in Kendall US 2,541,472, Schouwenaars GB 723,019, Illingsworth US 3,501,307, Berriman US 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 2,563,785, Evans US 3,761,276, Knott US 2,456,953 and Jouy US 3,511,662. Further patents include Davey US 2,592,250, which describes internal sensitive emulsions prepared by conversion, Porter US 3,206,313, which discloses direct positive emulsions of a particular core-shell type, Milton US 3,761,266, illustrating direct positive emulsions rich in chloride, Gilman US 3,761,267, 25 Atwell US 4,035,185, and Daubendiek US 4,504,570, which discloses direct positive emulsions of the internal latent image-forming type containing tabular grains.

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, JA-Apl. 75-39537, and GB 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US 4,727,017, and 40 other compounds such as benzenethiosulphonic acid, toluenethiosulphonic acid, benzenethiosulphonic acid and benzenethiosulphonic acid amide. A review of useful compounds is published in Research Disclosure N° 17643 (1978), Chapter VI.

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 45 easily be reached with direct positive emulsions. It is not easy to reconcile the various demands of high maximum density, good contrast, low minimum density and sufficient speed. More particularly direct positive emulsions of the internal sensitivity type can suffer from a second disadvantage known as rereversal on overexposure. 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 62229134 describes benzotriazoles in backing layers of 50 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 63029752, 01197742, 63040148 and 63040148. In JP-A 57096331 the addition after physical maturation to direct positive emulsions of specific mercaptotriazoles in order to improve raw stock stability is described.

55 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-P 3,761,276 cited above. Høyen US-P 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 acylhydrazide derivative. The invention described in US-P 5,254,443 disclosing masked stabilisers can be considered as a further improvement to the teachings of US-P 4,572,892.

The problem that may arise with fogging development of direct-positive emulsions of the internal latent image type is that said development is highly dependant on the circumstances during development. Especially in the presence of acylhydrazides higher development temperatures and development times tend to increase the action of the nucleating agents: as a consequence the amount of new developable crystals increases and the direct-positive sensitivity decreases. Attempts in favour of the image-wise blocking of the acceleration of nucleating actions are given in US-P 5,116,717 and EP-Applications 495 477 and 512 420, but a further improvement thereof is highly requested.

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, being high maximum density, low minimum density, good contrast and sensitivity.

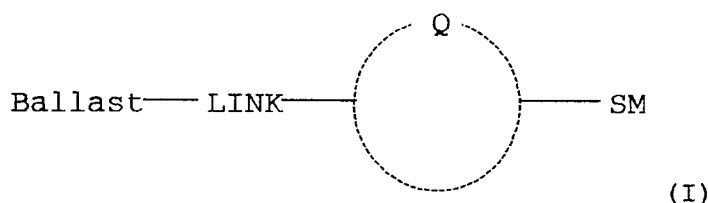
It is a further object of the present invention to provide a direct positive material with a better processing latitude, especially as a function of processing temperature and of processing time.

Other objects will become apparent from the description given hereinafter.

4. Summary of the invention.

The objects of the invention are attained by providing a photographic direct positive material, comprising a support and one or more radiation sensitive emulsion layers containing internal latent image-forming silver halide grains characterized in that a hydrophilic non-light-sensitive interlayer adjacent to said emulsion layer(s) and coated between said emulsion layer(s) and the support comprises a nucleation inhibitor releaser which is characterised by a half-life of from 1 to 180 seconds, more preferably of from 5 to 40 seconds, and still more preferably from 10 to 30 seconds, said half-life being defined as the time necessary to convert $(1-1/e)^{th}$ of the inhibitor releaser to its inhibitor in the developing step of the exposed material at a developer temperature of 36°C.

Said inhibitor releaser preferably corresponds to the general formula (I),



wherein

BALLAST means an inert hydrophobic aliphatic group limiting the diffusion of the molecule; LINK means a divalent linking group which contains at least one functional group which cleaves or hydrolyses during processing in an alkaline developing or activating bath; and Q represents the necessary atoms to complete a heterocyclic or aliphatic aromatic ring and which forms a photographically useful group or PUG, together with the terminal -SM group, wherein S represents sulphur and M represents an alkali metal or a NH_4 -group.

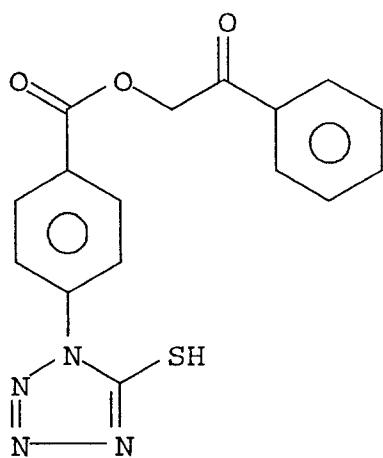
More preferably PUG represents a substituted or unsubstituted phenylmercaptotetrazole compound. A preferred one is 1-(p-carboxyphenyl)-5-mercaptotetrazole.

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. Most preferably an acylhydrazide nucleating agent is used which is preferably incorporated in an emulsion layer too.

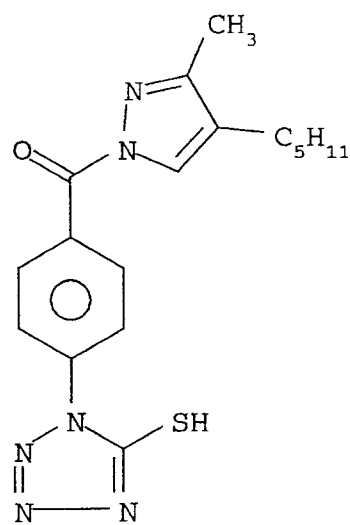
5. Detailed description of the invention.

The compounds represented by formula (I) comprising a preferred phenylmercaptotetrazole inhibiting group are forming a free stabilizing substituted or unsubstituted phenylmercaptotetrazole molecule under the alkaline pH conditions commonly occurring during the development step.

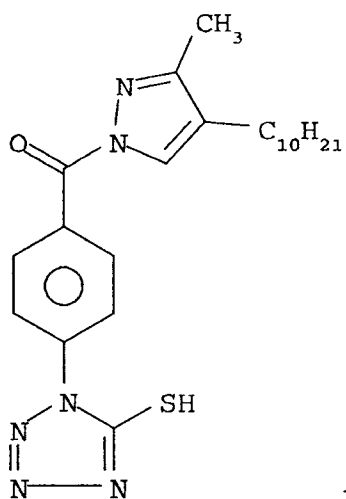
Examples of useful stabilizers according to the formula (I) are set forth hereinafter:



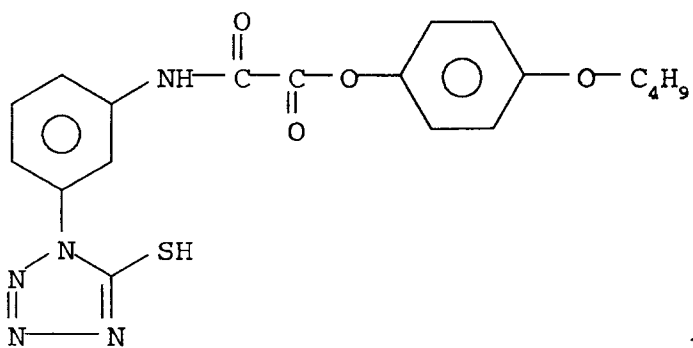
I.1



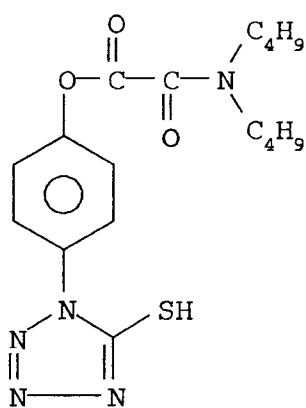
I.2



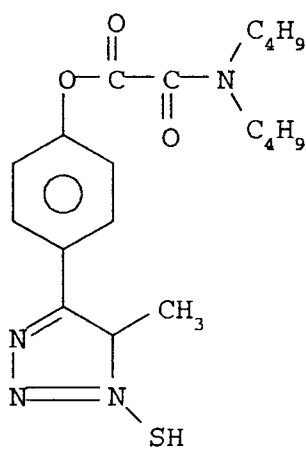
I.3



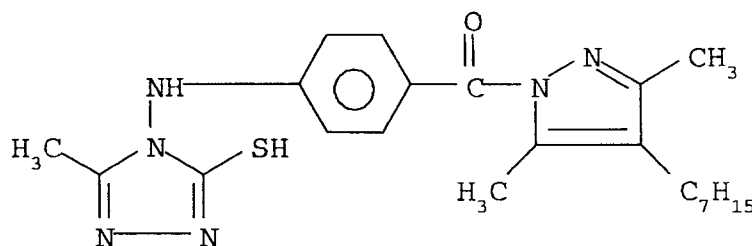
I.4



I.5



I.6



I. 7

In the practice of this invention the nucleator inhibiting releaser may be incorporated in at least one of the emulsion layers.

For reasons of kinetics, it is specifically contemplated that the said nucleator inhibiting releaser is incorporated in a layer adjacent to the emulsion layer and is situated between said emulsion layer and the support, in order to avoid losses of the active product in the developer and in order to make the product work effectively in the emulsion layer. As a consequence, according to the object of this invention, the nucleation will be inhibited some time after its start in order to avoid further nucleation at the surface of more and more new crystals. As already mentioned above an increasing developability of more and more emulsion crystals leads to a decrease in sensitivity of the direct-positive material in which said emulsion crystals are coated. It is important for the nucleator inhibiting releasing compound used in the photographic material according to this invention that the inhibiting moiety only becomes active after some initial development time. In this context the meaning of the "half-life of the nucleator inhibiting releaser" is important and is defined as "the time necessary to convert $(1-1/e)^{th}$ of the inhibitor releaser to its inhibitor in the developing step at a temperature of the developer of 36°C ".

The "half-life" can easily be determined by following the spectral changes of the inhibitor releaser in the developer or the developer conditions, like pH and the like, at 36°C .

It is clear that a short half-life versus the development time will result in a low maximum density as the development is blocked then rather quickly, whereas a long half-life will result in a normal maximum density and a high minimum density: preferred half-life times are from 5 to 40 seconds and still more preferably from 10 to 30 seconds.

Therefor the said compound is preferably incorporated in an adjacent layer, from which it takes some time to diffuse to the emulsion layer, where its active PUG is able to block the nucleating action of the nucleating agent(s).

The concentration of the compound according to the general formula (I) in the layer adjacent to the emulsion layer(s) is preferably comprised between 5×10^{-7} and 5×10^{-2} mole per mole of silver halide and more preferably between 5×10^{-5} and 5×10^{-3} .

Preferred latent image-forming silver halide emulsions are so-called core-shell emulsions consisting of a core and at least one shell having the same or different halide compositions. Both shell(s) and core can mutually independently be composed of silver bromide, silver chloride, silver chlorobromide, silver chloriodide, silver bromiodide and silver chlorobromiodide. 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 as disclosed in US-P 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 boundaries between a core and a shell of distinctly different halide composition, e.g. a silver bromide core and a silver bromiodide shell with a relatively 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. Preferred polyvalent metal dopants are metals from the group VIII of the Periodic System, e.g., Iridium, as disclosed in US 3,367,778, Rhodium or Ruthenium, as disclosed, e.g., in EP-S 0 336 425 and 0 336 426, in EP-A 0 617 323 and in US-P 4,643,965. 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

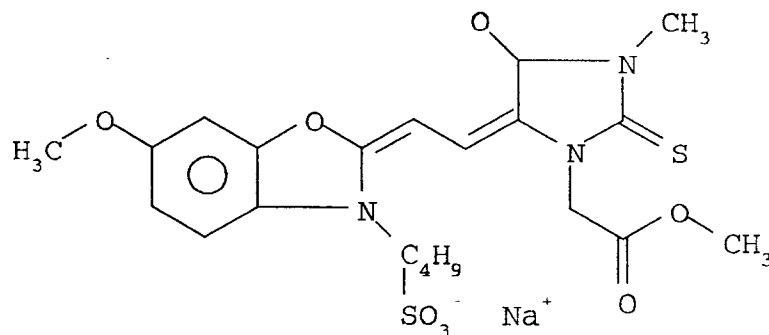
completion of the core and applying chemical sensitization or even fogging to this core, after which process the precipitation of the shell is resumed. The usual chemical ripening agents containing middle-chalcogen elements like sulphur, selenium and tellurium can be used as has been disclosed, e.g., in US-P 3,761,276. Preferably they are combined with compounds containing noble metal atoms, e.g., gold. Contrast can be controlled by optimizing the ratio of middlechalcogen amount to gold sensitizer amount as has been described in US-P 4,035,185. The core-shell emulsions used in the photographic direct-positive material according to this invention are emulsions wherein at least the core of said core-shell grains is chemically ripened.

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 required bromide or iodobromide grain shells are preferred. The shell portion of the grain must contain a sufficient percentage of the total silver halide in order to restrict 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 reversal speed and maximum density a moderate degree of surface sensitization using conventional techniques can be applied. This degree of chemical sensitization is usually 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.

A preferred orthochromatic spectral sensitizing dye (SD-1) is



SD-1

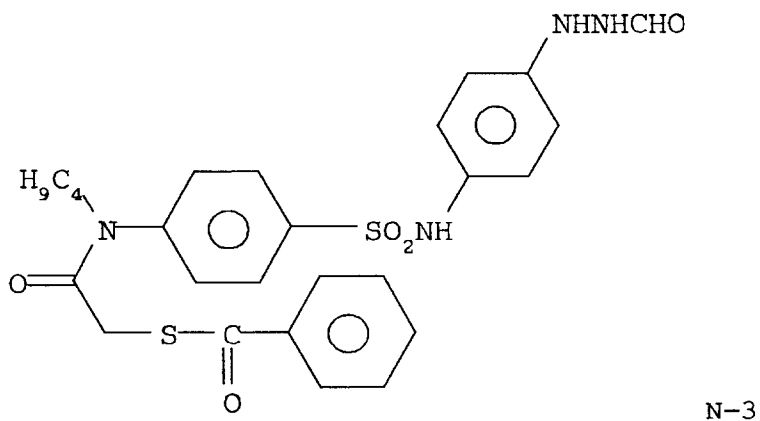
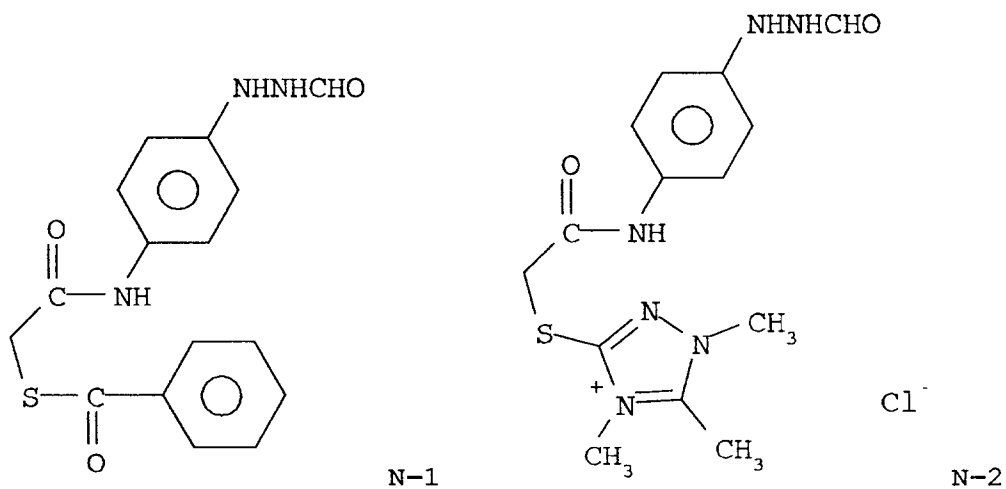
In order to promote the formation of a direct positive image the photographic materials of the present invention can be image-wise exposed and then subjected to uniform flash lighting during processing. Preferably however the direct positive image is formed with the aid of a so-called nucleating agent (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. Since in the preferred embodiment of this invention there is an undercoat non-light sensitive layer the nucleating agent can be incorporated therein, but preferably it is incorporated in the emulsion layer(s). When used in the silver halide emulsion layer(s) the development nucleators are present in a concentration of preferably 10^{-5} mole to 10^{-1} mol per mole of silver halide.

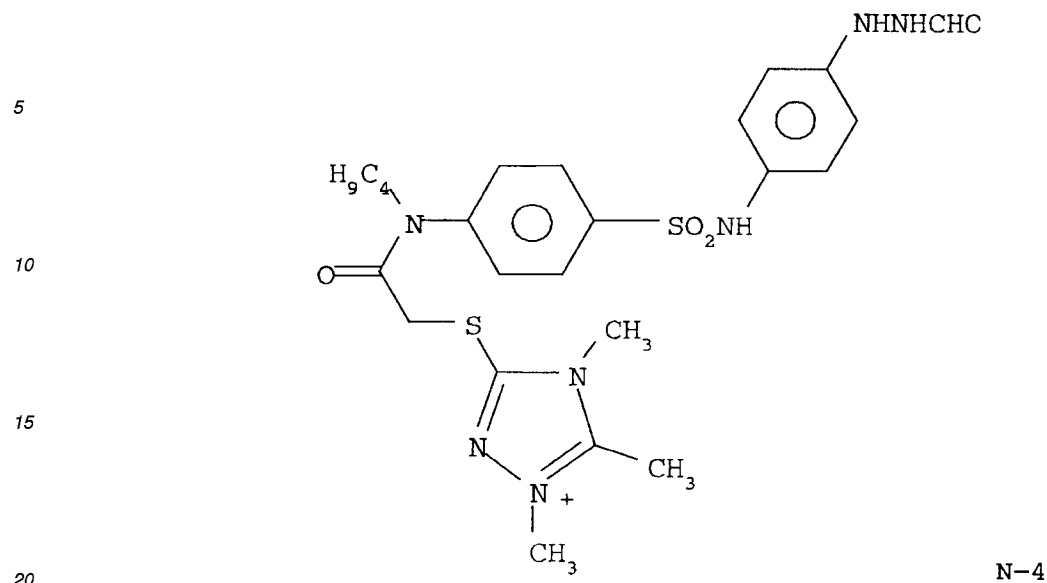
A review of suitable development nucleators for use in accordance with the present invention are the hydrazide-type compounds corresponding to the different general formulae N-1 to N-8 as has been described in US-P 5,254,443, which is incorporated herein by reference.

Other classes of suitable development nucleators are, e.g., propargylammonium salts, e.g., N-propargyl quinaldinium tosylate, 2-acetoxy-1,2-di(2-pyridyl)-ethanone, dihydroquinazolinium bromide, etc.

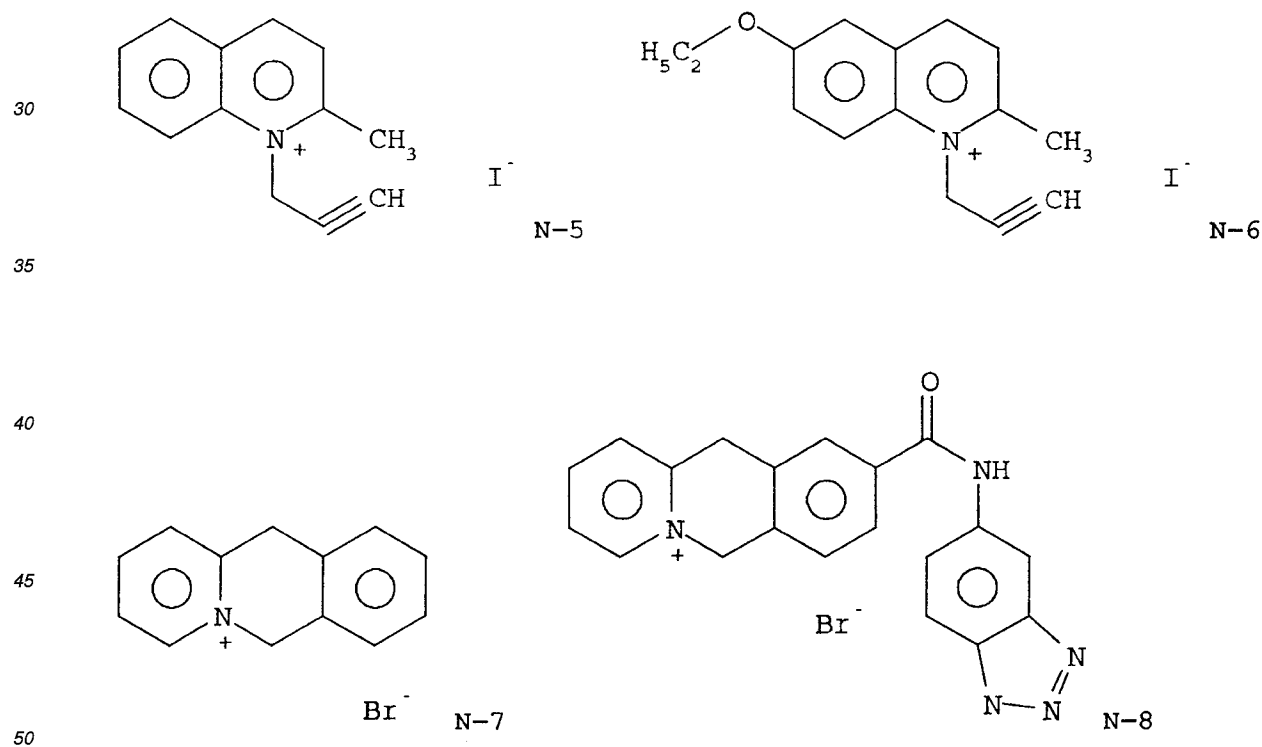
Other classes of suitable development nucleators have recently been described in EP-A's 0 634 693 and 0 634 692.

Acylhydrazides are preferred nucleating agents for use in photographic materials according to this invention. Preferred examples of such compounds are N-1 to N-4, the formulae of which are given hereinafter.





25 Another class of preferred nucleating agents comprises N-substituted cycloammonium quaternary salt. Preferred examples of such compounds are given in the formulae N-5 to N-8:



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. alcohol, 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 the 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.

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-propanol, 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 glycol alkylamines 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, sulphy, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonyl 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 sulphonyl 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, α - β -unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphonylalkyl (meth)acrylates, and styrene sulphonyl acids.

Spacing agents can be present of which, in general, the average particle size is comprised between 0.2 and 10 μ m. 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 besides an already mentioned protective antistress layer one or more non-light-sensitive hydrophilic colloid undercoat and/or backing layers can be present.

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 poly-

alkyleneoxides. Preferred developing agents are e.g. hydroquinone and derivatives, 3-pyrazolidinone derivatives like 1-phenyl-5-pyrazolidinone ("Phenidone") and analogues, 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 and 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-slug 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. Finally the solution can contain hardening agents including latent hardeners.

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, 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. Although limited to direct-positive materials comprising nucleation inhibitor releasers, the said releasers can also be useful in negative working materials, preferably in combination with hydrazides.

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

6. EXAMPLES

Example 1

A cubic silver bromide core-shell emulsion showing a final average grain size of 0.26 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 70 °C and at a pAg value of +106 mV versus a Ag/AgCl reference electrode. After addition of 50 % of the total silver the core grains were chemically sensitized by means of 19.4×10^{-3} mmole of sodium thiosulphate, 12.3×10^{-3} mmole of aurochloric acid and 27.5×10^{-3} mmole of p-toluenethiosulphonic 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-toluenethiosulphonic acid sodium salt, 17.2×10^{-3} mmole of sodium thiosulphate, 3×10^{-3} of aurochloric acid and 33.5×10^{-3} mmole of ammoniumthiocyanate, all expressed per mole of silver halide.

The finished emulsion was divided in different samples in order to prepare different coating solutions for the emulsion layer having the following composition:

- coating amount of the silver bromide emulsion: 3.4 g/m² expressed as the equivalent amount of silver nitrate
- coating amount of gelatin: 2.18 g/m²
- spectral sensitizing dye (1-methoxycarbonylmethyl-3-methyl-5-[2-(2,3) dihydro-6-methoxy-3-sulphonatobutyl-benzoxazole-2-ylidene-ethylidene]-thiohydantoin sodium salt): 13 mg/m²
- nucleating agent: N-formyl-4-[2-(benzoylthio)-acetamido]-phenyl hydrazide: 1 mg/m²
- nucleator inhibiting releaser (1-(2-sulphonatobenzoyl)-5-methylbenzotriazole potassium salt) : 93 mg/m²

The protective antistress layer was composed of:

- coating amount of gelatin: 1.80 g/m²
- an ammoniumperfluorocarbonate compound represented by the formula $\text{F}_{15}\text{C}_7\text{COONH}_4$: 0.6 ml
- MOBILCER Q (trademarked product from MOBIL OIL): 0.8 ml
- $(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_2-\text{CH}(\text{CH}_3)_2)(\text{OSO}_3\text{H})$: 0.32 ml
- 4-bis-vinylsulphonyl-methane: 250 mg
- polystyrene sulphonic acid as a polymeric thickener: amount in order as to reach a viscosity of 16-20 mPas.

Moreover the following coating solutions were prepared in order to coat a layer between the support and the emul-

sion layer:

- coating amount of gelatin: 1.20 g/m²
- surfactant according to the formula
- 5 C₈H₁₇-Phen-(O-CH₂-CH₂)₈-O-CH₂-COOH : 1 ml/m²
- polystyrene sulphonic acid as a polymeric thickener in an amount of 1 ml/m².

For the comparative coating (comp.) no stabilizer according to this invention was added to the gelatinous interlayer between the emulsion layer and the support, whereas for the coating according to this invention (inv.) 0.9 mg/m² of the compound according to formula I-1 was added.

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

Then 4 strips of each of the coatings (comp. and inv.) were exposed through a continuous wedge on a EG&G sensitometer using a 10⁻⁵ s flashlight and developed at different temperatures in a developer of following composition :

2-methylaminoethanol	100 ml
potassium sulphite (45 %)	360 ml
potassium hydroxide (50 wt%)	45 ml
potassium dihydrogeniumphosphate	65 g
potassium bromide	6 g
hydroquinone	74.9 g
methyl benzotriazole	0.23 g
acetic acid (99 wt%)	30 ml
4-hydroxymethyl-methylphenidone	12.5 g
Turpinal 2NZ	3 g
EDTA Na ₄ (40wt%)	5 ml
water to make	1 l

After development at different temperatures (resp. 32°C, 34°C, 36°C and 38°C) in the diluted developer (1+3) 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.

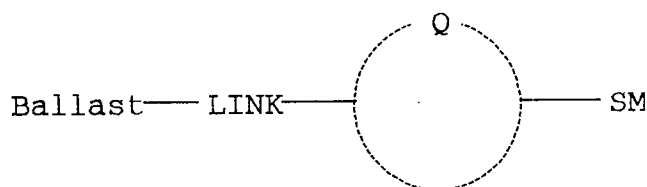
Table 1.

Sample	Dev. Temp. (°C)	Dmin (x100)	Sensitivity (0.1+Dmin)	Dmax (x100)
comp.	32	7	0.53	249
inv.	32	5	0.70	202
comp.	34	10	0.39	265
inv.	34	6	0.58	245
comp.	36	12	0.31	275
inv.	36	7	0.56	260
comp.	38	21	0.22	272
inv.	38	9	0.54	246
Note : sensitivity : relative sensitivity expressed as relative log Et-values; lower figure means higher sensitivity as a lower exposure dose is required.				

Table 1 illustrates the more extended development latitude for processing at different developer temperatures and a lower rereversal when the nucleator inhibiting releaser according to this invention is present in a layer, adjacent to the emulsion layer, as in this case, in the protective antistress layer.

Claims

1. Photographic direct positive material comprising a support and one or more radiation sensitive emulsion layers containing internal latent image-forming silver halide grains characterized in that a hydrophilic non-light-sensitive interlayer adjacent to said emulsion layer(s) and coated between said emulsion layer(s) and the support comprises a nucleation inhibitor releaser which is characterised by a half-life of from 1 to 180 seconds, said half-life being defined as the time necessary to convert $(1-1/e)^{\text{th}}$ of the inhibitor releaser to its inhibitor in the developing step of the exposed material at a developer temperature of 36°C.
2. Photographic direct positive material according to claim 1, wherein said releaser has a half-life of from 5 to 40 seconds.
3. Photographic direct positive material according to claim 1, wherein said releaser has a half-life of from 10 to 30 seconds.
4. Photographic direct positive material according to any of claims 1 to 3, wherein said nucleation inhibitor releaser corresponds to general formula (I) :



wherein

BALLAST means an inert hydrophobic aliphatic group limiting the diffusion of the molecule;

LINK means a divalent linking group which contains at least one functional group which cleaves or hydrolyses during processing in an alkaline developing or activating bath;

and

Q represents the necessary atoms to complete a heterocyclic or aliphatic aromatic ring and which forms a photo-graphically useful group or PUG, together with the terminal -SM group, wherein S represents sulphur and M represents an alkali metal or a NH_4 -group.

5. Photographic direct positive material according to claim 4, wherein the said PUG represents a substituted or unsubstituted phenylmercaptotetrazole compound.
6. Photographic direct positive material according to claim 4 or 5, wherein the said PUG represents 1-(p-carboxyphenyl)-5-mercaptotetrazole.
7. Photographic direct positive material according to any of claims 1 to 6, wherein said material further contains a nucleating agent.
8. Photographic direct positive material according to claim 7, wherein said nucleating agent is an acylhydrazide derivative.
9. Photographic direct positive material according to claim 7, wherein said nucleating agent is a propargylammonium salt.
10. Photographic direct positive material according to claim 7, wherein said nucleating agent is a N-substituted cycloammonium quaternary salt.

11. Photographic direct positive material according to claim 4, wherein said compound according to general formula (I) is present in a concentration comprised between 5×10^{-7} and 5×10^{-2} mole per mole of silver halide.
- 5 12. Photographic direct positive material according to claim 4, wherein said compound according to general formula (I) is present in a concentration comprised between 5×10^{-5} and 5×10^{-3} mole per mole of silver halide.
13. Photographic direct positive material according to any of claims 1 to 12 wherein said internal latent image forming silver halide grains are core-shell grains.
- 10 14. Photographic direct positive material according to claim 13, wherein at least the core of said core-shell grains is chemically ripened.
- 15 15. Photographic direct positive material according to claims 13 or 14, wherein said internal latent image-forming silver halide grains are internally doped with a polyvalent metal dopant.
16. Photographic direct positive material according to claim 15, wherein said polyvalent metal dopant is chosen from the metals of group VIII of the Periodic Tabel.
- 20 17. Method of developing an imagewise exposed photographic direct positive material according to any of claims 1 to 16, (a) in the presence of a nucleating agent, or (b) with light flashing of said material during processing.



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PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 95 20 1941 shall be considered, for the purposes of subsequent proceedings, as the European search report

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	EP-A-0 365 926 (KONICA CORPORATION) * page 16; claims * * page 19, line 23 - line 40 * ---	1-17	G03C1/485
X	US-A-4 550 070 (MIYASAKA ET AL.) * column 7, line 49 - column 11, line 10; claims * ---	1-5,7,8, 11-17	
A	DE-A-24 16 814 (AGFA-GEVAERT AG) * p.8, compound 1; p.4, 1.1-8 * -----	1-17	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
INCOMPLETE SEARCH			
<p>The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims</p> <p>Claims searched completely : Claims searched incompletely : Claims not searched : Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search		Date of completion of the search	Examiner
THE HAGUE		8 February 1996	Buscha, A
CATEGORY OF CITED DOCUMENTS			
<p>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</p> <p>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</p>			

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Reason for the incomplete search:

Independent claim 1 claims a material containing a certain type of chemical compound. However, the compound has not been characterized by a general formula as in claim 4 but in terms of its function and in terms of kinetic reaction parameters. Since the function of an additive in photographic technology is often manifold, depending on the type of material and the processing, and frequently not explicitly disclosed, it is not possible for the skilled man, to decide, whether a certain chemical compound would fall under the scope of claim 1. Likewise it cannot be proved nor excluded that compounds mentioned in the state of the art would fall under the scope of claim 1, simply because the kinetic reaction parameter of present claim 1 ("half-life") has not been measured and disclosed.

Therefore the search has been limited to the subject-matter of claims 4-17.