

(19)



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(11)

EP 0 473 209 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

02.01.1997 Bulletin 1997/01

(51) Int Cl.⁶: **G03C 1/485**

(21) Application number: **91201761.3**

(22) Date of filing: **08.07.1991**

(54) **Method of making direct-positive computer output images**

Verfahren zur Herstellung von direktpositiven Computerausgabebildern

Méthode pour la production d'images de sortie d'ordinateur autpositives

(84) Designated Contracting States:
BE DE FR GB

(30) Priority: **27.07.1990 EP 90202059**

(43) Date of publication of application:
04.03.1992 Bulletin 1992/10

(73) Proprietor: **AGFA-GEVAERT**
naamloze vennootschap
B-2640 Mortsel (BE)

(72) Inventor: **de Prijcker, Jozef Paulina**
B-9220 HAMME (BE)

(56) References cited:
EP-A- 0 331 185 **US-A- 3 718 470**

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Description

Field of the Invention

5 The present invention relates to a method of forming direct-positive computer output (COM) images having an enhanced maximum density and gradation and to photographic light-sensitive direct-positive silver halide emulsion elements for use according to that method.

Background of the Invention

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In silver halide photography a photographic method, according to which a positive image is made without the use of a negative image or an intermediary process producing a negative image, is called a direct-positive method and a photographic light-sensitive element and a photographic emulsion for use according to such direct-positive method are called direct-positive element and direct-positive emulsion respectively.

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Two main classes of methods for making direct-positive images are known. According to a first class of methods prefogged silver halide grains are exposed to light in the presence of a desensitizing agent and developed. Such methods have been described in e.g. US-A 3,364,026, US-A 3,501,305, and GB-A 707,704. According to the second class of methods a silver halide emulsion containing silver halide grains that have light-sensitive specks mainly inside the grains (generally called internal latent image-type silver halide emulsion) is subjected to an image-wise exposure and the exposed emulsion is surface-developed in the presence of a development nucleator or the exposed emulsion is overall light-flashed to fog before it is surface-developed.

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The present invention relates to the second class of methods and to photographic material comprising silver halide grains that have light-sensitive specks mainly inside the grains. Methods for making a direct-positive image by development of an exposed internal latent image-type silver halide emulsion in the presence of a development nucleator by means of a surface developer, and photographic emulsions and photographic light-sensitive elements used in such methods have been disclosed in i.a. GB-A 1,011,062, 1,151,363, 1,195,837, JA Patent Publication 29,405/68, and in US-A 2,456,953, 2,497,875, 2,497,876, 2,588,982, 2,592,250, 2,675,318, 3,227,552, 3,761,276, and 4,540,655.

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The present invention relates to direct-positive silver halide elements comprising unfogged silver halide emulsions.

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Because of their practical and economical usefulness in the field of printing out of computer information preference is given nowadays to the use of direct-positive elements and direct-positive emulsions.

Unsensitized direct-positive silver halide emulsions for recording computer information at the usual 460 nm give direct-positive images having a maximum density of about 1.4 and a gradation of only 1.22. However, an image having such a low maximum density has poor reading quality and the gradation is insufficient for a high image quality.

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It is known from EP-A 331,185 to form direct-positive images by image-wise exposing a photographic silver halide emulsion layer containing unfogged internal latent image-type silver halide grains and developing the exposed emulsion layer containing a simple cyanine or a carbocyanine dye having the longest wavelength absorption maximum on silver halide of not longer than 590 nm.

Although the maximum density and the gradation are slightly improved according to this process, they remain substantially unsatisfactory.

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It is also known from US-A 3,736,140 to produce a positive silver image comprising image-wise exposing for at least 0.01 s at an intensity of at least about 1×10^{-12} watt/cm² an unfogged primitive silver halide emulsion layer containing a methine or polymethine spectral sensitizing agent, the silver halide grains of the emulsion layer being free of chemically induced internal or surface sensitivity, and developing the image-wise exposed emulsion layer in the presence of a chemical fogging agent or alternatively light-flashing to fog the image-wise exposed emulsion layer.

45

However, it is known from "The Theory of the Photographic Process" by T.H. James, 4th edition, Macmillan Publishing Co., Inc., New York, p. 133 and following, that at short exposure times such as those commonly used in COM-recorders viz. 10^{-5} to 10^{-8} s the speed and gradation of photographic elements can be inferior to those obtained at longer exposure times. This phenomenon also occurs in photographic direct-positive elements comprising internal latent image-type silver halide emulsions that have not been fogged or ripened externally but which are fogged either by an overall post-exposure or by development in the presence of a development nucleator. Shortening of the development time may aggravate this phenomenon.

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SUMMARY OF THE INVENTION

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It is therefore an object of the present invention to provide a method of forming direct-positive computer output (COM) images having an enhanced density and gradation.

It is another object of the present invention to provide a photographic light-sensitive direct-positive silver halide emulsion element for use according to that method.

Other objects of the present invention will become apparent from the description hereinafter.

According to the present invention a method has been found for forming direct-positive COM images obtained by the steps of :

- 5 - image-wise exposing a photographic light-sensitive element comprising a support and at least one photographic emulsion layer comprising unfogged internal latent image-type silver halide grains to light in the wavelength range of from about 440 to about 480 nm for a short duration of 10^{-5} to 10^{-8} s at a high intensity of at least 0.1 mJ/m^2 , and then
- 10 - either (a) developing the image-wise exposed element in a surface developer in the presence of at least one development nucleator or (b) overall light-flashing to fog said image-wise exposed element and subsequent development thereof in a surface developer, wherein said method is characterised in that said photographic emulsion layer comprises at least one merocyanine dye, as herein defined.

15 The present invention also provides a photographic light-sensitive direct-positive element for making direct-positive images, said element comprising a highly antistatic and highly electroconductive support and at least one light-sensitive emulsion layer comprising unfogged internal latent image-type silver halide grains and a development nucleator, characterized in that said photographic emulsion layer comprises at least one merocyanine dye; as herein defined.

20 DETAILED DESCRIPTION OF THE INVENTION

By image-wise exposing a photographic light-sensitive element comprising a support and at least one photographic emulsion layer comprising unfogged internal latent image-type silver halide grains and at least one merocyanine dye to exposure light in the wavelength range of from about 440 to about 480 nm, preferably 460 nm, for a short duration of 10^{-5} to 10^{-8} s at a high intensity of at least 0.1 mJ/m^2 , and then either (a) developing the image-wise exposed element
 25 in a surface developer in the presence of at least one development nucleator contained in the photographic emulsion layer or in a hydrophilic colloid layer in water-permeable relationship with said photographic emulsion layer or in said surface developer, or (b) overall light-flashing to fog said image-wise exposed element prior to the development thereof in a surface developer, it was found unexpectedly that increases in D_{max} and gradation are obtained, which are substantially higher than the limited increases reached with cyanine dyes according to prior art methods. Moreover, no
 30 reduction in speed is obtained according to the present invention.

A further increase D_{max} and gradation can be obtained by adding at least one rhodacyanine dye in addition to said at least one merocyanine dye to the photographic emulsion.

Merocyanines used according to the present invention are dyes having a heterocyclic nucleus comprising a trivalent nitrogen atom, wherein said heterocyclic nucleus is linked via a carbon chain having an even number of carbon atoms
 35 according to the formula $=(\text{CH}-\text{CH})_n=$ wherein n is 0, 1, 2, 3... to a nucleus containing a ketomethylene structure, e.g. a rhodanine nucleus, a pyrazolin-5-one nucleus, a thiohydantoin nucleus, etc.. Merocyanines having a trivalent nitrogen atom and substituted thereon a member having the formula $-(\text{CH}_2)_n-\text{R}$ wherein R represents a 1-hydrazonoalkyl radical are excluded as said merocyanines also act as a nucleating agent, which is not within the scope of this invention. Such bifunctional merocyanines have been disclosed e.g. in US-A 3,718,470.

40 As the merocyanine dyes and the rhodacyanine dyes are not used as spectrally sensitizing dyes either they may have but need not have an absorption spectrum in the above defined wavelength range of the exposure light.

Examples of merocyanines dyes that can be used advantageously according to the present invention are the dyes listed in the following Table 1.

45

50

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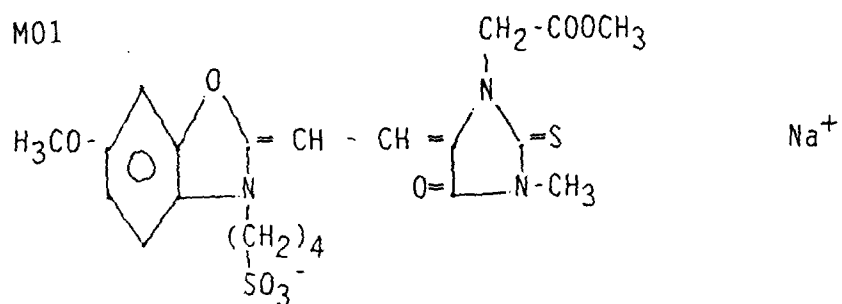
TABLE I

Dye N°

5

M01

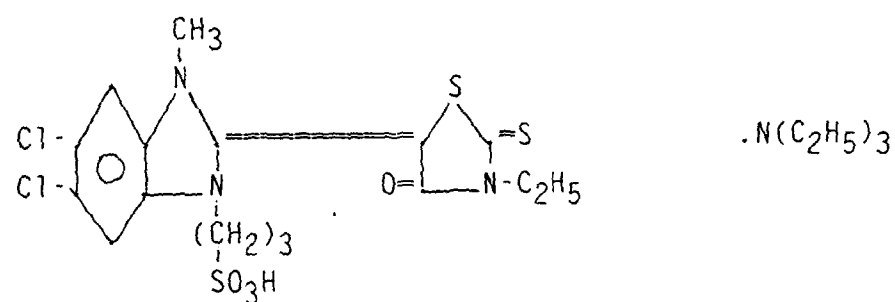
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M02

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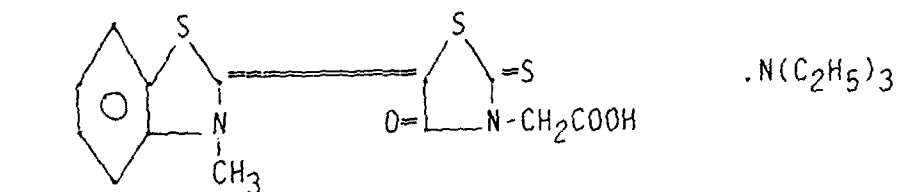


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M03

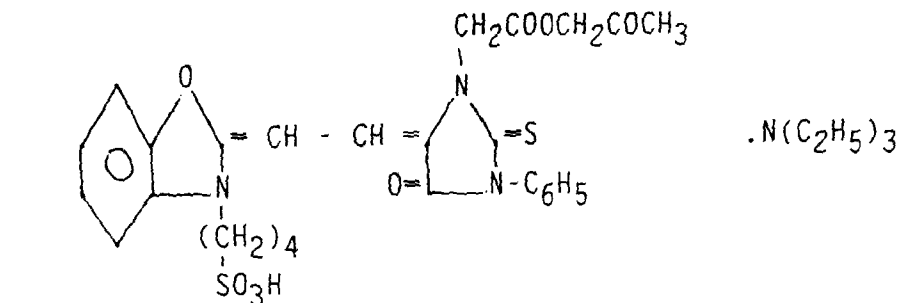
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M04

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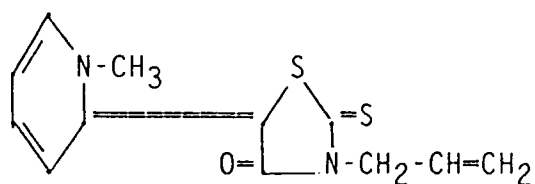


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M05

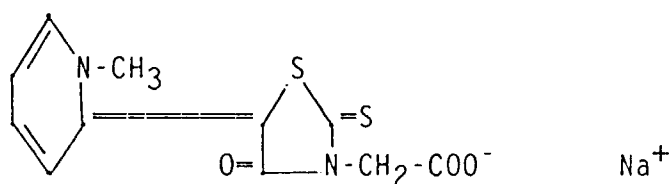
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M06

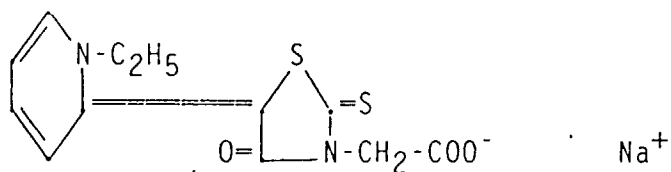
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M07

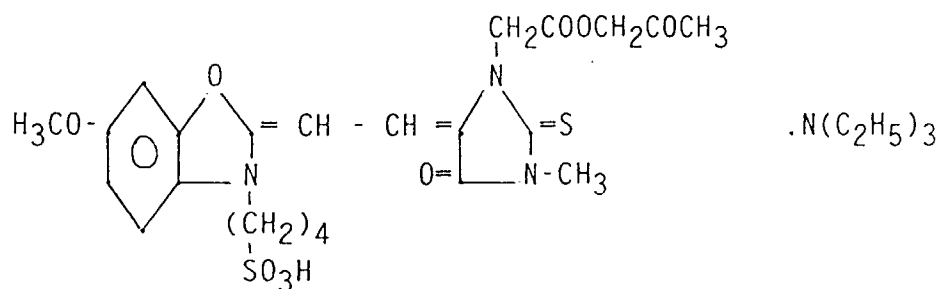
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M08

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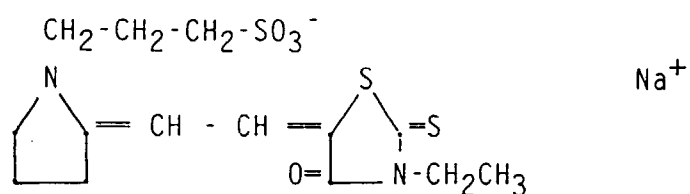


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M09

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Rhodacyanines are complex cyanines obtained e.g. by reaction of a simple merocyanine with a methyl halide or methyl sulphate followed by the condensation of the resulting reactive methylthio group with other compounds having a reactive methyl or methylene group.

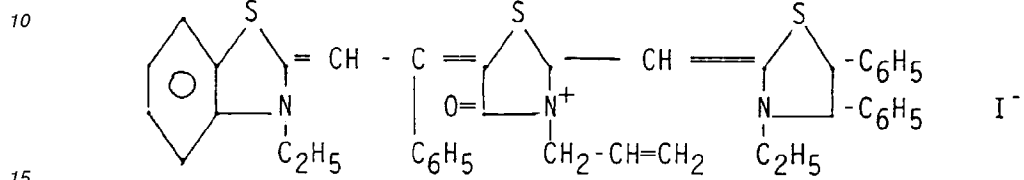
Examples of rhodacyanine dyes that can be used in addition to the merocyanine dyes are listed in the following

Table 2.

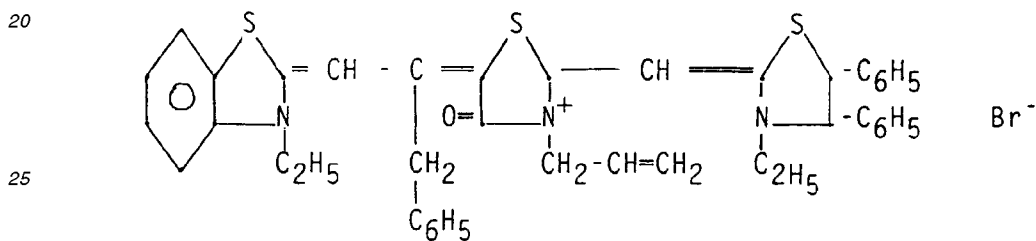
TABLE 2

5 Dye N°

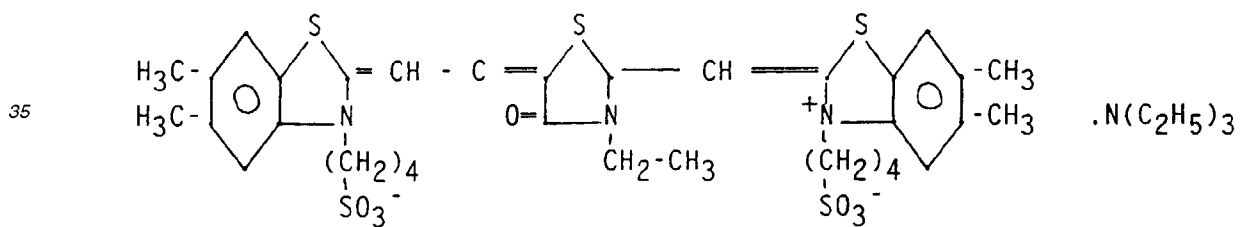
R01



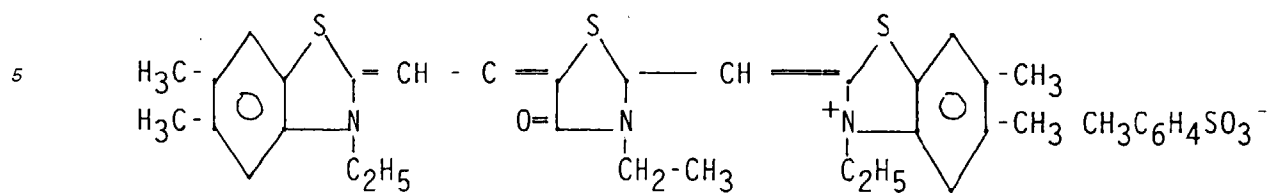
R02



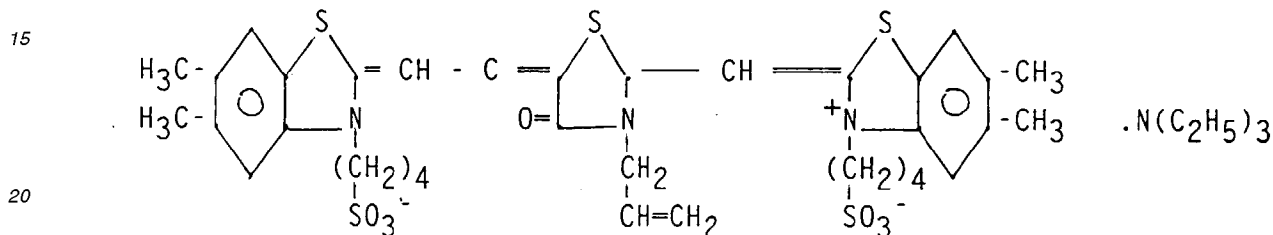
R03



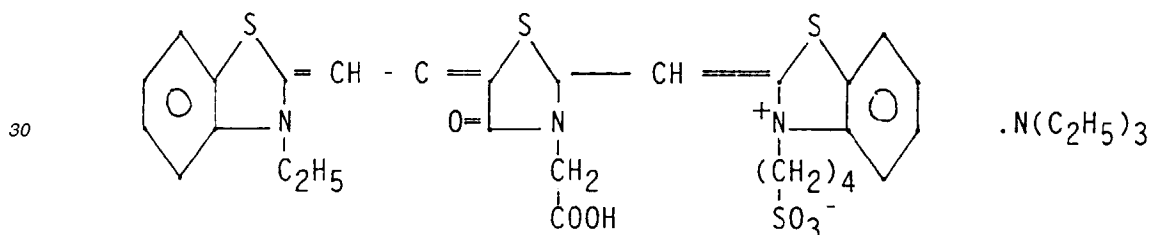
R04



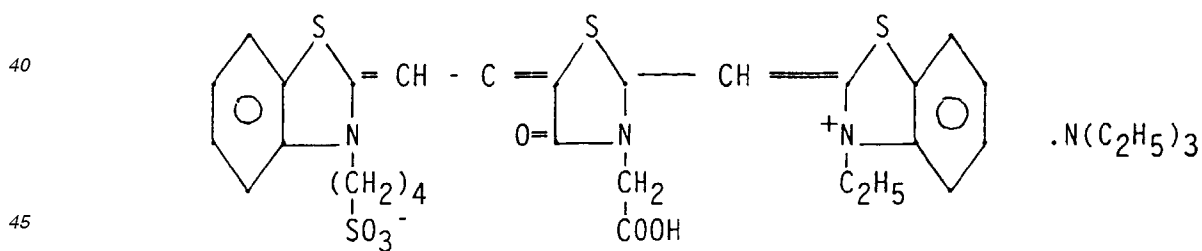
R05



R06



R07



Particulars about merocyanines and their preparation can be found in Photographic Chemistry by P. Glafkides, edited by the Fountain Press, London in 1960, Vol 2, page 844 and following. Details about rhodacyanines, also called complex merocyanines, and their preparation can also be found in the same document on page 857 and following.

The merocyanine dyes and possibly additionally rhodacyanine dyes are present in the photographic emulsion layer in a concentration almost equivalent to that used in ordinary negative silver halide emulsions. It is preferred that the merocyanine sensitizing dyes or alternatively the merocyanine and rhodacyanine sensitizing dyes are employed in a global concentration of from about 1.0×10^{-5} to about 3×10^{-3} mol per mol of silver halide, and particularly in a global concentration of from about 4×10^{-5} to 2×10^{-3} mol per mol of silver halide.

For carrying out the method of the present invention the at least one development nucleator may be incorporated in the developer or in a prebath applied to the exposed photographic element before development thereof. Preferably, however, the at least one development nucleator is incorporated into the silver halide emulsion layer or into a hydrophilic

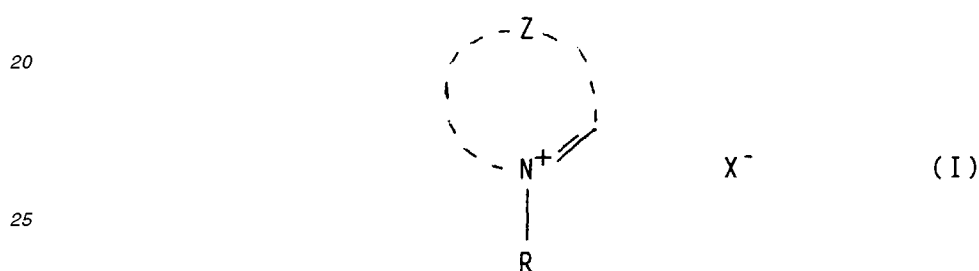
colloid layer in water-permeable relationship therewith.

The development nucleators for use in accordance with the present invention may be any of the compounds known for that purpose.

Suitable development nucleators are e.g.:

- 5 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,
 10 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, reactive N-substituted cycloammonium quaternary salts, and hydrazine-type compounds e.g. 1-diphenyl-hydrazine hydrochloride and 1,2-dipyridyl-hydrazine hydrochloride.

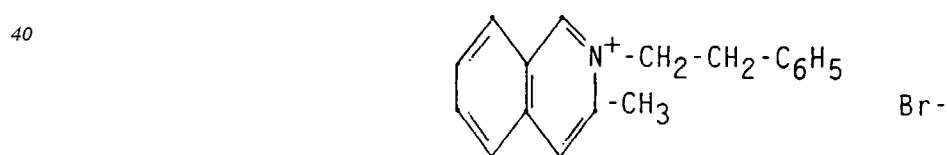
15 Suitable development nucleators of the class of reactive N-substituted cycloammonium quaternary salts correspond to the following general formula I:



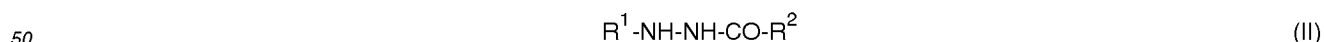
wherein :

- 30 R represents hydrogen, an alkyl group, a substituted alkyl group, an aralkyl group, a substituted aralkyl group, an alkaryl group, a substituted alkaryl group, an aryl group, or a substituted aryl group,
 Z represents the atoms needed to complete a heterocyclic nucleus or a substituted heterocyclic nucleus, which heterocyclic nucleus may carry a fused-on heterocyclic or carbocyclic ring, and
 35 X is an anion.

A representative development nucleator corresponding to general formula I has the following structural formula :



Other suitable development nucleators for use in accordance with the present invention are the hydrazine-type compounds corresponding to the following general formula II :



wherein :

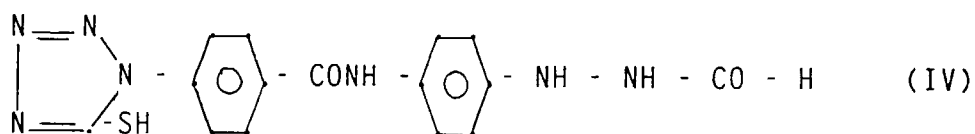
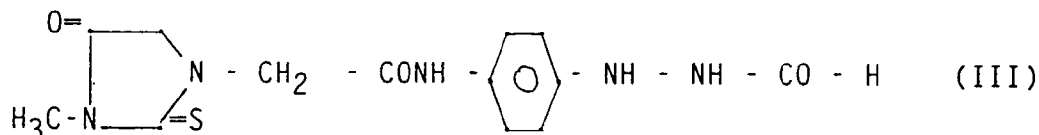
each of R^1 and R^2 (same or different) represent hydrogen, an alkyl group, a substituted alkyl group, an aryl group, or a substituted aryl group.

55 Preferred development nucleators for use in accordance with the present invention are phenyl hydrazides

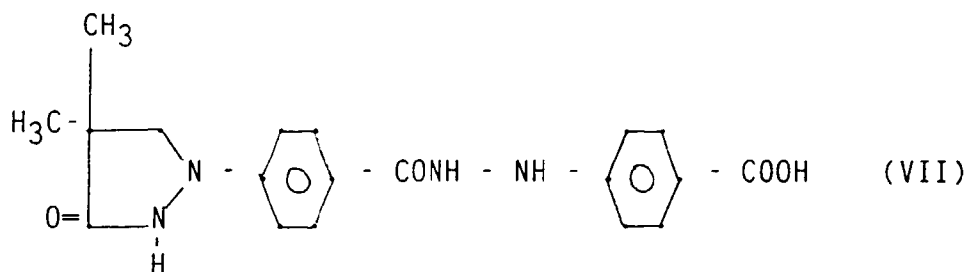
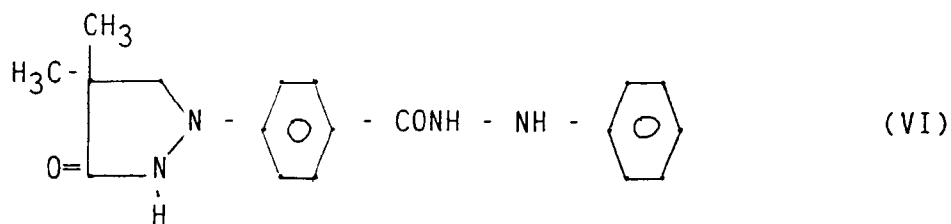
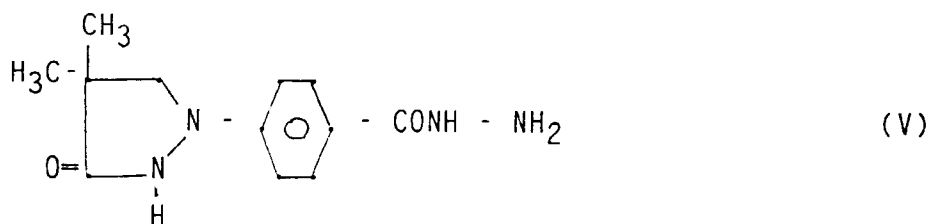
e.g. 1-formyl-2-phenyl-hydrazine, 1-p-acetamidophenyl-2-acetyl-hydrazine, and

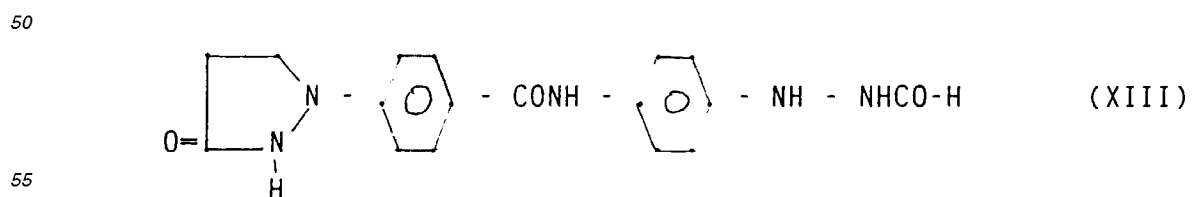
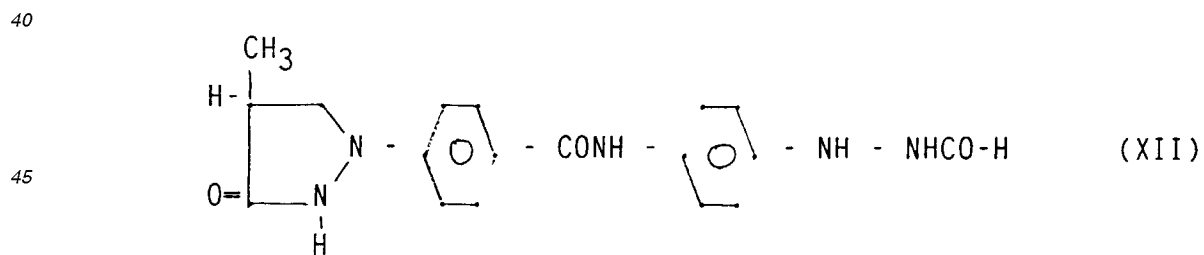
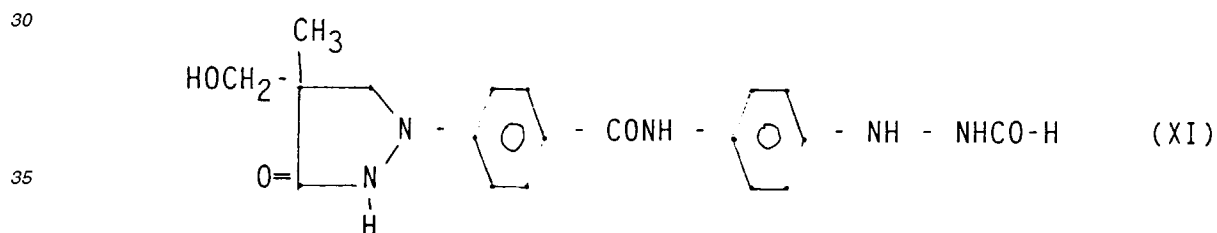
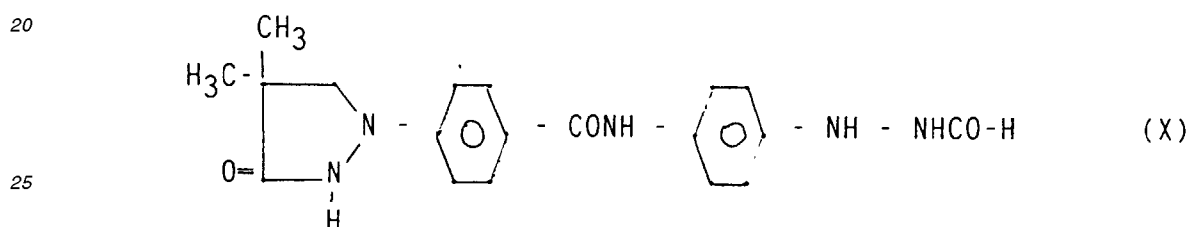
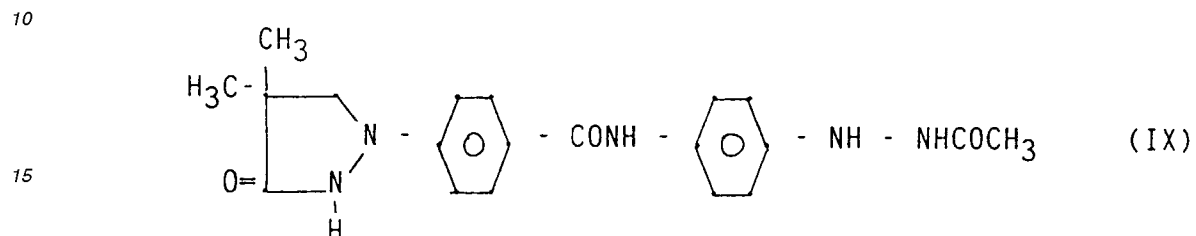
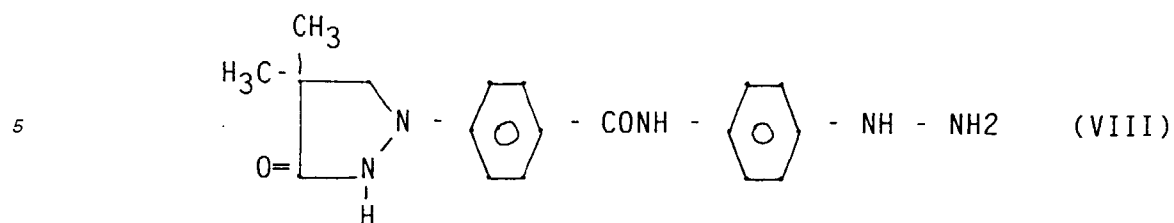
1-[2-(2,4-di-tert-pentyl-phenoxy)propionamidophenyl]-2-formyl-hydrazine.

Another class of suitable hydrazine-type development nucleators are hydrazines comprising a heterocyclic nitrogen-containing nucleus or a substituted heterocyclic nitrogen-containing nucleus e.g. a thiohydantoin nucleus and a mercaptotetrazolyl nucleus. Examples of such compounds are the following compounds III and IV:



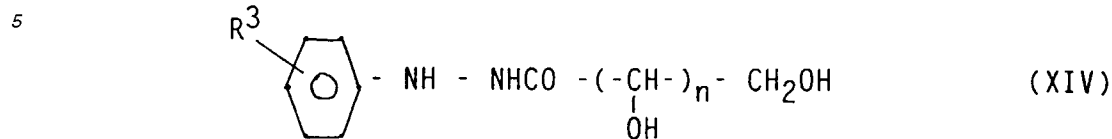
A preferred class of hydrazine-type development nucleators for use in accordance with the present invention, which comprise a heterocyclic nitrogen-containing nucleus are the hydrazines carrying a pyrazolidin-3-one-1-yl-phenyl group or a substituted pyrazolidin-3-one-1-yl-phenyl group. Examples of such preferred development nucleators are the compounds according to the following structural formulae V to XIII:





An interesting class of development nucleators corresponding to general formula II are the phenyl hydrazides

containing water-solubilizing polyhydroxy moieties. Representatives of this class correspond to the following general formula XIV :



wherein :

n is a positive integer ranging from 1 to 10 and

15 R³ is hydrogen, an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, a heterocyclic group, or a substituted heterocyclic group.

A suitable example of a heterocyclic group represented by R³ in general formula XIV is a pyrazolidin-3-one-1-yl group, which may be substituted.

20 Suitable examples of development nucleators corresponding to general formula XIV are the compounds, in which n is 4 or 5 and R³ stands for hydrogen.

Mixtures of at least 2 of the above-mentioned development nucleators can be used advantageously.

25 As mentioned before, nucleating amounts of the development nucleators are present during development of the photographic element and can be incorporated for that purpose e.g. into the light-sensitive silver halide emulsion layer or into a hydrophilic colloid layer in water-permeable relationship therewith. Alternatively, they can also be added to the developing bath or to a separate bath.

When used in the silver halide emulsion layer the development nucleators are present in a concentration of 10⁻⁴ mol to 10⁻¹ mol per mol of silver halide.

30 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 and added to said composition. For instance, 1.3 x 10⁻³ mol of the development nucleator is added in the form of a 3.5 % solution in N-methyl-pyrrolidone per mol of silver.

35 According to a preferred embodiment the development nucleator(s) are added in dispersed form to the hydrophilic colloid composition that will form said emulsion layer or said hydrophilic colloid layer. When these hydrazines are present in dispersed form in a hydrophilic colloid layer, preferably in the internal latent image-type silver halide emulsion layer, the direct-positive images obtained upon development have a very fine grain.

40 The development nucleator(s) can be incorporated into the hydrophilic colloid composition that will form said emulsion layer or said hydrophilic colloid layer by dissolving them 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, which is removed afterwards by evaporation.

45 The development nucleator(s) can be dispersed in hydrophilic colloid compositions with the aid of at least one known oil-former e.g. an alkyl ester of phthalic acid. The oil-formers can be used in widely varying concentrations e.g. in amounts ranging from about 0.1 to about 10 parts by weight and preferably from 0.5 to 2 parts by weight relative to the amount of the development nucleator(s) dispersed therewith.

50 It may be useful to combine the oil-former with at least one auxiliary solvent that is insoluble or almost insoluble in water and has a boiling point of at most 150°C, such as a lower alkyl acetate e.g. ethyl acetate.

55 According to a preferred embodiment of the present invention the development nucleator(s) are incorporated into the hydrophilic colloid composition that will form said silver halide emulsion layer or said hydrophilic colloid layer by mixing the development nucleator(s) in the absence of an oil-former and a solvent with an aqueous hydrophilic colloid solution, preferably an aqueous gelatin solution, passing the resulting mixture through a homogenizing apparatus, adding the dispersion obtained to said hydrophilic colloid composition that will form said emulsion layer or said hydrophilic colloid layer, and coating said hydrophilic colloid composition on a support.

The homogenizing apparatus can be any of the devices currently used for making dispersions e.g. an ultrasonic power generator, a mill such as a ball mill, a sand mill, and a colloid mill.

In the photographic light-sensitive direct-positive element according to the present invention the development nucleator(s) is(are) preferably present in the internal latent image-type silver halide emulsion layer. However, the development nucleator(s) can also be incorporated into a hydrophilic colloid layer that stands in water-permeable relationship with the internal latent image-type silver halide emulsion layer. Such a hydrophilic colloid layer can be any layer that makes part of the photographic light-sensitive direct-positive element according to the present invention. It can thus be i.a. a light-sensitive layer, an intermediate layer, a filter layer, a protective layer, an antihalation layer, an antistress layer, a subbing layer, or any other layer. In other words, any layer will do provided the development nucleator(s) is (are) not prevented from diffusing to the internal latent image-type silver halide emulsion layer.

The development nucleator(s) used according to the present invention preferably is(are) incorporated into the layer (s) in an amount that yields satisfactory maximum density values of e.g. at least 1.50 when the internal latent image-type emulsion is developed with a surface-developing solution. The amount may vary within wide limits and depends upon the nature of the silver halide emulsion, the chemical structure of the development nucleator(s), and on the developing conditions. Nevertheless, an amount of from about 0.1 to about 15 g per mol of silver halide in the internal latent image-type silver halide emulsion is generally effective, more preferably an amount of from about 0.6 to about 9 g per mol of silver halide. When the development nucleator(s) is(are) incorporated into a hydrophilic colloid layer that stands in water-permeable relationship with the internal latent image-type silver halide emulsion layer, it is adequate to incorporate the development nucleator(s) in the above amounts while taking into account the amount of silver contained in the associated internal latent image-type emulsion layer.

An internal latent image-type silver halide emulsion is an emulsion, the maximum density of which obtained when developing it with an "internal type" developing solution exceeds the maximum density that is achievable when developing it with a "surface-type" developing solution. The internal latent image-type emulsions that are suited for use in accordance with the present invention yield a maximum density that, when these emulsions have been coated on a transparent support and are exposed to light for a fixed time of from 1/100 to 1 s and then developed for 3 min at 20°C with the internal-type Developing Solution A as described hereinafter, is higher by at least 5 times than the maximum density obtained when the silver halide emulsion exposed as described above is developed for 4 min at 20°C with the surface-type Developing Solution B as described hereinafter.

Internal-type Developing Solution A

| | |
|-----------------------------------|------|
| hydroquinone | 15 g |
| monomethyl-p-aminophenol sulphate | 15 g |
| anhydrous sodium sulphite | 50 g |
| potassium bromide | 10 g |
| sodium hydroxide | 25 g |
| crystalline sodium thiosulphate | 20 g |
| Water to make | 1 l |

Surface-type Developing Solution B

| | |
|------------------------------|-------|
| p-hydroxyphenylglycine | 10 g |
| crystalline sodium carbonate | 100 g |
| water to make | 1 l |

Internal latent image-type silver halide emulsions that can be used in accordance with the present invention have been described in e.g. US-A 2,592,250, 3,206,313, 3,271,157, 3,447,927, 3,511,662, 3,737,313, 3,761,276, GB-A 1,027,146, and JA Patent Publication No. 34,213/77. However, the silver halide emulsions used in the present invention are not limited to the silver halide emulsions described in these documents.

The internal latent image-type silver halide emulsions that are suited for use in the method of the present invention are emulsions that have not been prefogged externally and that have not been ripened chemically, as described e.g. in US-A 3,761,276 and 3,850,637.

The photographic emulsions can be prepared according to different methods as described e.g. by P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

The photographic silver halide emulsions used in the method of the present invention can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method, the double-jet method, or the conversion method. The conversion method has proved to be particularly suitable. According to this method a more soluble silver halide is converted into a less soluble silver halide. For instance a silver chloride emulsion is converted in the presence of water-soluble bromide and possibly iodide, the amounts of which are selected with regard to the finally required composition, into a silver chlorobromiodide or a silver bromiodide emulsion. This conversion is preferably carried out very slowly in several consecutive steps i.e. by converting a part of the more soluble silver halide at a time. Another technique by which emulsions with an increased internal latent image sensitivity can be prepared has been described in GB-A 1,011,062.

The silver halide particles of the photographic emulsions used in the method of the present invention may have a regular crystalline form such as a cubic or octahedral form or they may have a transition form. They may also have an irregular crystalline form such as a spherical form or a tabular form, or may otherwise have a composite crystal form comprising a mixture of said regular and irregular crystalline forms.

The silver halide grains may have a multilayered grain structure. According to a simple embodiment the grains may comprise a core and a shell, which may have different halide compositions and/or may have undergone different modifications such as the addition of dopes. Besides having a differently composed core and shell the silver halide grains may also comprise different phases inbetween.

Two or more types of silver halide emulsions that have been prepared differently can be mixed for forming a photographic emulsion for use in the method of the present invention.

The average size of the silver halide grains may range from 0.1 to 2.0 μm , preferably from 0.3 to 0.8 μm .

The size distribution of the silver halide particles of the photographic emulsions used in the method of the present invention can be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size.

In addition to silver halide the emulsions may also comprise organic silver salts such as e.g. silver benzotriazolate and silver behenate.

The silver halide crystals can be doped with Rh^{3+} , Ir^{4+} , Cd^{2+} , Zn^{2+} , Pb^{2+} .

The photographic emulsions may comprise substances that will provide iodide and/or bromide ions (in excess of any such ions provided by the light-sensitive emulsion itself) during the development of the exposed emulsions. Such compounds and the method using them have been described in GB-A 1,195,837.

The emulsion can be left unwashed or it can be desalted in the usual ways e.g. by dialysis, by flocculation and re-dispersing, or by ultrafiltration.

The light-sensitive silver halide emulsions used in the method of the present invention have not been sensitized chemically. Chemical sensitization can be performed as described i.a. in the above-mentioned "Chimie et Physique Photographique" by P. Glafkides, in the above-mentioned "Photographic Emulsion Chemistry" by G.F. Duffin, in the above-mentioned "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968).

Density-increasing compounds may be incorporated into the photographic light-sensitive direct-positive silver halide element, preferably into an internal latent image-type silver halide emulsion layer thereof, although they may be incorporated also into a hydrophilic colloid layer that stands in water-permeable relationship with the internal latent image-type silver halide emulsion layer. Suitable density-increasing compounds are formic acid, oxalic acid, glyoxylic acid, or salts of these, and polyethylene glycols. When incorporated into the photographic element the density-increasing compound is present in amounts of from 4 to 600 mg/m^2 , preferably from 40 to 300 mg/m^2 . When the density-increasing compound is incorporated into a hydrophilic colloid layer it is present therein in the form of a salt e.g. sodium or potassium formiate or oxalate.

It is also possible to incorporate the density-increasing compound into a hydrophilic colloid layer that does not stand in direct water-permeable relationship with the internal latent image-type silver halide emulsion layer e.g. because an impermeable support constitutes a barrier between said emulsion layer and said hydrophilic colloid layer. In that case the density-increasing compound can during treatment of the exposed material with a developing solution or a prebath diffuse via said developing solution or said prebath towards the silver halide emulsion layer and have its effect there. Such layers are e.g. layers that have been coated on the rear side of the support and which may serve different purposes. Examples of such layers are e.g. a back layer, an anti-curling layer, and an antistatic layer.

The density-increasing compound may also be added to the developing solution in amounts of from 0.2 to 30 g/l, preferably from 1 to 10 g/l. The density-increasing compound may also be added to another processing solution e.g. a prebath. When the density-increasing compound is added to the developing solution or to a prebath it is present therein in acid form or in the form of a salt.

A preferred density-increasing compound is oxalic acid, because it has the highest density-increasing effect and

can thus be used in lower concentrations.

For processing the photographic element according to the present invention. Specifically, the processing method used according to the present invention basically includes a surface development step and a fixing step. A stopping step and a rinsing step can be included as well, if desired. The processing temperature is usually selected within the range of from 18°C to 50°C. However, temperatures lower than 18°C and temperatures higher than 50°C can be employed, if desired. The processing time may vary within broad ranges provided the mechanical strength of the materials to be processed is not adversely influenced and no decomposition takes place.

The hydroquinone-type developing solution used for developing an exposed photographic element in accordance with the present invention may comprise at least one alkanolamine, which may be chosen from primary, secondary, and tertiary alkanolamines. Suitable alkanolamines are i.a. N,N,N-triethanolamine, 2-amino-2-hydroxymethyl-propan-1,3-diol, N-methyl-diethanolamine, N-ethyl-diethanolamine, diisopropanolamine, N,N-diethanolamine, 3,3'-amino-dipropanol, 2-amino-2-methyl-propan-1,3-diol, N-propyl-diethanolamine, N-butyl-diethanolamine, N,N-dimethyl-ethanolamine, N,N-diethyl-ethanolamine, N,N-diethylN,N-diethyl-isopropanolamine, 1-amino-propan-2-ol, N-ethanolamine, N-methyl-ethanolamine, N-ethylN-ethyl-ethanolamine, N-ethyl-propanolamine, 3-amino-propanol, 3-dimethylamino-propanol, 4-amino-butanol, and 5-amino-pentan-1-ol.

The alkanolamine or a mixture of alkanolamines may be present in the developing solution in amounts of from 1 to 100 g/l, preferably from 10 to 60 g/l.

In the developing solution used in the method of the present invention, a hydroquinone alone or a combination of a hydroquinone with a secondary developing agent of the class of 1-phenyl-3-pyrazolidinone compounds and p-N-methyl-aminophenol can be used as developing agent. Specific examples of hydroquinones include hydroquinone, methylhydroquinone, t-butyl-hydroquinone, chloro-hydroquinone, and bromohydroquinone.

Particularly useful 1-phenyl-3-pyrazolidinone developing agents that can be used in combination with a hydroquinone are 1-phenyl-3-pyrazolidinone, 1-phenyl-4-methyl-3-pyrazolidinone, 1-phenyl-4-ethyl-5-methyl-3-pyrazolidinone, and 1-phenyl-4,4-dimethyl-3-pyrazolidinone.

N-methyl-p-aminophenol and 2,4-diaminophenol can be used in combination with a hydroquinone as a developing agent.

When the secondary developing agent used in the processing method of the present invention is one of the class of the 1-phenyl-3-pyrazolidinone compounds it is preferably present in an amount of 2 to 20 g per litre. When the secondary developing agent is p-N-methyl-aminophenol it is preferably present in an amount of 10 to 40 g per litre.

The developing solution comprises a preservative such as a sulphite e.g. sodium sulphite in an amount ranging from 45 g to 160 g per litre.

The developing solution comprises alkali-providing substances such as hydroxides of sodium and potassium, alkali metal salts of phosphoric acid and/or silicic acid e.g. trisodium phosphate, orthosilicates, metasilicates, hydrodisilicates of sodium or potassium, and sodium carbonate. The alkali-providing substances can be substituted in part or wholly by alkanolamines.

The developing solution may comprise a buffering agent such as a carbonate e.g. sodium carbonate, potassium carbonate, trisodium phosphate, and sodium metaborate.

For the purpose of decreasing the formation of fog (D_{min}) the developing solution may further contain an inorganic anti-fogging agent such as a bromide e.g. potassium bromide and/or an organic anti-fogging agent such as a benzimidazole e.g. 5-nitro-benzimidazole, a benzotriazole like benzotriazole itself and 5-methyl-benzotriazole.

The developing solution may contain other ingredients such as i.a. toning agents, development accelerators, oxidation preservatives, surface-active agents, defoaming agents, water-softeners, anti-sludge agents, hardeners including latent hardeners, and viscosity-adjusting agents.

Regeneration of the developing solution according to known methods is, of course, possible.

The development may be stopped - though this is often not necessary - with an aqueous solution having a low pH. An aqueous solution having a pH not higher than 3.5 comprising e.g. acetic acid and sulphuric acid, and containing a buffering agent is preferred.

Buffered stop bath compositions comprising a mixture of sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate are preferred.

Conventional fixing solutions may be used. Examples of useful fixing agents include organic sulphur compounds known as fixing agents, as well as a thiosulphate, a thiocyanate, etc. The fixing solution may contain a water-soluble aluminium salt as a hardening agent.

The stopping solution may be an aqueous solution having a low pH. An aqueous solution having a pH not higher than 3.5 comprising e.g. acetic acid and sulphuric acid, and containing a buffering agent is preferred.

The photographic light-sensitive direct-positive silver halide element of the present invention comprises an internal latent image-type silver halide emulsion layer, which preferably is a gelatin silver halide emulsion layer. However, instead of gelatin or in admixture with gelatin a variety of other hydrophilic colloids can be used as the binder for the silver halide.

Other suitable hydrophilic colloids that can be used as the binder for the silver halide are synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof, in particular copolymers thereof. Other synthetic substitutes for gelatin are latices such as a latex of poly(ethyl acrylate). Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose derivatives, saccharides, starch, and alginates. In general, the semi-synthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents or by grafting of polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates. The presence of such other binders often has a favourable photographic effect on the formation of the direct-positive image. For instance, the addition of polyvinyl pyrrolidone and of said latex of poly(ethyl acrylate) often increases the maximum density of the direct-positive image.

Suitable additives for improving the dimensional stability of the photographic element can also be incorporated together with the hydrophilic colloid. Suitable examples of this type of compounds include i.a. dispersions of a water-soluble 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, sulphonyl (meth)acrylates, and styrene sulphonic acids.

The binder should dispose of an acceptably high number of functional groups, which by reaction with an appropriate hardening agent can provide a sufficiently resistant layer. Such functional groups are especially the amino groups, but also carboxylic groups, hydroxy groups, and active methylene groups.

The gelatin can be lime-treated or acid-treated gelatin. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin can also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966).

Various compounds can be added to the photographic emulsion to prevent the reduction in sensitivity or fog formation during preparation, storage, or processing of the photographic element. A great many compounds are known for these purposes, and they include homopolar or salt-like compounds of mercury with aromatic or heterocyclic rings such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Other suitable stabilizers are azaindenes, preferably tetra- or penta-azaindenes, especially those substituted with hydroxy or amino groups e.g. 4-hydroxy-6-methyl- 1,3,3a,7-tetra-azaindene. Compounds of this kind have been described by Birr in Z. Wiss. Photogr. Photophys. Photochem. 47, 2-27 (1952). Other suitable stabilizers are i.a. heterocyclic mercapto compounds e.g. 1-phenyl-5-mercaptotetrazole, 3-methyl-benzothiazole, quaternary benzothiazole derivatives, benzotriazole. Specific examples of stabilizers have been mentioned by K. Mees in The Theory of the Photographic Process, 3rd ed. 1966 by reference to the papers that first reported such compounds, and in addition, have been described in i.a. US-A 1,758,576, 2,110,178, 2,131,038, 2,173,628, 2,304,962, 2,324,123, 2,394,198, 2,444,605, 2,444,606, 2,444,607, 2,444,608, 2,476,536, 2,566,245, 2,694,716, 2,697,040, 2,697,099, 2,708,162, 2,728,663, 2,728,664, 2,728,665, 2,824,001, 2,843,491, 2,886,437, 3,052,544, 3,137,577, 3,220,839, 3,226,231, 3,236,652, 3,251,691, 3,252,799, 3,287,135, 3,326,681, 3,420,668, and 3,622,339, GB-A 893,428, 403,789, 1,173,609, and 1,200,188.

The silver halide emulsions may comprise other ingredients e.g. development accelerators, wetting agents, and hardeners. The binder of the silver halide emulsion layer and/or of other hydrophilic colloid layers can, especially when the binder used is gelatin, 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 and the phosphorus compounds described in EP published Application N° 0408143.

Compounds that release iodine ions e.g. potassium iodide can be incorporated into the photographic silver halide emulsion. Additionally, the developing solution used in the method of the present invention may also contain iodine ions.

The photographic light-sensitive direct-positive element of the present invention may contain a water-soluble dye in a hydrophilic colloid layer as a filter dye or for other various purposes such as for the prevention of irradiation or anti-halation. Such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Of these, oxonol dyes, hemioxonol dyes, and merocyanine dyes are useful.

When a hydrophilic colloid layer of the photographic light-sensitive direct-positive element of the present invention contains a dye or an UV-absorbing agent, these compounds may be mordanted by means of a cationic polymer e.g. polymers described in GB-A 1,468,460 and 685,475, US-A 2,675,316, 2,839,401, 2,882,156, 3,048,487, 3,184,309,

3,445,231, and 3,986,875, DE-A 1,914,362.

The photographic light-sensitive direct-positive element of the present invention may 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, 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, and as compounds improving the photographic characteristics e.g. higher contrast and development acceleration.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-A 3,038,805, 4,038,075, and 4,292,400.

The photographic light-sensitive direct-positive element of the present invention may further comprise in the silver halide emulsion layer various other additives such as e.g. UV-absorbers, matting agents or spacing agents, lubricants, and plasticizers.

Suitable UV-absorbers are i.a. aryl-substituted benzotriazole compounds as described in US-A 3,533,794, 4-thiazolidone compounds as described in US-A 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

Suitable spacing agents are e.g. finely divided silica particles and polymer beads as described US-A 4,614,708.

In general, the average particle size of spacing agents is comprised between 0.2 and 10 μm . Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made i.a. 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-A 4,614,708.

A matting agent and/or a lubricant may be added to an emulsion layer and/or a protective layer of the photographic light-sensitive direct-positive element of the present invention. Suitable matting agents are e.g. water-dispersible vinyl polymers such as poly(methyl methacrylate) having an appropriate particle size of from 0.2 to 6 μm and inorganic compounds e.g. silver halide and strontium barium sulphate. The lubricant is used to improve the slidability of the photographic element. Suitable examples of lubricants are e.g. liquid paraffin, waxes such as esters of higher fatty acids, polyfluorinated hydrocarbons or derivatives thereof, silicones such as polyalkylpolysiloxanes, polyarylpolysiloxanes, polyalkylarylpolysiloxanes and alkyleneoxide addition derivatives thereof.

A variety of photographic supports can be employed for the photographic light-sensitive direct-positive element of the present invention. The silver halide emulsion can be coated onto one side or both sides of the support. For use in COM-film the support should be highly antistatic and should therefore be highly electroconductive. Suitable supports are e.g. cellulose acetate films such as cellulose triacetate film and cellulose diacetate film, cellulose nitrate films, polyethylene terephthalate films, and polystyrene films.

In the first step for making a direct-positive image according to the present invention the photographic light-sensitive direct-positive element is exposed image-wise. This exposure is a high-intensity exposure to light in the wavelength range of from about 440 to about 480 nm at an intensity of at least 0.1 mJ/m² and for short times such as those commonly used in COM-recorders viz. 10⁻⁵ to 10⁻⁸ s.

In a second step for making a direct-positive image the image-wise exposed silver halide element is soaked with, e.g. immersed in, a developing solution. For instance, the image-wise exposed silver halide material is conducted through a tray containing a developing solution.

The developing agents may also be incorporated partially or completely into the photographic light-sensitive silver halide element. They may be incorporated during the preparation stage of the material or at a later stage by means of a processing liquid with which the photographic element is wet prior to the development of the direct-positive image. In this way the surface developer can be reduced to a mere alkaline liquid that is substantially free from developing agents. Such an alkaline aqueous liquid, often called "activator" offers the advantage of having a longer activity i.e. of being less rapidly exhausted. The preliminary processing liquid may contain at least a part of the development nucleator and may also contain other ingredients that otherwise would have been incorporated into the developing solution.

Wetting of the photographic element by means of a processing liquid comprising development nucleator and/or density-increasing compound may be performed according to any conventional method such as by soaking or by moistening one single side of the material e.g. by means of a lick roller, by spreading a paste e.g. contained in a pod, or by spraying.

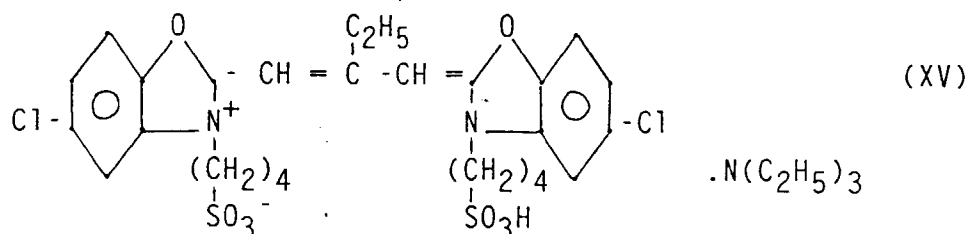
According to an alternative second step for making a direct-positive image the image-wise exposed silver halide element is given an overall flash with a high intensity light to fog said image-wise exposed silver halide element and is then developed in a surface developer.

The photographic light-sensitive silver halide element used in the method of the present invention is of particular use in COM recording but may serve other purposes according to which direct-positive images can be made i.a. in graphic arts recording processes, silver salt diffusion transfer reversal processes, microfilm recording processes, laser recording processes, cathode-ray recording processes, and phototype-setting processes.

The present invention will be explained in greater detail by reference to the following examples. The present invention should, however, not be construed as being limited thereto.

EXAMPLE 1 (comparative)

An internal latent image-type direct-positive gelatin silver halide emulsion was prepared by conversion of a silver chloride emulsion in the presence of water-soluble bromide and iodide to form grains having a core of silver chloride (4 mol%) and a shell of silverbromiodide (95/1 mol%). The average grain diameter was 0.4 μm. The silver halide emulsion was sensitized with a cyanine ortho-sensitizing dye according to the structural formula XV:



The amount of sensitizer was 300 mg per 200 g of silver nitrate.

A dispersion of the development nucleator corresponding to structural formula X was made by passing a mixture of 300 g of a 20% aqueous solution of gelatin and 60 g of the development nucleator for 120 min through a sand mill.

The dispersion was added to the silver halide emulsion in a concentration of 200 mg per 5 g of silver halide.

The resulting emulsion was coated on a cellulose triacetate support at a ratio of 6.5 g of silver halide per m² and dried.

A first sample of the light-sensitive element obtained was exposed for 10⁻⁵ s to white light emitted by a U460 flashlight sold by EG&G ING, 45 William street, Wellesley, Ma.02181, USA and then developed for 60 s with a hydroquinone-type developing solution (bath) at a temperature of 35°C, said developing solution comprising the following ingredients :

| | |
|-------------------------|--------|
| demineralized water | 700 ml |
| hydroquinone | 24 g |
| 3-dimethylaminopropanol | 40 ml |
| sodium sulphite | 110 g |
| sodium hydroxide | 18 g |
| sodium carbonate | 40 g |
| potassium bromide | 3 g |

demineralized water to make
(pH-value : 11.5)

1 1

- 5 The sensitometric curve obtained with the first Sample is shown in the accompanying Figure 1.
A second sample of the same light-sensitive element was exposed for 10^{-2} s to white light emitted by an above-mentioned U460 flashlight commercially available from E.G. & G. through a L453 filter and then developed in the same way as the first sample.
- 10 The sensitometric curve obtained with the second Sample is shown in the accompanying Figure 2.
The Dmax and Dmin values, gradation, and speed of Samples 1 and 2 were measured and are listed in Table 3. The values given for speed are expressed in log E. The higher the speed value, the lower the speed.

TABLE 3

| Sample | Dmin | Dmax | Speed | Gradation | Exposure |
|--------|------|------|-------|-----------|-------------|
| 1 | 11 | 194 | 180 | 1.15 | 10^{-5} s |
| 2 | 11 | 214 | 102 | 2.15 | 10^{-2} s |

- 20 In order to obtain acceptable Dmax and speed values at shorter development times e.g. 45 s, it was necessary to change the development nucleator. For instance, with 1-formyl-2-phenyl-hydrazine as development nucleator a shorter development time was possible than with the development nucleator corresponding to structural formula X. In Table 4 the results obtained with Sample 3 are shown. Sample 3 was identical to Sample 1 except that the development nucleator 1-formyl-2-phenyl-hydrazine was used instead of the development nucleator corresponding to structural formula X. Sample 3, which was also sensitized with dye XV, was exposed for 10^{-5} s to white light emitted by a U460 flashlight and the development time was 45 s at 35°C.

TABLE 4

| Sample | Dmin | Dmax | Speed | Gradation |
|--------|------|------|-------|-----------|
| 3 | 12 | 145 | 180 | 1.66 |

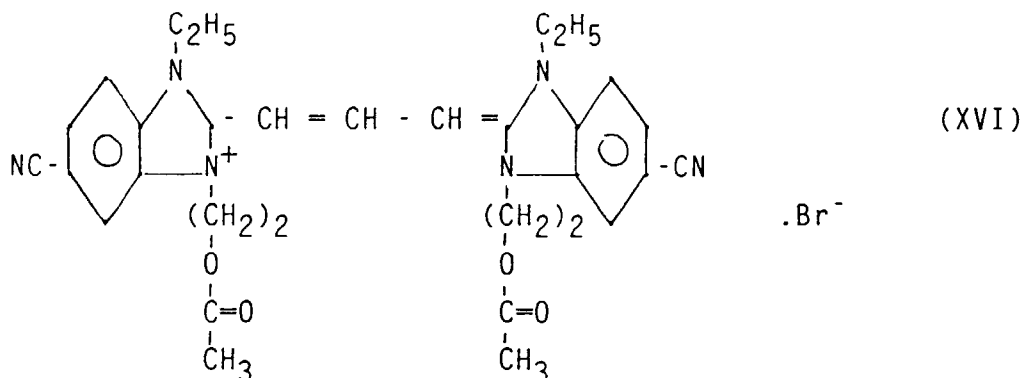
- 30 The gradation values obtained with these ortho-sensitized emulsions were too low for COM applications, which require a value of at least 1.70.
- 35 EXAMPLE 2 (comparative)

- An internal latent image-type direct-positive gelatin silver halide emulsion was prepared by conversion of a silver chloride emulsion in the presence of water-soluble bromide and iodide to form grains having a core of silver chloride (4 mol%) and a shell of silverbromiodide (95/1 mol%). The average grain diameter was 0.4 μm . The silver halide emulsion was divided into 3 equal portions called Batch 2A, Batch 2B, and Batch 2C hereinafter.
- 40 Batch 2A was left unsensitized. Batch 2B was sensitized with the cyanine ortho-sensitizing dye corresponding to the above structural formula XV. Batch 2C was sensitized with the cyanine ortho-sensitizing dye corresponding to the following structural formula XVI :

45

50

55



20 The amount of sensitizer used in Batch 2B and in Batch 2C was 300 mg per weight of silver halide equivalent to 200 g of silver nitrate.

A dispersion of the development nucleator 1-formyl-2-phenylhydrazine was added to each of Batches 1 to 3 in a concentration of 200 mg per 5 g of silver halide.

25 Each of the resulting Batches 2A to 2C was coated on a cellulose triacetate support at a ratio of 6.5 g of silver halide per m² and dried.

Each of the Batches 2A to 2C was exposed for 10-5 s to white light emitted by an above-mentioned U460 flashlight and then developed for 45 s with the hydroquinone-type developing solution described in Example 1 at a temperature of 35°C.

25 The D_{max} and D_{min} values, gradation, and speed of Batches 2A to 2C were measured and are listed in Table 5. The values given for speed are expressed in log E. The higher the speed value, the lower the speed.

TABLE 5

30

| Batch | D _{min} | D _{max} | Speed | Gradation |
|-------|------------------|------------------|-------|-----------|
| 2A | 0.08 | 1.41 | 194 | 1.22 |
| 2B | 0.12 | 1.45 | 180 | 1.66 |
| 2C | 0.09 | 1.38 | 213 | 1.26 |

35 The results listed in Table 5 show that the maximum density and the gradation are slightly improved according to this prior art method, but remain substantially unsatisfactory for COM applications.

EXAMPLE 3

40 Three batches of silver halide emulsions were prepared, coated, exposed, and developed as described in Example 2.

Batch 3A was left unsensitized and consequently was identical to Batch 2A of Example 2.

45 Batches 3B and 3C were sensitized with different concentrations of the merocyanine dye M01 of Table 1. The amounts of sensitizer used are indicated in mg in Table 6 and are per weight of silver halide equivalent to 200 g of silver nitrate.

The D_{max} and D_{min} values, gradation, and speed of Batches 3A to 3C were measured and are listed in Table 6.

TABLE 6

50

| Batch | mg of M01 | D _{min} | D _{max} | Speed | Gradation |
|-------|-----------|------------------|------------------|-------|-----------|
| 3A | none | 0.08 | 1.41 | 194 | 1.22 |
| 3B | 168 | 0.14 | 1.98 | 190 | 1.66 |
| 3C | 420 | 0.16 | 1.66 | 180 | 1.87 |

55 The results listed in Table 6 show that the maximum density and gradation values obtained with merocyanine dye are better than those obtained with cyanine dye.

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EXAMPLE 4

A core-shell silver bromide emulsion was prepared by double jet precipitation. The core consisted of 0.24 μm octahedral silver bromide grain sensitized chemically for 4.5 h at 50°C with 4.1 mg of sodium thiosulphate, 7.6 mg of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, and 5.8 mg of the sodium salt of p-toluenethiosulphonic acid. After precipitation of a shell on the core octahedral grains sizing 0.3 μm were obtained. The resulting core-shell emulsion was sensitized chemically for 4 h at 46°C with 2.2 mg of sodium thiosulphate, 1 mg of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, and 2 mg ammonium thiocyanate.

The silver halide emulsion obtained was divided into 4 portions called Batch 4A, Batch 4B, Batch 4C, and Batch 4D.

These batches were sensitized with different concentrations of the merocyanine dye M01 of Table 1. The amounts of sensitizer used are indicated in mg per mol of silver nitrate in Table 7 hereinafter. Each batch contained 6.64 mmol of the nucleating agent 1-formyl-2-phenylhydrazide per mol of silver nitrate.

Each of the resulting Batches A to D was coated on a polyester film support at a silver coverage of 3.6 g expressed as silver nitrate per m^2 . A protective layer containing 1.04 g of gelatin per m^2 was applied and formaldehyde was used as hardener.

Each of the resulting Batches A to D was exposed for 10⁻⁵ s to white light emitted by an above-mentioned U460 flashlight and then developed for 45 s with the hydroquinone-type developing solution at a temperature of 35°C, said developing solution comprising the following ingredients :

| | |
|---|--------|
| demineralized water | 500 ml |
| p-N-methyl-aminophenol | 15 g |
| sodium hydroxide | 17.5 g |
| sodium sulphite | 110 g |
| 41% aqueous solution of ethylenediaminetetraacetic acid | 2 ml |
| sodium carbonate | 40 g |
| sodium bromide | 10 g |
| hydroquinone | 24 g |
| oxalic acid | 2 g |
| 2-methylamino-ethanol | 40 ml |
| demineralized water to make (pH-value : 11.7) | 1 l |

The Dmax and Dmin values and the speed of Batches A to D were measured and are listed in Table 7.

TABLE 7

| Batch | mg of M01 | Dmin | Dmax | Speed |
|-------|-----------|------|------|-------|
| 4A* | 224 | 0.2 | 2.7 | 156 |
| 4B | 449 | 0.04 | 0.9 | 118 |
| 4C | 673 | 0.08 | 1.7 | 130 |
| 4D | 898 | 0.08 | 2.8 | 147 |

* means that in that particular case a development time of 90 s was required to obtain a maximum density higher than 2.

The results listed in table 7 show that the maximum density is better with high concentrations of the merocyanine dye. The rereversal obtained in Batches B to D is also lower than for Batch A. Rereversal is the negative image that is obtained when the exposure is extended (over-exposure).

EXAMPLE 5

Six batches of silver halide emulsions were prepared, coated, exposed, and developed as described in Example 2.

Batch 5A was left unsensitized and consequently was identical to Batch 2A of Example 2.

Batches 5B, 5C, 5D, 5E, and 5F were sensitized with a combination of the merocyanine dye M01 and the rhodacyanine dye R01 in different concentrations. The amounts of sensitizer used are indicated in mg in Table 8 and are per weight of silver halide equivalent to 200 g of silver nitrate.

The Dmax and Dmin values, gradation, and speed of Batches 5A to 5F were measured and are listed in Table 8.

TABLE 8

| Batch | mg M01 | mg R01 | Dmin | Dmax | Speed | Gradation |
|-------|--------|--------|------|------|-------|-----------|
| 5A | none | none | 0.08 | 1.41 | 194 | 1.22 |
| 5B | 168 | 121 | 0.14 | 2.85 | 215 | 2.63 |
| 5C | 294 | 121 | 0.14 | 2.70 | 210 | 2.50 |
| 5D | 420 | 121 | 0.15 | 2.75 | 208 | 2.94 |
| 5E | 630 | 121 | 0.24 | 2.88 | 207 | 3.12 |
| 5F | 168 | 283 | 0.15 | 2.70 | 230 | 3.40 |

The results listed in Table 8 show that the maximum density and gradation values obtained with a combination of a merocyanine dye and a rhodacyanine dye are considerably better than those obtained with cyanine dyes.

Claims

1. Method for forming direct-positive COM images obtained by the steps of :

- image-wise exposing a photographic light-sensitive element comprising a support and at least one photographic emulsion layer comprising unfogged internal latent image-type silver halide grains to light in the wavelength range of from about 440 to about 480 nm for a short duration of 10^{-5} to 10^{-8} s at a high intensity of at least 0.1 mJ/m^2 , and then
- either (a) developing the image-wise exposed element in a surface developer in the presence of at least one development nucleator or (b) overall light-flashing to fog said image-wise exposed element prior to the development thereof in a surface developer,

wherein said method is characterized in that said photographic emulsion layer comprises at least one merocyanine dye, having a heterocyclic nucleus comprising a trivalent nitrogen atom, except for a trivalent nitrogen atom having substituted thereon a member having the formula $-(\text{CH}_2)_n\text{-R}$ wherein R represents a 1-hydrazonoalkyl radical, the said heterocyclic nucleus being linked via a carbon chain having an even number of carbon atoms according to the formula $=(\text{CH-CH})_n=$ wherein n is 0, 1, 2, 3... to a nucleus containing a ketomethylene structure.

2. A method according to claim 1, wherein said photographic emulsion layer also comprises at least one rhodacyanine dye.

3. A method according to claim 1 or 2, wherein said at least one development nucleator is contained in said at least one photographic emulsion layer or in a hydrophilic colloid layer in water-permeable relationship with said photographic emulsion layer or in said surface developer.

4. A method according to any of claims 1 to 3, wherein said at least one development nucleator is 1-formyl-2-phenyl hydrazine.

5. Photographic light-sensitive direct-positive element for forming direct-positive images, said element comprising a highly antistatic and highly electroconductive support and at least one light-sensitive emulsion layer comprising unfogged internal latent image-type silver halide grains and a development nucleator, wherein said photographic emulsion layer comprises at least one merocyanine dye, having a heterocyclic nucleus comprising a trivalent nitrogen atom, except for a trivalent nitrogen atom having substituted thereon a member having the formula $-(\text{CH}_2)_n\text{-R}$ wherein R represents a 1-hydrazonoalkyl radical, the said heterocyclic nucleus being linked via a carbon chain having an even number of carbon atoms according to the formula $=(\text{CH-CH})_n=$ wherein n is 0, 1, 2, 3... to a nucleus containing a ketomethylene structure.

6. A photographic direct-positive element according to claim 5, wherein said photographic emulsion layer also comprises at least one rhodacyanine dye

7. A photographic direct-positive element according to claim 5 or 6, wherein said development nucleator has been added in dispersed form to the hydrophilic colloid composition that will form said emulsion layer or a hydrophilic

colloid layer in water-permeable relationship therewith.

Patentansprüche

- 5
1. Verfahren zur Herstellung von direktpositiven COM-Bildern, die in den folgenden Stufen erhalten werden :
- die bildmäßige Belichtung eines photographischen lichtempfindlichen Elements, das einen Träger und wenigstens eine photographische, unverschleierte Innenlatentbild-Silberhalogenidkörner enthaltende Emulsionsschicht enthält, mit Licht im Wellenbereich von etwa 440 bis etwa 480 nm für einen kurzen Zeitraum von 10^{-5} bis 10^{-8} s bei einer hohen Intensität von wenigstens $0,1 \text{ mJ/m}^2$, und danach
 - entweder (a) die Entwicklung des bildmäßig belichteten Elements in einem Oberflächenentwickler in der Gegenwart von wenigstens einem Entwicklungskeimbildner oder (b) die verschleiernde Gesamtanbelichtung des bildmäßig belichteten Elements und die darauffolgende Entwicklung dieses Elements in einem Oberflächenentwickler, wobei dieses Verfahren sich dadurch kennzeichnet, daß die photographische Emulsionsschicht wenigstens einen Merocyaninfarbstoff enthält, der einen heterocyclischen Ring mit einem dreiwertigen Stickstoffatom, ausgenommen einem dreiwertigen Stickstoffatom mit einem darauf substituierten Glied entsprechend der Formel $-(\text{CH}_2)_n-\text{R}$, in der R ein I-Hydrazonalkylradikal bedeutet, enthält, wobei der heterocyclische Ring mittels einer eine gerade Anzahl von Kohlenstoffatomen enthaltenden Kohlenstoffkette entsprechend der Formel $=(\text{CH}-\text{CH})_n=$, in der n 0, 1, 2, 3... ist, mit einem Ring mit einer Ketomethylenstruktur verbunden ist.
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2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die photographische Emulsion ebenfalls wenigstens einen Rhodacyaninfarbstoff enthält.
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3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß in der (den) photographischen Emulsionsschicht (en), in einer hydrophilen in wasserdurchlässigem Verhältnis zur photographischen Emulsionsschicht stehenden Kolloidschicht oder im Oberflächenentwickler wenigstens ein Entwicklungskeimbildner enthalten ist.
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4. Verfahren nach irgendeinem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß diese(r) Entwicklungskeimbildner 1-Formyl-2-phenylhydrazin ist (sind).
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5. Photographisches lichtempfindliches Direktpositivelement zur Herstellung von Direktpositivbildern, wobei dieses Element einen sehr antistatischen und sehr elektrisch leitfähigen Träger und wenigstens eine lichtempfindliche Emulsionsschicht mit unverschleierten Innenlatentbild-Silberhalogenidkörnern und einen _ Entwicklungskeimbildner enthält, dadurch gekennzeichnet, daß die photographische Emulsionsschicht wenigstens einen Merocyaninfarbstoff mit einem heterocyclischen Ring mit einem dreiwertigen Stickstoffatom, ausgenommen einem dreiwertigen Stickstoffatom mit einem darauf substituierten Glied entsprechend der Formel $-(\text{CH}_2)_n-\text{R}$, in der R ein 1-Hydrazonalkylradikal bedeutet, enthält, wobei der heterocyclische Ring mittels einer eine gerade Anzahl von Kohlenstoffatomen enthaltenden Kohlenstoffkette entsprechend der Formel $=(\text{CH}-\text{CH})_n=$, in der n 0, 1, 2, 3... ist, mit einem Ring mit einer Ketomethylenstruktur verbunden ist.
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6. Photographisches lichtempfindliches Direktpositivelement nach Anspruch 5, dadurch gekennzeichnet, daß die photographische Emulsionsschicht ebenfalls wenigstens einen Rhodacyaninfarbstoff enthält.
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7. Photographisches lichtempfindliches Direktpositivelement nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß der Entwicklungskeimbildner in dispergierter Form der hydrophilen kolloidalen Zusammensetzung, die die Emulsionsschicht oder eine hydrophile, kolloidale, in wasserdurchlässigem Verhältnis dazu stehende Schicht bilden wird, zugesetzt ist.
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Revendications

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1. Procédé pour la formation d'images autopositives de sortie d'ordinateur sur microfilm (COM) obtenues par les étapes consistant à :
- exposer sous forme d'image un élément photographique sensible à la lumière comprenant un support et au moins une couche d'émulsion photographique renfermant des grains d'halogénure d'argent non voilés du type à image latente interne, à la lumière dans la gamme d'ondes d'environ 440 à environ 480 nm pendant une

courte durée de 10^{-5} à 10^{-8} s à une intensité élevée d'au moins $0,1 \text{ mJ/m}^2$, et ensuite

- soit (a) développer l'élément exposé suivant une image dans un révélateur superficiel en présence d'au moins un agent de nucléation pour le développement, soit (b) le flasher intégralement à la lumière pour voiler cet élément exposé suivant une image avant son développement dans un révélateur superficiel,

5 ce procédé étant caractérisé en ce que ladite couche d'émulsion photographique renferme au moins un colorant mérocyanine, présentant un noyau hétérocyclique comprenant un atome d'azote trivalent, à l'exception d'un atome d'azote trivalent sur lequel à été substitué un élément de la formule $-(\text{CH}_2)_n\text{-R}$, dans laquelle R représente un radical 1-hydrazonoalkyle, ledit noyau hétérocyclique étant lié à un noyau contenant une structure cétométhylénique, par une chaîne carbonée présentant un nombre pair d'atomes de carbone conformément à la formule $=(\text{CH}-\text{CH})_n$, dans laquelle n est égal à 0, 1, 2

10 2. Procédé suivant la revendication 1, caractérisé en ce que ladite couche d'émulsion photographique renferme également au moins un colorant rhodacyanine.

15 3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que ledit agent de nucléation pour le développement est contenu dans ladite couche d'émulsion photographique ou dans une couche colloïdale hydrophile en relation de perméabilité à l'eau avec ladite couche d'émulsion photographique ou dans ledit révélateur superficiel.

20 4. Procédé suivant l'une quelconque des revendications 1 à 3, caractérisé en ce que ledit agent de nucléation pour le développement est la 1-formyl-2-phénylhydrazine.

25 5. Élément photographique autositif sensible à la lumière pour la formation d'images autositives, cet élément comprenant un support hautement antistatique et hautement électroconducteur et au moins une couche d'émulsion sensible à la lumière renfermant des grains d'halogénure d'argent non voilés du type à image latente interne et un agent de nucléation pour le développement, caractérisé en ce que ladite couche d'émulsion photographique renferme au moins un colorant mérocyanine, présentant un noyau hétérocyclique comprenant un atome d'azote trivalent, à l'exception d'un atome d'azote trivalent sur lequel à été substitué un élément de la formule $-(\text{CH}_2)_n\text{-R}$, dans laquelle R représente un radical 1-hydrazonoalkyle, ledit noyau hétérocyclique étant lié à un noyau contenant une structure cétométhylénique, par une chaîne carbonée présentant un nombre pair d'atomes de carbone conformément à la formule $=(\text{CH}-\text{CH})_n$, dans laquelle n est égal à 0, 1, 2

30 6. Élément photographique autositif suivant la revendication 5, caractérisé en ce que ladite couche d'émulsion photographique renferme également au moins un colorant rhodacyanine.

35 7. Élément photographique autositif suivant la revendication 5 ou 6, caractérisé en ce que ledit agent de nucléation pour le développement a été ajouté sous forme dispersée à la composition colloïdale hydrophile qui formera ladite couche d'émulsion ou une couche colloïdale hydrophile en relation de perméabilité à l'eau avec celle-ci.

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