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(54) **Method for the formation of images.**

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**EP-A- 0 238 271**  
**EP-A- 0 308 212**  
**EP-A- 0 316 864**  
**GB-A- 2 002 530**

**PATENT ABSTRACTS OF JAPAN, vol. 8, no. 275 (P-321)[1712], 15th December 1984; & JP-A-59 142 543**

**PATENT ABSTRACTS OF JAPAN, vol. 9, no. 273 (P-401)[1996], 30th October 1985; & JP-A-60 119 547**

**AGFA-GEVAERT N.V., advertising material "Rapiline 95", no. 21.5748, July 1985, 4 pages, Mortsels, BE**

**AGFA-GEVAERT N.V., advertising material "Scopix 12", no. MR/681/3215, June 1981, 6 pages, Mortsels, BE**

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**EP 0 331 319 B1**

## Description

The present invention relates to a method for the formation of images which is capable of rapid processing and does not cause problems such as roller transfer marks.

In the field of silver halide light-sensitive photographic materials, there has, in recent years, been a growing demand for even more rapid processing: i.e., increasing the processing quantity within the same period of processing time.

The above tendency is also seen in the field of radiographic light-sensitive materials such as medical X-ray films. With a rapid increase in the number of diagnoses due to the strict enforcement of regular medical examinations, the number of examination items is increased in order to even more precisely carry out diagnoses, thus increasing the radiographing quantity of X-ray films.

It is advantageous also for the automatic processor to speed up the processing of X-ray films. For example, even if the processor is a compact-type automatic processor, if its processing speed is increased, its processing capacity per unit time then increases, while if its processing capacity need not be increased, then the processor can be of an even smaller size, thus contributing to space-saving.

However, while rapid processing has the above-mentioned significant advantages there are problems yet to be solved.

Rapid processing requires an increased film-transport speed but, if an automatic processor, e.g., a roller-transport-type automatic processor, is used, it tends to cause roller transfer marks on the surface of processed film. In the processing of a light-sensitive film, gelatin fragments from the section of the leading end or trailing end of the film being processed become attached onto transport rollers, and the gelatin fragments are then transferred from the rollers onto the surface of the subsequent film, whereby the fragments appear in the form of linear stain marks in the roller transport direction.

EP-A-238,271 discloses a silver halide photographic material comprising at least one hydrophilic colloidal layer on a support, wherein the photographic material has a water content of from 10 to 20 g/m<sup>2</sup> upon completion of the washing step during processing with a roller transport type automatic processor.

EP-A-308,212 discloses a method for processing a silver halide light-sensitive photographic material by a super-rapid process and also discloses an automatic processing machine for use in such a process. The image-wise exposed silver halide light-sensitive photographic material comprises a support and a photographic component layer provided on at least one side of the support. The material is processed under conditions satisfying the equation

$$50 \leq I^{0.75} \times T \leq 124$$

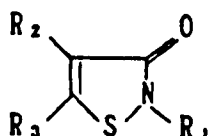
wherein I and T have the meanings given below.

EP-A-316,864 discloses a method of processing a silver halide photographic light-sensitive material in a roller-transporting type processing equipment, comprising the steps of developing, fixing, washing and drying. The photographic material is comprised of a support having thereon at least one hydrophilic layer including a silver halide emulsion layer containing at least one compound selected from silver chloride, silver bromochloride and silver bromochloriodide each containing silver chloride of not less than 60 mol% and water content of the photographic material just after the washing step is 5 to 16g/m<sup>2</sup>.

EP-A-308,212 and EP-A-316,864 are part of the state of the art by virtue of Article 54(3) EPC.

The present invention provides a method for the formation of images which, as a result of solving the above problems, is capable of forming images by rapid processing and which reduces roller transfer marks.

The present invention provides a method of forming a photographic image by processing an imagewise exposed silver halide light-sensitive photographic material in an automatic processor, wherein said light-sensitive photographic material contains at least one compound of formula [I] or formula [II] below;



[I]

wherein R<sub>1</sub> is a hydrogen atom, a straight-chain or branched-chain alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkylamido group, an arylamido

group, an alkylthioamido group, an arylthioamido group, an alkylsulfoamido or an arylsulfoamido group;  $R_2$  and  $R_3$  are independently a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, a cyano group, an alkylthio group, an arylthio group, an alkylsulfoxido group, an alkylsulfonyl group, an alkylsulfinyl group or a heterocyclic group; such that the above-mentioned alkyl, cycloalkyl, alkenyl, heterocyclic, aralkyl and aryl groups may be substituted, and that  $R_2$  and  $R_3$  may together form a divalent group to complete a ring, but not including 5-chloroisothiazoline-3-one;



wherein  $R_4$  is a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or a hydroxymethyl group and  $R_5$  is a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms, such that the above-mentioned groups  $R_4$  and  $R_5$  may be substituted, but not including 1,1-dimethylol-1-bromo-1-nitromethane, under a condition satisfying the equation given below;

$$50 \leq l^{0.75} \times T \leq 124,$$

wherein  $l$  is the length (in metres) between the axis of the first roller at the film inlet in the insertion section and the axis of the final roller at the film outlet in the drying section of a roller-transport-type automatic processor and is more than 0.7m and less than 3.1m,  $T$  is the time in seconds necessary for said silver halide light-sensitive photographic material to pass through said length,  $l$ .

It is assumed that the above compounds selectively function to prevent the section of film from being subjected to deterioration such as erosion by microbes and the like.

Figure 1 and Figure 2 show the constructions of the automatic processors that are used in Examples of this invention.

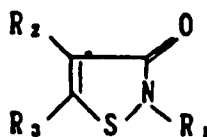
Figure 3 shows the construction of the cutting machine that is used in the examples.

The indication numbers that are used in Figures 1 and 2 are as follows: 1...the first roller at the inlet for inserting a light-sensitive material, 2...the final roller at the outlet in the drying section, 3a...developer bath, 3b...fixer bath, 3c...wash water bath, 4...a light-sensitive material, 5...squeegee section, 6...drying section, and 7...drying air outlet port.

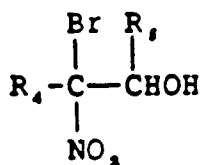
The present invention will be illustrated in detail.

Firstly, those compounds having Formulas [I] and [II] to be used in this invention will be explained. The formulas are as follows:

#### Formula [I]



wherein  $R_1$  is a hydrogen atom or a straight-chain or branched-chain alkyl, cycloalkyl, alkenyl, aralkyl, aryl, heterocyclic, alkylamido, arylamido, alkylthioamido, arylthioamido, alkylsulfoamido or arylsulfoamido group; and  $R_2$  and  $R_3$  each independently represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, a cyano group, an alkylthio group, an arylthio group, an alkylsulfoxido group, an alkylsulfonyl group, an alkylsulfinyl group or a heterocyclic group, such that the above alkyl, cycloalkyl, alkenyl, heterocyclic, aralkyl and aryl groups each may be substituted, and that  $R_2$  and  $R_3$  may together form a divalent group to complete a ring, which may be aromatic; with the proviso that the compound of Formula I is not 5-chloroisothiazoline-3-one. Compounds of Formula I can be synthesised by the method disclosed in EP-1,555,415;

**Formula [II]**

wherein R<sub>4</sub> represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or a hydroxymethyl group; and R<sub>5</sub> represents a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms; such that the above-mentioned groups for R<sub>4</sub> and R<sub>5</sub> may independently be substituted and provided that the compound of formula II is not 1,1-dimethylol-1-bromo-1-nitromethane. Compounds of formula II may be synthesised by referring to:

Henry, Recueil des travaux chimiques des Ray-Bas, 16 251.

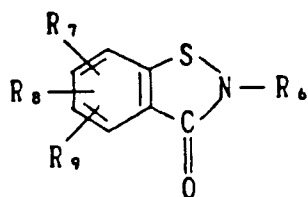
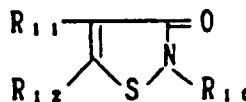
Maas, Chemisches Zentralblatt, 1899 I 173.

E. Schmidt, Berichte der Deutschen Chemischen Gesellschaft, 52 397.

E. Schmidt, *ibid* 55 317

Henry, Chemisches Zentralblatt, 1897 II 338.

As the compound of formula [I], those compounds having the following formulas [III] and [IV] are more preferably used.

**Formula [III]****Formula [IV]**

wherein R<sub>6</sub> represents a hydrogen atom, an alkyl group or an alkoxy group; R<sub>7</sub>, R<sub>8</sub>, and R<sub>9</sub>, each represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a cyano group or a nitro group; R<sub>10</sub> represents a hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a -CONHR<sub>13</sub> group (wherein R<sub>13</sub> is an alkyl, aryl, alkylthio, arylthio, alkylsulfonyl or arylsulfonyl group) or a heterocyclic group; R<sub>11</sub> and R<sub>12</sub> each represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, a cyano group, an alkylthio group, an arylthio group, an alkylsulfoxido group, an alkylsulfinyl group, an alkylsulfonyl group or a heterocyclic group; provided that the alkyl group and the alkyl portion of the alkoxy group represented by the R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> or R<sub>9</sub> are preferably straight-chain or branched-chain alkyl groups having from 1 to 6 carbon atoms, and that the above-mentioned groups for R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub> and R<sub>12</sub> may independently have a substituent.

Typical examples of the compounds having Formula [III] are given below, but the compounds are not limited to the examples.

Exemplified Compounds:

Benzoisothiazoline-3-one, 2-methyl-benzoisothiazoline-3-one, 2-ethyl-benzoisothiazoline-3-one, 2-(n-propyl)-benzoisothiazoline-3-one, 2-(n-butyl)-benzoisothiazoline-3-one, 2-(sec-butyl)-benzoisothiazoline-3-one, 2-(t-butyl)-benzoisothiazoline-3-one, 2-methoxy-benzoisothiazoline-3-one, 2-ethoxy-benzoisothiazoline-3-one, 2-(n-propyloxy)-benzoisothiazoline-3-one, 2-(butyloxy)-benzoisothiazoline-3-one, 5-chloro-benzoisothiazoline-3-one, 5-methyl-benzoisothiazoline-3-one, 6-ethoxy-benzoisothiazoline-3-one, 6-cyano-benzoisothiazoline-3-one, and 5-nitro-benzoisothiazoline-3-one.

In the R<sub>10</sub> of Formula [IV], the number of carbon atoms of each of the alkyl group and alkenyl group is generally 1 to 36, and more preferably 1 to 18. The number of carbon atoms of the cycloalkyl group is generally 3 to 12, and more preferably 3 to 6. Each of the alkyl, cycloalkyl, alkenyl, aralkyl, aryl and heterocyclic groups represented by the R<sub>10</sub> may have a substituent which may be selected from among

halogen atoms and groups including nitro, cyano, thiocyno, aryl, alkoxy, aryloxy, carboxy, sulfoxy, alkylcarbonyl, arylcarbonyl, alkoxycarbonyl, aryloxycarbonyl, sulfo, acyloxy, sulfamoyl, carbamoyl, acylamino, diacylamino, ureido, thioureido, urethane, thiourethane, sulfonamido, heterocyclic, arylsulfonyloxy, alkylsulfonyloxy, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylsulfinyl, arylsulfinyl, alkylamino, dialkylamino, anilino, N-alkylanilino, N-arylanilino, N-acylamino, hydroxy and mercapto, for example.

In Formula [IV], the number of carbon atoms of the alkyl group represented by the  $R_{11}$  or  $R_{12}$  is generally 1 to 18, and more preferably 1 to 9, and that of the cycloalkyl group represented by the same is generally 3 to 18, and more preferably 3 to 6. Each of these groups represented by the  $R_{11}$  or  $R_{12}$  may have a substituent, which is, for example, a halogen atom or a nitro, sulfo, aryl or hydroxy group.

The following are typical examples of the compounds having Formula [IV], but the compounds are not limited to the examples.

#### Exemplified Compounds:

2-(N-methylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-methylcarbamoyl)-3-isothiazolinone, 2-(N-methylthiocarbamoyl)-3-isothiazolinone, 4-bromo-5-methyl-2-(N-methylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylthio-2-(N-methylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylsulfinyl-2-(N-methylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylsulfonyl-2-(N-methylcarbamoyl)-3-isothiazolinone, 2-(N-n-butylcarbamoyl)-3-isothiazolinone, 2-(N-t-octylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-phenylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylthio-2-(N-phenylcarbamoyl)-3-isothiazolinone, 4-bromo-5-methyl-2-(N-3-chlorophenylcarbamoyl)-3-isothiazolinone, 5-bromomethyl-2-(N-3-chlorophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-3-chlorophenylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylthio-2-(N-3-chlorophenylcarbamoyl)-3-isothiazolinone, 2-(N-3-chlorophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-2-chlorophenylcarbamoyl)-3-isothiazolinone, 5-bromomethyl-2-(N-2-chlorophenylcarbamoyl)-3-isothiazolinone, 4-bromo-5-methyl-2-(N-3,4-dichlorophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-3,4-dichlorophenylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylthio-2-(N-3,4-dichlorophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-4-tosylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylthio-2-(N-4-tosylcarbamoyl)-3-isothiazolinone, 4-bromo-5-methyl-2-(N-4-tosylcarbamoyl)-3-isothiazolinone, 2-(N-n-propylcarbamoyl)-3-isothiazolinone, 2-(N-ethylcarbamoyl)-3-isothiazolinone, 2-(N-i-propylcarbamoyl)-3-isothiazolinone, 4-bromo-2-(N-methylcarbamoyl)-3-isothiazolinone, 2-(N-4-methoxyphenylcarbamoyl)-3-isothiazolinone, 2-(N-2-methoxyphenylcarbamoyl)-3-isothiazolinone, 2-(N-3-nitrophenylcarbamoyl)-3-isothiazolinone, 2-(N-3,4-dichlorophenylcarbamoyl)-3-isothiazolinone, 2-(N-n-dodecylcarbamoyl)-3-isothiazolinone, 2-(N-2,5-dichlorophenylcarbamoyl)-3-isothiazolinone, 2-(N-carboethoxymethylcarbamoyl)-3-isothiazolinone, 2-(N-4-nitrophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-ethylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-ethylthiocarbamoyl)-3-isothiazolinone, 5-chloro-2-(N-ethylcarbamoyl)-3-isothiazolinone, 2-n-propyl-3-isothiazolinone, 2-t-butyl-3-isothiazolinone, 2-n-butyl-3-isothiazolinone, 2-cyclohexyl-3-isothiazolinone, 2-n-octyl-3-isothiazolinone, 2-t-octyl-3-isothiazolinone, 2-benzyloxy-3-isothiazolinone, 3-chloro-2-methyl-3-isothiazolinone, 3-chloro-2-benzyl-3-isothiazolinone, 4,5-dichloro-2-methyl-3-isothiazolinone, 2,4-dimethyl-3-isothiazolinone, 4-methyl-2-(3,4-dichlorophenyl)-3-isothiazolinone, 2-(3,4-dichlorophenyl)-3-isothiazolinone, 4,5-dichloro-2-benzyl-3-isothiazolinone, 4-bromo-5-chloro-2-methyl-3-isothiazolinone, 4-bromo-2-methyl-3-isothiazolinone, 2-hydroxymethyl-3-isothiazolinone, 2-( $\beta$ -diethylaminoethyl)-3-isothiazolinone, 2-n-propyl-3-isothiazolinone hydrochloride, 5-chloro-2-methyl-3-isothiazolinone hydrochloride, 2-ethyl-3-isothiazolinone hydrochloride, 2-methyl-3-isothiazolinone hydrochloride, 2-benzyl-3-isothiazolinone hydrochloride, 2-n-dodecyl-3-isothiazolinone, 2-n-tetradecyl-3-isothiazolinone, 2-(4-chlorobenzyl)-3-isothiazolinone, 2-(2-chlorobenzyl)-3-isothiazolinone, 2-(2,4-dichlorobenzyl)-3-isothiazolinone, 2-(3,4-dichlorobenzyl)-3-isothiazolinone, 2-(4-methoxybenzyl)-3-isothiazolinone, 2-(4-methylbenzyl)-3-isothiazolinone, 2-(2-ethoxyhexyl)-3-isothiazolinone, 2-(2-phenylethyl)-3-isothiazolinone, 2-(2-phenylethyl)-4-chloro-3-isothiazolinone, 2-(1-phenylethyl)-3-isothiazolinone, 2-n-decyl-3-isothiazolinone, 2-n-octyl-3-isothiazolinone, 2-t-octyl-4-chloro-3-isothiazolinone, 2-t-octyl-4-bromo-3-isothiazolinone, 2-n-nonyl-3-isothiazolinone, 2-n-octyl-5-chloro-3-isothiazolinone, 2-(4-nitrophenyl)-3-isothiazolinone, 2-(4-carboethoxyphenyl)-3-isothiazolinone, 5-chloro-2-methyl-3-isothiazolinone monochloroacetate, 4,5-dichloro-2-methyl-3-isothiazolinone monochloroacetate, 2-ethyl-3-isothiazolinone monochloroacetate, 2-n-propyl-3-isothiazolinone monochloroacetate, and 2-benzyl-3-isothiazolinone monochloroacetate.

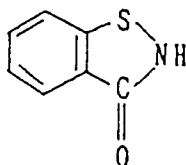
Any of these 1,2-benzisothiazoline-3-one compounds of Formula [III] to be used in this invention is generally contained in said photographic material in a proportion of  $1 \times 10^{-5}$  to 10% by weight relative to the total amount of hydrophilic colloid contained in the photographic material, and particularly preferably from  $1 \times 10^{-4}$  to 1% by weight relative to the total amount of hydrophilic colloid contained in the photographic material. Also, any of these isothiazoline-3-one compounds of Formula [IV] is generally contained in said

photographic material in a proportion of from  $1 \times 10^{-4}$  to 10% by weight relative to the total amount of hydrophilic colloid contained in the photographic material, and particularly preferably from  $3 \times 10^{-4}$  to 1% by weight relative to the total amount of hydrophilic colloid contained in the photographic material. It goes without saying that the amount of these compounds added is allowed to be outside the range mentioned above, depending on, for example, the kind of light-sensitive material to be used, the layer to which the compound is to be added and coating method.

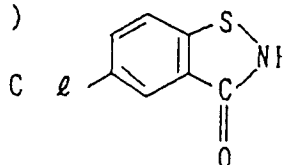
Any of these compounds may be dissolved into water or a solvent, not adversely affecting photographic characteristics; suitable organic solvents include alcohols such as methanol, ethanol and isopropanol, ketones such as acetone, glycols such as ethylene glycol and propylene glycol, esters such as ethyl acetate, and the solution may be added to a hydrophilic colloid, may be coated on the protective layer, or may be incorporated into a photographic light-sensitive material by immersing the photographic light-sensitive material into the solution. Alternatively, the compound may be dissolved into a high-boiling solvent, a low-boiling solvent or a mixture of these solvents, then emulsifiedly dispersed in the presence of a surface active agent, and then added to a liquid containing a hydrophilic colloid or coated over the protective layer. Otherwise, the compound may be incorporated into a high-polymer compound such as butyl polyacrylate, then dispersed in the presence of a surface active agent, and the dispersed liquid is then added to a liquid containing a hydrophilic colloid or coated over the protective layer.

Particularly suitable examples of the compounds having Formula [III] are as follows:

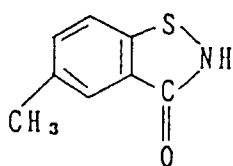
( 1 )



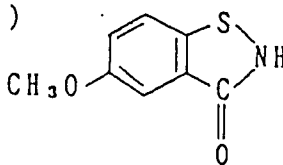
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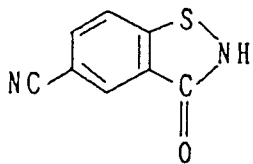
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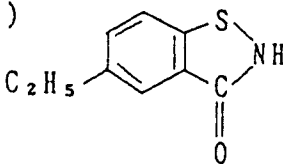
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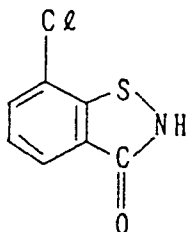
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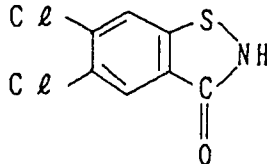
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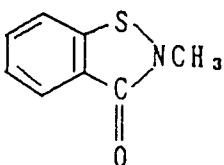
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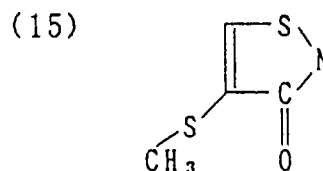
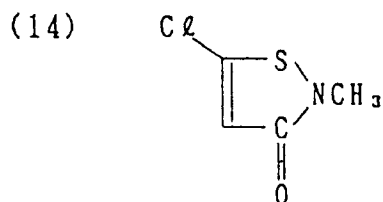
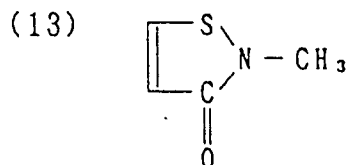
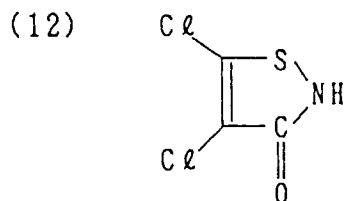
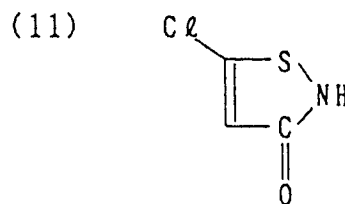
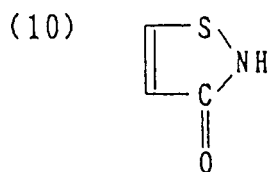
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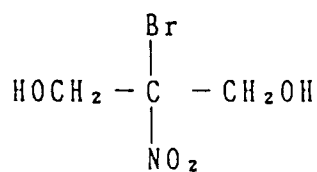


Further, particularly suitable examples of the compounds having Formula [IV] are as follows:

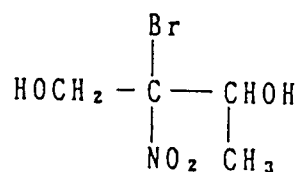


Subsequently, examples of the compounds having Formula [II] will be given below, but the compounds are not limited to the following examples.

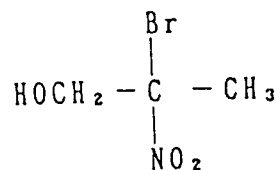
(16)



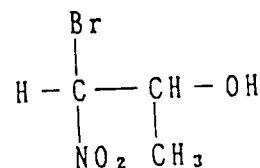
(17)



(18)



(19)



These compounds may be synthesized by making reference to known literature, and some of them are commercially available.

In this invention, the image formation is carried out by using a roller-transport-type automatic processor of which the foregoing  $\ell$  and T meet the following conditions:

$$\ell^{0.75} \times T = 50 \text{ to } 124$$

$$0.7 < \ell < 3.1$$

The above  $\ell$  can be found on the basis of, e.g., a light-sensitive material comprising a 175 $\mu$ m-thick polyethylene terephthalate support having photographic component layers thereon.

The above T implies the whole period of time the leading end of a sheet of film takes to travel from the insertion of it in the first roller at the film inlet, passing through the developer bath, crossover section, fixer bath, crossover section, wash water bath, crossover section and drying section, until the ejection of it from the final roller at the film outlet in the drying section of an automatic processor; in other words, the quotient (sec.) obtained by dividing the whole length (in meters) of the processing line by the line transport speed (meters/sec.).

The reason why the crossover section passage time is included, well-known to those skilled in the art, is that even in the crossover section, substantial processing is considered to be still going on due to the preceding process' liquid contained in the swelled gelatin layer of the film in transit.

The whole number of the transport rollers of the automatic processor for use in the image forming method of this invention, when expressed in terms of the value obtained dividing the  $\ell$ , the whole processing line's length of the automatic processor, by the number of the rollers, is desirable to be in the range of from 0.01 to 0.04. Also, the processing time proportions and ranges required in the individual processing positions are desired to be as follows:

|                                     |           |
|-------------------------------------|-----------|
| Insertion + developing + crossover: | 25 to 40% |
| Fixing + crossover:                 | 12 to 25% |
| Washing + crossover:                | 10 to 25% |
| Squeeze + drying:                   | 25 to 45% |
| Total                               | 100 %     |

The size of each roller to be used, in its transport-functional part, is desirable to be 12mm to 60mm in diameter and 30cm to 110cm in length. The roller may be made of various materials; for example, bakelite-type materials which may contain glass powder, metal powder or plastic powder) or rubber-type materials (e.g., neoprene, isoprene, silicone rubber) may be used for the rollers in the developing, fixing, washing and drying sections, and repellent and elastic silicone rubber or highly water-absorbing synthetic leather such as the commercial product called 'Kurarino' (Kuraray Co., Ltd.) may be preferably used for the rollers in the crossover and squeeze sections.

In this invention, the above  $\ell$  is in the range of from 0.7m to 3.1m so that satisfactory results can be obtained. If the  $\ell$  is less than 0.7m, the individual processes become small with the number of the rollers to be used being reduced, thus reducing the sensitivity of or affecting the transportability of the light-sensitive material being processed. In contrast, if the  $\ell$  is larger than 3.1m, the transport speed is increased to excess, whereby not only is the film liable to get scratched but the durability of the automatic processor deteriorates abruptly.

If the product of  $\ell^{0.75}$  and T is less than 50, the sensitivity of the film in processing is abruptly lowered, and, in a film containing not less than 10mg/m<sup>2</sup> of a sensitizing dye per side of its support, the residual dye stain also becomes a problem.

This problem is what we have found as a result of our investigation. Preferably, the product of  $\ell^{0.75}$  and T should be not less than 76.

On the other hand, if the product of  $\ell^{0.75}$  and T exceeds 124, the graininess of a photographic image deteriorates despite almost no increase in the sensitivity, and the fog begins to increase.

In practising this invention, various additives may be added to the developer solution and fixer solution to be used in the automatic processor.

Typical additives to be added to the developer solution include an antifoggant; a development accelerator comprised of an alkali agent such as sodium hydroxide, sodium carbonate or potassium carbonate; an inorganic or organic restrainer such as potassium bromide, 2-methylbenzimidazole or methylbenzothiazole; a water softener such as a polyphosphate; and an anti-surface-overdevelopment agent comprising a small amount of an iodide or mercapto compound. In addition, if necessary, a preservative such as a sulfite; a buffer such as a carbonate, boric acid, a borate or an alkanolamine; an

alkali agent such as a hydroxide or a carbonate; a dissolving aid such as polyethylene glycol or an ester thereof; a pH control agent comprised of an organic acid such as acetic acid; a sensitizer such as a quaternary ammonium salt; or a surface active agent, for example, may be used.

5 The developer solution may contain a hardening agent. As the hardening agent, a dialdehyde-type hardening agent may be suitably used.

The developer solution may also contain a chelating agent such as, e.g., ethylenediaminetetraacetic acid or an alkali metal salt thereof, a polyphosphate or a nitriloacetate.

10 The developing temperature is generally determined in relation to the developing time. In this invention, the developing temperature and developing time are preferably 30 to 40 °C and 6 to 20 seconds, respectively.

The fixer bath to be used in the fixing process of this invention is generally an aqueous solution containing, e.g., a thiosulfate and a water-soluble aluminum compound, and the solution may also contain a polybasic acid such as citric acid, or tartaric acid, and its pH is preferably about 3.5 to 5.0 (at 20 °C).

15 In the method of this invention, the developing process may be followed by a stop process. However, the stop process is excluded from general roller-transport-type automatic processors, so that part of the developer solution is carried out into the fixer solution, whereby the pH of the fixer solution may sometimes be raised. For this reason, the pH of the fixer solution is preferably adjusted to 3.6 to 4.7 (at 20 °C).

20 As the fixing agent, a thiosulfate such as ammonium thiosulfate or sodium thiosulfate is generally used. Of these ammonium thiosulfate is particularly suitably used from the fixing speed point of view. The amount of the fixing agent, although allowed to be arbitrarily varied, is normally from 0.1 to 5 moles per liter.

A water-soluble aluminum salt may be used which functions principally as a hardening agent in the fixer solution. This is a compound which is generally known as a hardening agent for acid hardening fixing solutions, and examples of it include aluminum chloride, aluminum sulfate and potassium alum. The fixing temperature and time in this invention are preferably 20 ° to 35 °C and 4 to 15 seconds, respectively.

25 A photographic material that has been developed and fixed is generally washed and then dried. The washing takes place in order to almost completely remove the silver salt that has been dissolved by fixing, and is preferably carried out for a period of 5 to 12 seconds at 20 ° to 50 °C. The drying is to take place at a temperature of 40 ° to 100 °C for an appropriate period of time. The drying time, although allowed to be arbitrarily varied according to ambient conditions, is normally from 5 to 15 seconds.

30 Examples of the roller-transport-type automatic processor suitably usable in practicing this invention are given in Figure 1 and Figure 2.

35 In Figures 1 and 2, 1 is the first roller at the film inlet in the insertion section, 2 is the final roller at the film outlet in the drying section, 3a is a developer bath, 3b is a fixer bath, 3c is a wash water bath, 4 is a light-sensitive material to be processed, 5 is a squeegee section, 6 is a drying section, and 7 is a drying air outlet port.

## EXAMPLES

40 The present invention will be illustrated in greater detail by the following Examples. It goes without saying that this invention is not limited to and by the Examples.

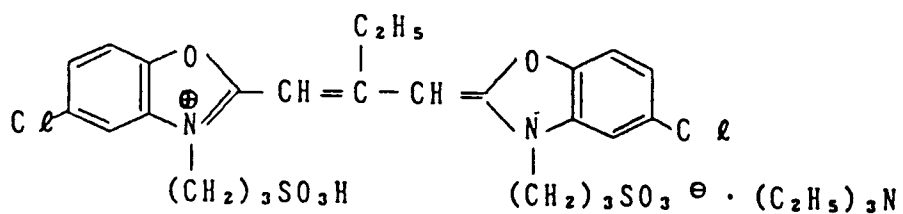
### EXAMPLE-1

45 A silver iodobromide emulsion of which the average silver iodide content is 2.0 mole% was subjected to gold-sulfur sensitization by using a chloroaurate, sodium thiosulfate and ammonium thiocyanate, stabilized by using 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, and spectrally sensitized by using the following Sensitizing Dyes A and B:

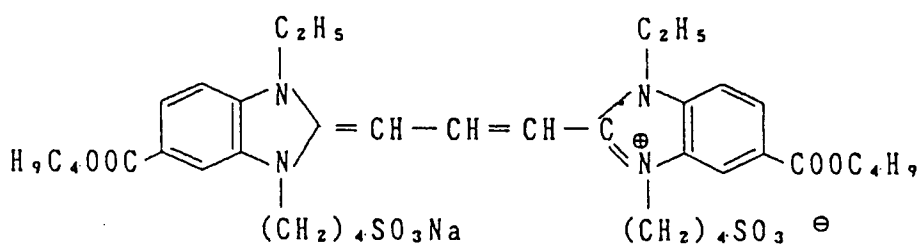
50

55

## Sensitizing Dye A

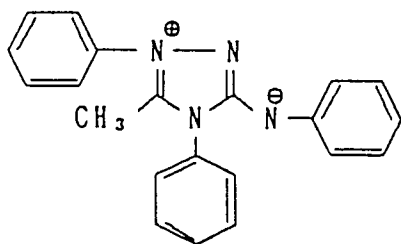


## Sensitizing Dye B



To the thus obtained emulsion were added the following additives to thereby prepare an emulsion liquid (silver halide coating liquid). The following adding amounts are values per mole of silver halide.

1,1-Dimethylol-1-bromo-1-nitromethane 70 mg



150 mg

t-Butyl-catechol 400 mg

Polyvinyl-pyrrolidone (molecular wt. 10,000) 1.0 g

Styrene-maleic anhydride copolymer 2.5 g

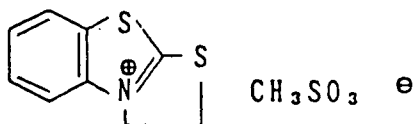
Trimethylolpropane 10 g

Diethylene glycol 5 g

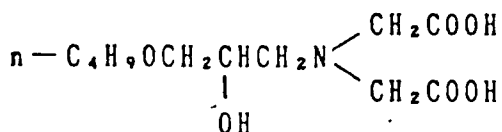
Nitrophenyl-triphenyl-phosphonium chloride 50 mg

Ammonium 1,3-hydroxybenzene-4-sulfonate 4 g

Sodium 2-mercaptobenzimidazole-5-sulfonate 1.5 mg



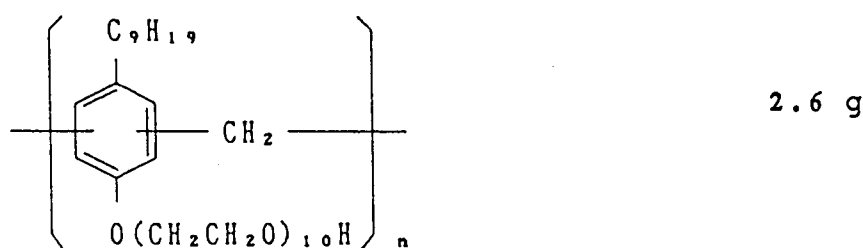
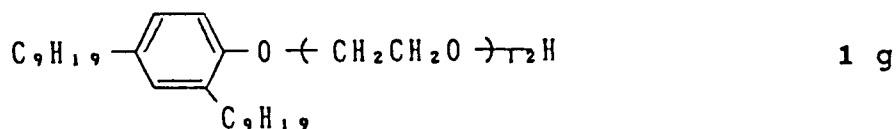
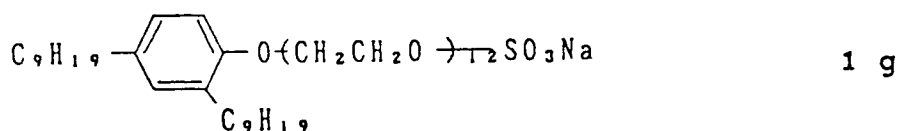
70 mg



1 g

Compounds of Formula [I] or [II] as defined herein or comparative compounds as shown in Table 1 were added in the amounts as given in Table 1 to the emulsion.

On the other hand, a protective layer coating liquid containing matting agents comprised of 1g/liter of polymethyl methacrylate having an average particle size of 3.5μm and 30g/liter of colloidal silica and the following compounds as surface active agents was prepared.



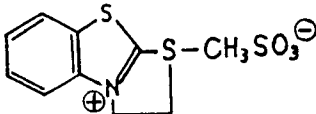
(A mixture of ones with n of 2 to 5)

Further, a mixture of formaldehyde and glyoxal in equimolar amounts was added as a hardening agent.

The thus prepared emulsion and the protective layer coating liquid were coated simultaneously, in the order of the emulsion layer and protective layer from the support side, at a coating speed of 90m/min on both sides of a 175 $\mu$ m-thick polyethylene terephthalate film support, both sides of which were subbed with an aqueous copolymer-dispersed liquid obtained by diluting to 10% by weight a copolymer comprised of three different monomers: 50% by weight of glycidyl methacrylate, 10% by weight of methyl acrylate, and 40% by weight of butyl methacrylate, whereby samples No.1 through No.33 were obtained. The coating weight of silver of each sample was 40mg/dm<sup>2</sup>. The gelatin coating weight of the emulsion layer was 2.0g/m<sup>2</sup>, and that of the protective layer was 1.0g/m<sup>2</sup>. The gelatin that was used in each layer was lime-treated Ossein gelatin.

Each of the thus obtained samples unexposed was processed in the following developer solution and fixer solution by the automatic processor shown in Figure 1.

## &lt;Developer Solution&gt;

|    |                                                                                     |         |
|----|-------------------------------------------------------------------------------------|---------|
| 5  | Potassium sulfite                                                                   | 70 g    |
|    | Trisodium hydroxyethylethylenediamine-                                              |         |
|    | triacetate                                                                          | 8 g     |
| 10 | 1,4-Dihydroxybenzene                                                                | 28 g    |
|    | Boric acid                                                                          | 10 g    |
|    | 5-Methyl-benzotriazole                                                              | 0.04 g  |
| 15 | 1-Phenyl-5-mercaptotetrazole                                                        | 0.01 g  |
|    | Sodium metabisulfite                                                                | 5 g     |
| 20 | Acetic acid (90 %)                                                                  | 13 g    |
|    | Triethylene glycol                                                                  | 15 g    |
|    | 1-Phenyl-3-pyrazolidone                                                             | 1.2 g   |
| 25 | S-Nitroindazole                                                                     | 0.2 g   |
| 30 |  | 0.001 g |
| 35 | Glutaraldehyde                                                                      | 4.0 g   |
|    | Disodium ethylenediaminetetraacetate                                                | 2.0 g   |
|    | Potassium bromide                                                                   | 4.0 g   |
| 40 | 5-Nitrobenzimidazole                                                                | 1.0 g   |
|    | Water to make 1,000 ml                                                              |         |
| 45 | pH adjusted to 10.50 with potassium hydroxide.                                      |         |

50

55

| (Fixer Solution)                             |       |
|----------------------------------------------|-------|
| Sodium thiosulfate (5 H <sub>2</sub> O)      | 45 g  |
| Disodium ethylenediaminetetraacetate         | 0.5 g |
| Ammonium thiosulfate                         | 150 g |
| Anhydrous sodium sulfite                     | 8 g   |
| Potassium acetate                            | 16 g  |
| Aluminum sulfate (10-18 H <sub>2</sub> O)    | 27 g  |
| Sulfuric acid (50 wt %)                      | 6 g   |
| Citric acid                                  | 1 g   |
| Boric acid                                   | 7 g   |
| Glacial acetic acid                          | 5 g   |
| Water to make 1,000 ml                       |       |
| pH adjusted to 4.0 with glacial acetic acid. |       |

In addition, each sample was cut into pieces by the cutting machine shown in Figure 3, wherein A1 and A2 indicate cutting blades, and B indicates a light-sensitive material (sample). Evaluation of the roller transfer marks on each sample was made by expressing in terms of the difference  $\Delta D$  between the densities, measured by an automatic densitometer, of the roller transfer marks and of their ambient areas.

The obtained results are as given in Table 1.

Table 1

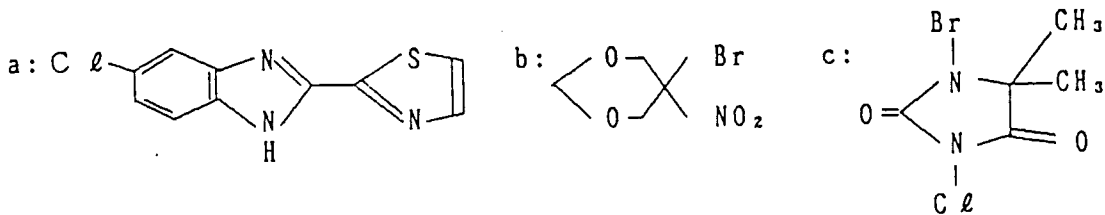
| Sample No. | Processing time T(sec) | $D^{0.75} \times T$ | Exemplified compound (or comparative cpd.) |                                   | $\Delta D$ | Remarks     |
|------------|------------------------|---------------------|--------------------------------------------|-----------------------------------|------------|-------------|
|            |                        |                     | No.                                        | Added amt(mg) per gram of gelatin |            |             |
| 1          | 20                     | 100                 | -                                          | -                                 | 0.08       | Comparative |
| 2          | 56.3                   | 120                 | -                                          | -                                 | 0.08       | Comparative |
| 3          | 65.7                   | 140                 | -                                          | 1.0                               | 0.04       | Comparative |
| 4          | 56.3                   | 120                 | 1                                          | 1.0                               | 0.00       | Invention   |
| 5          | 47.5                   | 105                 | 1                                          | 1.0                               | 0.01       | Invention   |
| 6          | 37.6                   | 80                  | 1                                          | 1.0                               | 0.01       | Invention   |
| 7          | 65.7                   | 140                 | 2                                          | 1.0                               | 0.04       | Comparative |
| 8          | 56.3                   | 120                 | 2                                          | 1.0                               | 0.00       | Invention   |
| 9          | 47.0                   | 100                 | 2                                          | 1.0                               | 0.01       | Invention   |
| 10         | 35.7                   | 76.0                | 2                                          | 1.0                               | 0.01       | Invention   |
| 11         | 61.0                   | 130                 | 3                                          | 1.0                               | 0.04       | Comparative |
| 12         | 44.6                   | 95                  | 3                                          | 1.0                               | 0.01       | Invention   |
| 13         | 44.6                   | 95                  | 4                                          | 1.0                               | 0.00       | Invention   |
| 14         | 44.6                   | 95                  | 5                                          | 1.0                               | 0.00       | Invention   |
| 15         | 44.6                   | 95                  | 6                                          | 1.0                               | 0.00       | Invention   |
| 16         | 44.6                   | 95                  | 7                                          | 1.0                               | 0.01       | Invention   |
| 17         | 56.3                   | 120                 | 10                                         | 1.0                               | 0.02       | Invention   |
| 18         | 44.6                   | 95                  | 10                                         | 1.0                               | 0.01       | Invention   |

(Continued)

Table 1 (continued)

| 5  | Sample No. | Processing time T(sec) | Exemplified compound<br>(or comparative cpd.) | Exemplified compound<br>(or comparative cpd.) |                                   | AD   | Remarks     |
|----|------------|------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------|------|-------------|
|    |            |                        |                                               | No.                                           | Added amt(mg) per gram of gelatin |      |             |
|    | 19         | 32.9                   | 70                                            | 10                                            | 1.0                               | 0.00 | Invention   |
| 10 | 20         | 56.3                   | 120                                           | 10                                            | 10.0                              | 0.01 | Invention   |
|    | 21         | 44.6                   | 95                                            | 10                                            | 5.0                               | 0.01 | Invention   |
|    | 22         | 32.9                   | 70                                            | 10                                            | 0.5                               | 0.01 | Invention   |
|    | 23         | 56.3                   | 120                                           | 11                                            | 1.0                               | 0.02 | Invention   |
| 15 | 24         | 44.6                   | 95                                            | 11                                            | 1.0                               | 0.01 | Invention   |
|    | 25         | 32.9                   | 70                                            | 11                                            | 1.0                               | 0.02 | Invention   |
|    | 26         | 44.6                   | 95                                            | 13                                            | 1.0                               | 0.02 | Invention   |
| 20 | 27         | 44.6                   | 95                                            | 14                                            | 1.0                               | 0.01 | Invention   |
|    | 28         | 44.6                   | 95                                            | 16                                            | 1.0                               | 0.02 | Invention   |
|    | 29         | 44.6                   | 95                                            | 17                                            | 1.0                               | 0.02 | Invention   |
|    | 30         | 44.6                   | 95                                            | 18                                            | 1.0                               | 0.02 | Invention   |
| 25 | 31         | 44.6                   | 95                                            | a*                                            | 1.0                               | 0.08 | Comparative |
|    | 32         | 44.6                   | 95                                            | b*                                            | 1.0                               | 0.08 | Comparative |
|    | 33         | 44.6                   | 95                                            | c*                                            | 1.0                               | 0.08 | Comparative |

\*Comparative Compounds:



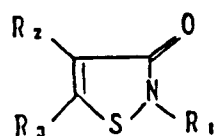
As is apparent from the results shown in Table 1, the samples to which the image forming method of this invention was applied show little or no roller-transfer marks, and thus the effect of this invention is significant.

### EXAMPLE 2

Similar experiments to Example 1 were performed by using the automatic processor shown in Figure 2 ( $\ell = 0.73(\text{m})$ ). As a result, quite the same effect as in Example 1 was obtained.

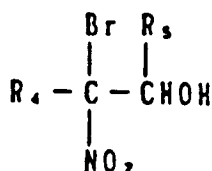
## Claims

1. A method of forming a photographic image by processing an imagewise exposed silver halide light-sensitive photographic material in an automatic processor, wherein said light-sensitive photographic material contains at least one compound of formula [I] or formula [II] below;



[I]

wherein R<sub>1</sub> is a hydrogen atom, a straight-chain or branched-chain alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkylamido group, an arylamido group, an alkylthioamido group, an arylthioamido group, an alkylsulfoamido or an arylsulfoamido group; R<sub>2</sub> and R<sub>3</sub> are independently a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, a cyano group, an alkylthio group, an arylthio group, an alkylsulfoxido group, an alkylsulfonyl group, an alkylsulfinyl group or a heterocyclic group; such that the above-mentioned alkyl, cycloalkyl, alkenyl, heterocyclic, aralkyl and aryl groups may be substituted, and that R<sub>2</sub> and R<sub>3</sub> may together form a divalent group to complete a ring, but not including 5-chloroisothiazoline-3-one;



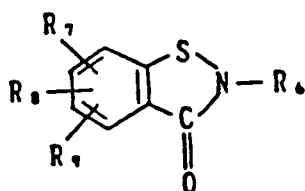
[II]

wherein R<sub>4</sub> is a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms or a hydroxymethyl group and R<sub>5</sub> is a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms, such that the above-mentioned groups R<sub>4</sub> and R<sub>5</sub> may be substituted, but not including 1,1-dimethylol-1-bromo-1-nitromethane, under a condition satisfying the equation given below;

$$50 \leq l^{0.75} \times T \leq 124,$$

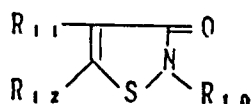
wherein l is the length (in metres) between the axis of the first roller at the film inlet in the insertion section and the axis of the final roller at the film outlet in the drying section of a roller-transport-type automatic processor and is more than 0.7m and less than 3.1m, T is the time in seconds necessary for said silver halide light-sensitive photographic material to pass through said length, l.

- The method of claim 1, wherein the compound of formula [I] is a 1,2-benzisothiazoline-3-one compound of formula [III] or an isothiazoline-3-one compound of formula [IV];



[III]

wherein R<sub>6</sub> is a hydrogen atom, an alkyl group, or an alkoxy group; R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are independently a halogen atom, an alkyl group, an alkoxy group, a cyano group or a nitro group, such that the above-mentioned groups, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> may independently be substituted;



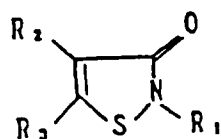
[IV]

R<sub>10</sub> is a hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a - CONHR<sub>13</sub> group or a heterocyclic group, wherein R<sub>13</sub> is an alkyl group, an aryl group, an alkylthio group, an arylthio group, an alkylsulfonyl group or an arylsulfonyl group, such that the above-mentioned groups for R<sub>10</sub> may be substituted; R<sub>11</sub> and R<sub>12</sub> are independently a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group, a cyano group, an alkylthio group, an arylthio group, an alkylsulfoxido group, an alkylsulfinyl group or an alkylsulfonyl group, such that the above-mentioned groups for R<sub>11</sub> and R<sub>12</sub> may be substituted.

3. The method of claim 2, wherein the 1,2-benzisothiazoline-3-one compound of formula [III] is contained in said photographic material in an amount from  $1 \times 10^{-5}$  to 10% by weight relative to the total amount of hydrophilic colloid contained in said photographic material.
4. The method of claim 3, wherein the content of the compound is  $1 \times 10^{-4}$  to 1 % by weight.
5. The method of any one of claims 2 to 4 wherein the thiazoline-3-one compound of formula [IV] is contained in said photographic material in an amount from  $1 \times 10^{-4}$  to 10% by weight relative to the total amount of hydrophilic colloid contained in said photographic material.
6. The method of claim 5, wherein the content of the compound is  $3 \times 10^{-4}$  to 1 % by weight.

#### Patentansprüche

1. Verfahren zur Erzeugung eines photographischen Bildes durch Behandeln eines bildgerecht belichteten lichtempfindlichen photographischen Silberhalogenid-Aufzeichnungsmaterials in einer automatischen Behandlungsvorrichtung, wobei das lichtempfindliche photographische Aufzeichnungsmaterial mindestens eine Verbindung der Formel [I] oder der Formel [II]



[I]

worin bedeuten:

R<sub>1</sub> ein Wasserstoffatom, eine gerad- oder verzweigt-kettige Alkylgruppe, eine Cycloalkylgruppe, eine Alkenylgruppe, eine Aralkylgruppe, eine Arylgruppe, eine heterocyclische Gruppe, eine Alkylamido-Gruppe, eine Arylamido-Gruppe, eine Alkylthioamido-Gruppe, eine Arylthioamido-Gruppe, eine Alkylsulfoamido- oder eine Arylsulfoamido-Gruppe;

R<sub>2</sub> und R<sub>3</sub> unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Alkylgruppe, eine Cycloalkylgruppe, eine Arylgruppe, eine Cyanogruppe, eine Alkylthio-Gruppe, eine Arylthio-Gruppe, eine Alkylsulfoxid-Gruppe, eine Alkylsulfonyl-Gruppe, eine Alkylsulfinyl-Gruppe oder eine heterocyclische Gruppe, wobei die zuvor genannten Alkyl-, Cycloalkyl-, Alkenyl-, heterocyclischen, Aralkyl- und Arylgruppen substituiert sein können und wobei R<sub>2</sub> und R<sub>3</sub> zusammen einen Ring vervollständigende zweiwertige Gruppe bilden können, mit Ausnahme von 5-Chlorisothiazolin-3-on;



worin bedeuten:

R<sub>4</sub> ein Wasserstoffatom, eine Alkylgruppe mit 1 bis 4 Kohlenstoffatom(en) oder eine Hydroxymethylgruppe und R<sub>5</sub> ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 4 Kohlenstoffatom(en), wobei die zuvor genannten Gruppen R<sub>4</sub> und R<sub>5</sub> substituiert sein können, ausschließlich 1,1-Dimethylol-1-brom-1-nitromethan,

enthält und die Behandlung unter der folgenden Gleichung:

$$50 \leq 1^{0,75} \times T \leq 124$$

worin bedeuten:

I die Länge (in m) zwischen der Achse der ersten Walze am Filmeinlaß im Einführabschnitt und der Achse der letzten Walze am Filmauslaß in dem Trocknungsabschnitt einer automatischen Behandlungsvorrichtung mit Walzentransport in der Größenordnung von mehr als 0,7 und weniger als 3,1 m und T die Zeit (in s), die das lichtempfindliche photographische Silberhalogenid-Aufzeichnungsmaterial zum Durchtritt durch die Länge I benötigt, genügenden Bedingungen erfolgt.

2. Verfahren nach Anspruch 1, wobei die Verbindung der Formel [I] aus einer 1,2-Benzisothiazolin-3-on-Verbindung der Formel [III] oder einer Isothiazolin-3-on-Verbindung der Formel [IV] besteht:



worin bedeuten:

R<sub>6</sub> ein Wasserstoffatom, eine Alkylgruppe oder eine Alkoxygruppe;

R<sub>7</sub>, R<sub>8</sub> und R<sub>9</sub> unabhängig voneinander ein Halogenatom, eine Alkylgruppe, eine Alkoxygruppe, eine Cyanogruppe oder eine Nitrogruppe, wobei die zuvor genannten Gruppen R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> und R<sub>9</sub> substituiert sein können;



worin bedeuten:

R<sub>10</sub> ein Wasserstoffatom, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkenylgruppe, eine Arylgruppe, eine Arylgruppe, eine -CONHR<sub>13</sub>-Gruppe oder eine heterocyclische Gruppe, wobei R<sub>13</sub> für eine Alkylgruppe, eine Arylgruppe, eine Alkylthiogruppe, eine Arylthiogruppe, eine Alkylsulfonylgruppe oder eine Arylsulfonylgruppe steht, wobei die zuvor genannten Gruppen R<sub>10</sub> substituiert sein können;

R<sub>11</sub> und R<sub>12</sub> unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Alkylgruppe, eine Cycloalkylgruppe, eine Arylgruppe, eine heterocyclische Gruppe, eine Cyanogruppe, eine Alkylthiogruppe, eine Arylthiogruppe, eine Alkylsulfoxidgruppe, eine Alkylsulfinylgruppe oder eine Alkylsulfonylgruppe, wobei die zuvor genannten Gruppen R<sub>11</sub> und R<sub>12</sub> substituiert sein können.

3. Verfahren nach Anspruch 2, wobei die 1,2-Benzisothiazolin-3-on-Verbindung der Formel [III] in dem photographischen Aufzeichnungsmaterial in einer Menge von  $1 \times 10^{-5}$  bis 10 Gew.-%, bezogen auf die Gesamtmenge an in dem photographischen Aufzeichnungsmaterial enthaltenem hydrophilen Kolloid vorhanden ist.

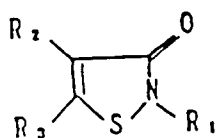
4. Verfahren nach Anspruch 3, wobei der Gehalt an der Verbindung  $1 \times 10^{-4}$  bis 1 Gew.-% beträgt.

5. Verfahren nach einem der Ansprüche 2 bis 4, wobei die Thiazolin-3-on-Verbindung der Formel [IV] in dem photographischen Aufzeichnungsmaterial in einer Menge von  $1 \times 10^{-4}$  bis 10 Gew.-%, bezogen auf die Gesamtmenge an in dem photographischen Aufzeichnungsmaterial enthaltenem hydrophilen Kolloid vorhanden ist.

6. Verfahren nach Anspruch 5, wobei der Gehalt der Verbindung  $3 \times 10^{-4}$  bis 1 Gew.-% beträgt.

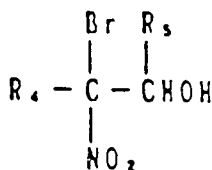
## Revendications

1. Procédé de formation d'une image photographique par traitement d'un matériau photographique photosensible à base d'halogénure d'argent, exposé pour la formation d'une image, dans un dispositif de traitement automatique, le matériau photographique photosensible contenant au moins un composé de formule [I] ou de formule [II] ci-après :



[I]

dans laquelle  $R_1$  est un atome d'hydrogène, un groupe alkyle à chaîne droite ou ramifiée, un groupe cycloalkyle, un groupe alcényle, un groupe aralkyle, un groupe aryle, un groupe hétérocyclique, un groupe alkylamido, un groupe arylamido, un groupe alkylthioamido, arylthioamido, un groupe alkylsulfonylamido ou un groupe arylsulfonylamido ;  $R_2$  et  $R_3$  représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe alkyle, un groupe cycloalkyle, un groupe aryle, un groupe cyano, un groupe alkylthio, un groupe arylthio, un groupe alkylsulfoxydo, un groupe alkylsulfonyl, un groupe alkylsulfinyl ou un groupe hétérocyclique ; les groupes alkyle, cycloalkyle, alcényle, hétérocyclique, aralkyle et aryle mentionnés ci-dessus pouvant être substitués, et  $R_2$  et  $R_3$  pouvant former ensemble un groupe divalent pour compléter un cycle, mais à l'exclusion de la 5-chloroisothiazoline-3-one ;



[II]

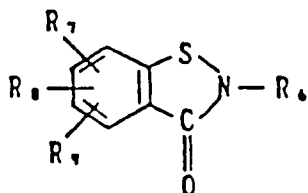
dans laquelle  $R_4$  est un atome d'hydrogène, un groupe alkyle ayant 1 à 4 atomes de carbone ou un groupe hydroxyméthyle, et  $R_5$  est un atome d'hydrogène ou un groupe alkyle ayant 1 à 4 atomes de carbone, les groupes  $R_4$  et  $R_5$  mentionnés ci-dessus pouvant être substitués, mais à l'exclusion du 1,1-diméthylol-1-bromo-1-nitrométhane, dans des conditions satisfaisant l'équation ci-après :

$$50 \leq l^{0.75} \times T \leq 124$$

dans laquelle  $l$  représente la longueur (en mètres) comprise entre l'axe du premier cylindre à l'entrée du film dans la section d'insertion et l'axe du dernier cylindre à la sortie du film dans la section de séchage d'un dispositif de traitement automatique du type à transport par cylindre,  $l$  étant supérieure à 0,7 m et inférieure à 3,1 m,  $T$  représente le temps en secondes nécessaire pour que ledit matériau

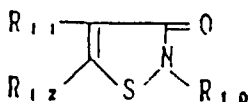
photographique photosensible à base d'halogénure d'argent traverse ladite longueur  $\lambda$ .

2. Procédé selon la revendication 1, dans lequel le composé de formule [I] est la 1,2-benzisothiazoline-3-one de formule [III] ou une isothiazoline-3-one de formule [IV] :



[III]

dans laquelle  $R_6$  est un atome d'hydrogène, un groupe alkyle ou un groupe alcoxy ;  $R_7$ ,  $R_8$  et  $R_9$  représentent indépendamment un atome d'halogène, un groupe alkyle, un groupe alcoxy, un groupe cyano ou un groupe nitro, les groupes  $R_6$ ,  $R_7$ ,  $R_8$  et  $R_9$  mentionnés ci-dessus pouvant indépendamment être substitués ;

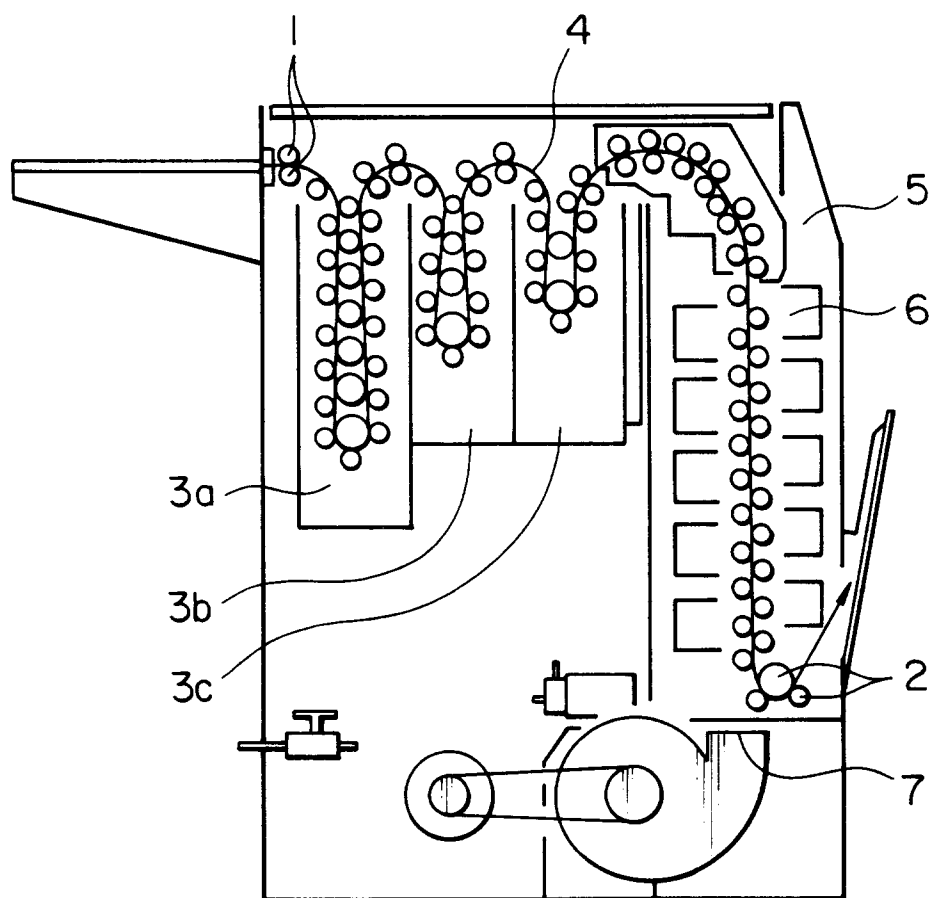


[IV]

$R_{10}$  représente un atome d'hydrogène, un groupe alkyle, un groupe cycloalkyle, un groupe alcényle, un groupe aralkyle, un groupe aryle, un groupe  $-\text{CONHR}_{13}$  ou un groupe hétérocyclique,  $R_{13}$  représentant un groupe alkyle, un groupe aryle, un groupe alkylthio, un groupe arylthio, un groupe alkylsulfonyl ou un groupe arylsulfonyl, les groupes mentionnés ci-dessus pour  $R_{10}$  pouvant être substitués ;  $R_{11}$  et  $R_{12}$  représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe alkyle, un groupe cycloalkyle, un groupe aryle, un groupe hétérocyclique, un groupe cyano, un groupe alkylthio, un groupe arylthio, un groupe alkylsulfoxydo, un groupe alkylsulfinyle ou un groupe alkylsulfonyl, les groupes mentionnés ci-dessus pour  $R_{11}$  et  $R_{12}$  pouvant être substitués.

3. Procédé selon la revendication 2, dans lequel la 1,2-benzisothiazoline-3-one de formule [III] est contenue dans ledit matériau photographique en une proportion de  $1 \times 10^{-5}$  à 10 % en poids par rapport à la quantité totale de colloïde hydrophile contenu dans ledit matériau photographique.
4. Procédé selon la revendication 3, dans lequel la teneur en ledit composé est de  $1 \times 10^{-4}$  à 1 % en poids.
5. Procédé selon l'une quelconque des revendications 2 à 4, dans lequel la thiazoline-3-one de formule [IV] est contenue dans ledit matériau photographique en une proportion de  $1 \times 10^{-4}$  à 10 % en poids par rapport à la quantité totale de colloïde hydrophile contenu dans ledit matériau photographique.
6. Procédé selon la revendication 5, dans lequel la teneur en ledit composé est de  $3 \times 10^{-4}$  à 1 % en poids.

FIG. 1



$l = 2.74(m)$

FIG. 3

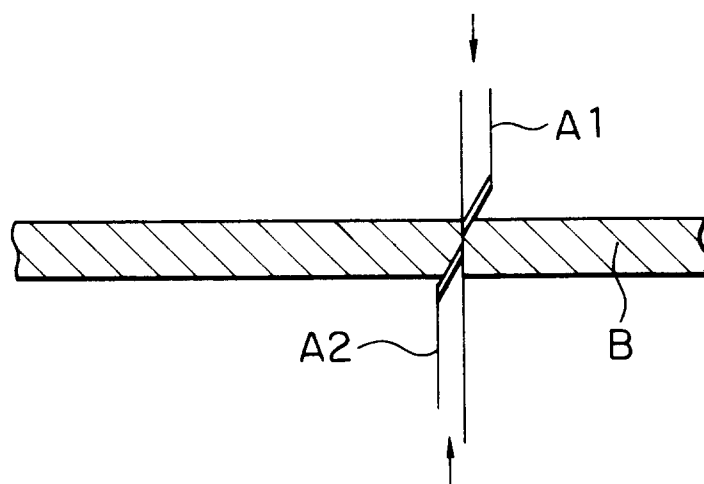


FIG. 2

