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- (54) Method for the formation of images.
- 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 selected from the group consisting of those represented by formula [I] and formula [II] below:

$$\begin{array}{c}
R_z \\
R_z
\end{array}$$

wherein  $R_1$  is selected from 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 arylsulfoamido group, an arylsulfoamido and an arylsulfoamido group;  $R_2$  and  $R_3$  are independently selected from 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, and a heterocyclic group; provided that the above-mentioned alkyl, cycloalkyl, alkenyl, heterocyclic aralkyl and aryl groups may have a substituent, and that said  $R_2$  and  $R_3$  may be a divalent group and form a ring;

wherein  $R_4$  is selected from a hydrogen atom and a lower alkyl group or a hydroxymethyl group; and  $R_5$  is selected from a hydrogen atom and a lower alkyl group; under a condition satisfying an equation given below;

 $50 \le \ell^{0.75} \times T \le 124$ ,

wherein  $\ell$  is length of a passage for said silver halide light-sensitive to be transported for processing, and is more than 0.7m and less than 3.1m,

T is time in terms of second necessary for said silver halide light-sensitive photographic material to pass through said passage.

#### METHOD FOR THE FORMATION OF IMAGES

#### FIELD OF THE INVENTION

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

#### BACKGROUND OF THE INVENTION

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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, rapid processing has the above-mentioned significant advantage but has problems yet to be solved.

That is, the rapid processing requires an increased film-transport speed. In this instance, if an automatic processor, e.g., a roller-transport-type automatic processor, is used, it tends to cause such troubles as roller transfer marks appearing 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 are 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.

#### SUMMARY OF THE INVENTION

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It is an object of the present invention to provide 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 hardly causes troubles such as roller transfer marks.

As a result of our continued investigation, it has now been found that the above object can be accomplished by a method for the formation of images which comprises the processing of a silver halide light-sensitive material, in which said light-sensitive material contains at least one compound arbitrarily selected from the group consisting of those compounds having the following Formula [II] and those compounds having the following Formula [II], and said processing of said light-sensitive material is performed by a roller-transport-type automatic processor under conditions corresponding to the following equation:

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

 $0.7 < \ell < 3.1$ 

wherein  $\ell$  is the length (in meters) between the core of the first roller at the film inlet in the insertion section and the core of the final roller at the film outlet in the drying section of a roller-transport-type automatic processor, and T is a period of time (in seconds) necessary for a film to pass the above  $\ell$ .

As a result of our various investigations, we have found that the compounds of Formulas [I] and [III] of the invention alone are effective to the above object, and the present invention has been made on the basis of this knowledge. The action of this invention is not necessarily clear, but we assume 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.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

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

Figure 3 is a drawing showing the construction of the cutting machine that is used in the examples.

The indication numbers that are used in these drawings of 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.

#### **DETAILED DESCRIPTION OF THE INVENTION**

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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:

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### Formula [I]

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wherein R<sub>1</sub> represents 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<sub>2</sub> and R<sub>3</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 alkylsulfonyl group or a heterocyclic group, provided that the above alkyl, cycloalkyl, alkenyl, heterocyclic, aralkyl and aryl groups each may have a substituent, and the R<sub>2</sub> and R<sub>3</sub> are allowed to form a ring together. The ring to be formed by both R<sub>2</sub> and R<sub>3</sub> may be an aromatic ring.

## Formula [II]

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wherein  $R_4$  represents a hydrogen atom, a lower alkyl group having from 1 to 4 carbon atoms or a hydroxymethyl group; and  $R_5$  represents a hydrogen atom or a lower alkyl group having from 1 to 4 carbon atoms; provided that the above-mentioned groups for  $R_4$  and  $R_5$  may independently have a substituent.

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

## Formula [III]

#### Formula [IV]

$$\begin{array}{c|c}
R_{8} & & & \\
R_{9} & & & \\
\hline
R_{12} & & & \\
\hline
R_{12} & & & \\
\hline
R_{13} & & & \\
\hline
R_{14} & & & \\
\hline
R_{15} & & & \\
\hline$$

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wherein  $R_6$  represents a hydrogen atom, an alkyl group or an alkoxy group;  $R_7$ ,  $R_8$  and  $R_9$  each represents a hydrogen atom, a halogen atom, an alkyl group, an alkoxy group, a cyano group or a nitro group;  $R_{10}$  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  $R_{13}$  is an alkyl, aryl, alkylthio, arylthio, alkylsulfonyl or arylsulfonyl group) or a heterocyclic group;  $R_{11}$  and  $R_{12}$  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 alkylsulfoxido group, an alkylsulfonyl group or a heterocyclic group; provided that the alkyl group and the alkyl portion of the alkoxy group represented by the  $R_6$ ,  $R_7$ ,  $R_8$  or  $R_9$  are preferably straight-chain or branched-chain alkyl groups having from 1 to 6 carbon atoms, and that the abovementioned groups for  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  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, 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 1 to 36, and more preferably 1 to 18. The number of carbon atoms of the cycloalkyl group is 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, thiocyano, 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, alkylsulfinyl, arylsulfinyl, alkylamino, dialkylamino, anilino, N-alkylanilino, N-arylanilino, N-acylamino, hydroxy, mercapto and the like groups.

In Formula [IV], the number of carbon atoms of the alkyl group represented by the  $R_{11}$  or  $R_{12}$  is 1 to 18, and more preferably 1 to 9, and that of the cycloalkyl group represented by the same is 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, hydroxy or the like group.

The following are typical examples of the compounds having Formula [IV], but the compounds of this invention 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-methylsulfinyl-2-(N-methylcarbamoyl)-3-isothiazolinone, 4-cyano-5-methylsulfinyl-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-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-5methyl-2-(N-3,4-dichlorophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-3,4-dichlorophenylcarbamoyl)-3isothiazolinone, 4-cyano-5-methylthio-2-(N-3,4-dichlorophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-4-dichlorophenylcarbamoyl)-3-isothiazolinone, 5-methyl-2-(N-4-dichlorophenylcarbamoyl) 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)-3-2-(N-4-methoxyphenylcarbamoyl)-3-isothiazolinone, 2-(N-2-methoxyphenylcarbamoyl)-3isothiazolinone, 2-(N-3,4-dichlorophenylcarbamoyl)-3-2-(N-3-nitrophenylcarbamoyl)-3-isothiazolinone, isothiazolinone, 2-(N-2,5-dichlorophenylcarbamoyl)-3-2-(N-n-dodecylcarbamoyl)-3-isothiazolinone, isothiazolinone, zolinone, 2-(N-4-nitrophenylcarbamoyl)-3-2-(N-carboethoxymethylcarbamoyl)-3-isothia thiazolinone, 5-methyl-2-(N-ethylthiocarbamoyl)-s-5-methyl-2-(N-ethylcarbamoyl)-3-isothiazolinone, isothiazolinone, 5-chloro-2-(N-ethylcarbamoyl)-3-isothiazolinone, 2-n-propyl-3-isothiazoline, 2-t-butyl-3isothiazolinone, isothiazolinone, 2-n-butyl-3-isothiazolinone, 2- cyclohexyl-3-isothiazolinone, 2-n-octyl-3-isothiazolinone, 2-toctyl-3-isothiazolinone, 2-benzyloxy-3-isothiazolinone, 3-chloro-2-methyl-3-isothiazolinone, 3-chloro-2benzyl-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-3isothiazolinone, 4-bromo-5-chloro-2-methyl-3-isothiazolinone, 4- bromo-2-methyl-3-isothiazolinone, 2hydroxymethyl-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, 2hydrochloride, 2-benzyl-3-isothiazolinone hydrochloride, 2-n-dodecyi-3methyl-3-isothiazolinone isothiazolinone, 2-n-tetradecyl-3-isothiazolinone, 2-(4-chlorobenzyl)-3-isothiazolinone, 2-(2-chlorobenzyl)-3-2-(2,4-dichlorobenzyl)-3-isothiazolinone, 2-(3,4-dichlorobenzyl)-3-isothiazolinone, 2-(4methoxybenzyl)-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-isothia zolinone, 2- n-decyl-3-isothiazolinone, 2-n-octyl-3-isothiazolinone, 2-t-octyl-4-chloro-3-isothiazolinone, 2-toctyl-4-bromo-3-isothiazolinone, 2-n-nonyl-3-isothiazolinone, 2-n-octyl-5-chloro-3-isothiazolinone, 2-(4nitrophenyl)-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.

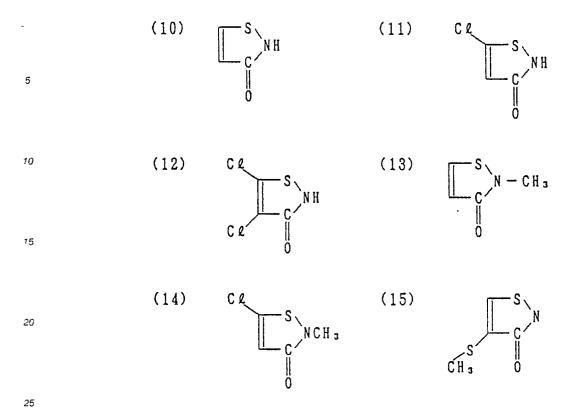
Any of these 1,2-benzoisothiazoline-3-one compounds of Formula [III] to be used in this invention is contained in said photographic material in a proportion of 1x10<sup>-5</sup> to 10% by weight relative to the total amount of hydrophilic colloid contained in the photographic material, and particularly preferably from 1x10<sup>-4</sup> 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 contain in said photographic material in a proportion of preferably from 1x10<sup>-4</sup> to 10% by weight relative to the total amount of hydrophilic colloid contained in the photographic material, and particularly preferably from 3x10<sup>-4</sup> to 1% by weight relative to the total amount of hydrophilic colloid contained in the photographic material. It goes without saying that the adding amount of these compounds is allowed to be outside the range mentioned above, depending on the kind of the light-sensitive material to be used, the layer to which the compound is to be added, coating method, and the like.

Any of these compounds may be dissolved into water or a solvent, not adversely affecting photographic characteristics, out of organic solvents including alcohols such as methanol, ethanol, isopropanol, etc., ketones such as acetone, glycols such as ethylene glycol, propylene glycol, etc., esters such as ethyl acetate, and the like, 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 in the manner of 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) . (3) (5) (7) (9) 

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.

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$$HOCH_2 - C - CH_2OH$$
  $HOCH_2 - C - CHOH$   $NO_2$   $HOCH_3$ 

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(18)
$$HOCH_{2} - C - CH_{3}$$

$$HOCH_{2} - CH_{3}$$

$$HOCH_{3} - CH_{3}$$

$$HOCH_{3} - CH_{3}$$

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 £ and T meet the following conditions:

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

(16)

 $0.7 < \ell < 3.1$ 

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The above £ 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 %

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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 (allowed to 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, whereby 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 deteriorating the sensitivity of or affecting the transportability of the light-sensitive material being processed. On the contrary, 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 is abruptly deteriorated.

If the product of  $\mathfrak{t}^{0.75}$  and T is less than 50, the sensitivity of the film in processing is abruptly lowered, and besides, in a film containing not less than  $10 \text{mg/m}^2$  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  $t^{0.75}$  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 becomes largely deteriorated despite almost no increase in the sensitivity, and besides, the fog begins to increase.

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

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, potassium carbonate, etc.; an inorganic or organic restrainer such as potassium bromide, 2-methylbenzimidazole, methylbenzothiazole, etc.; a water softener such as a polyphosphate; and an anti-surface-overdevelopement agent comprising a slight 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, an alkanolamine, etc.; an alkali agent such as a hydroxide, a carbonate, etc.; 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; a surface active agent, and the like, may be used.

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.

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

The fixer bath to be used in the fixing process of this invention is 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, tartaric acid or the like, and its pH is preferably about 3.5 to 5.0 (at 20°C).

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 desirable to be adjusted to about 3.6 to 4.7 (at 20°C).

As the fixing agent, a thiosulfate such as ammonium thiosulfate, sodium thiosulfate or the like is generally used. Of these the ammonium thiosulfate is particularly suitably used from the fixing speed point of view. The using amount of the fixing agent, although allowed to be arbitrarily varied, is normally from about 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 the hardening agent for acid hardening fixing solutions, and examples of it include, e.g., aluminum chloride, aluminum sulfate, potassium alum, and the like. The fixing temperature and time in this invention are preferably, e.g., 20° to 35°C and 4 to 15 seconds, respectively.

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 desirable to take place for a period of about 5 to 12 seconds at about 20° to 50°C. The drying is to take place at a temperature of about 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 about 5 to 15 seconds.

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

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.

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#### **EXAMPLES**

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**

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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:

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## Sensitizing Dye A

C P CH = C - CH 
$$=$$
 $C \neq H_5$ 
 $C \neq H_5$ 

# Sensitizing Dye B

$$\begin{array}{c} C_{2}H_{5} \\ \\ N \\ \\ H_{9}C_{4}00C \\ \\ O \\ CH_{2})_{4}SO_{3}Na \\ \end{array} \begin{array}{c} C_{2}H_{5} \\ \\ \\ CO0C_{4}H_{9} \\ \\ CH_{2})_{4}SO_{3} \\ \\ \end{array}$$

To the thus obtained emulsion were added the following additives to thereby prepare an emulsion liquid 30 (silver halide coating liquid). The following adding amounts are values per mole of silver halide.

	1,1-Dimethylol-1-bromo-1-nitromethane	70 mg
5	CH <sub>3</sub> N O	<b>150</b> mg
	t-Butyl-catechol	400 mg
15	Polyvinyl-pyrrolidone (molecular wt. 10,000)	1.0 g
	Styrene-maleic anhydride copolymer	<b>2.5</b> g
	Trimethylolpropane	10 g
20	Diethylene glycol	<b>5</b> g
	Nitrophenyl-triphenyl-phosphonium chloride	50 mg
25	Ammonium 1,3-hydroxybenzene-4-sulfonate	<b>4</b> g
	Sodium 2-mercaptobenzimidazole-5-sulfonate	1.5 mg
30		
35	S CH 3 SO 3 P	70 mg
	CH 2 COOH	
	n — C4H 9OCH 2CHCH 2N CH 2COOH	1 g

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

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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.

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$$C_9H_{19}$$
  $\longrightarrow$   $O(CH_2CH_2O)$   $\longrightarrow$   $O(CH_2CH_2O)$ 

$$C_{9}H_{19} \longrightarrow 0 \leftarrow CH_{2}CH_{2}O \xrightarrow{}_{12}H$$

$$C_{9}H_{19}$$

## (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 175µm-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/dm². The gelatin coating weight of the emulsion layer was  $2.0g/m^2$ , and that of the protective layer was  $1.0g/m^2$ . The gelatin that was used in each layer was limetreated Osein 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.

# 

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

<fixer solution=""></fixer>		
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.		

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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	Processing	€0.75x T		plified compound	40	Domowless
No.	time T(sec)	(m sec)	No.	Added amt(mg) per gram of gelatin	ΔD	Remarks
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

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(Continued)

Table 1 (continued)

	_	PA 11- 5		olified compound		
Sampl No.		€°·75x T (m sec)		omparative cpd.) Added amt(mg) per gram of gelatin	ΔD	Remarks
19	32.9	70	10	1.0	0.00	Invention
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
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
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
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 ( $\ell = 0.73(m)$ ). As a result, quite the same effect as in Example 1 was obtained.

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#### Claims

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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 selected from the group consisting of those represented by formula [I] and formula [II] below;

$$\begin{array}{c}
R_2 \\
R_3
\end{array}$$

wherein R<sub>1</sub> is selected from 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 and an arylsulfoamido group; R<sub>2</sub> and R<sub>3</sub> are independently selected from 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, and a heterocyclic group; provided that the above-mentioned alkyl, cycloalkyl, alkenyl, heterocyclic, aralkyl and aryl groups may have a substituent, and that said R<sub>2</sub> and R<sub>3</sub> may be a divalent group and form a ring;

wherein R<sub>4</sub> is selected from a hydrogen atom and a lower alkyl group having from 1 to 4 carbon atoms or a hydroxymethyl-group and R<sub>5</sub> is selected from a hydrogen atom and a lower alkyl group having from 1 to 4 carbon atoms, provided that the above-mentioned groups R<sub>4</sub> and R<sub>5</sub> may have a substituent; under a condition satisfying the equation given below;  $50 \le \ell^{0.75} \times T \le 124$ ,

wherein £ is length of a passage for said silver halide light-sensitive photographic material to be transported for processing, and is more than 0.7m and less than 3.1m, T is time in terms of seconds necessary for said silver halide light-sensitive photographic material to pass through said passage.

2. The method of claim 1, wherein the compound of formula [I] is selected from 1,2-benzoisothiazoline-3-one compounds represented by formula [III] and isothioazoline-3-one compounds of formula [IV];

$$R = \begin{cases} R & \text{S} \\ R & \text{S} \end{cases} \qquad \qquad [III]$$

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

$$\begin{array}{c|c}
R_{11} & & 0 \\
R_{12} & & & \\
\end{array}$$
[IV]

 $R_{13}$  is selected from a hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, an aralkyl group, an aryl group, a - CONHR<sub>13</sub> group and a heterocyclic group, wherein  $R_{13}$  is selected from an alkyl group, an aryl group, an alkylthio group, an arylthio group, an alkylsulfonyl group, and an arylsufonyl group, provided that the above-mentioned groups for  $R_{10}$  may independently have a substituent;  $R_{11}$  and  $R_{12}$  are independently selected from 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, and an alkylsulfonyl group, provided that the above-mentioned groups for  $R_{11}$  and  $R_{12}$  may independently have a substituent.

3. The method of claim 1, wherein the 1,2-benzoisothiazoline-3-one compound of formula [III] is contained in said photographic material at a proportion of 1 x  $10^{-5}$  to 10% by weight relative to the total amount of hydrophilic colloid contained in said photographic material.

4. The method of claim 1, wherein the thiazoline-3-one compounds of formula [IV] is contained in said photographic material at a proportion of 1  $\times$  10<sup>-4</sup> to 10% by weight relative to the total amount of hydrophilic colloid contained in said photographic material.

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5. The method of claim 3, wherein the content of the compound is  $1 \times 10^{-4}$  to 10% by weight. 6. The method of claim 3, wherein the content of the compound is  $3 \times 10^{-4}$  to 10% by weight.

FIG. I

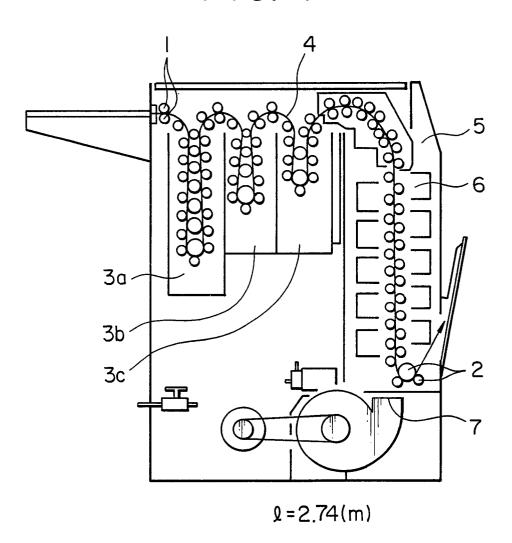
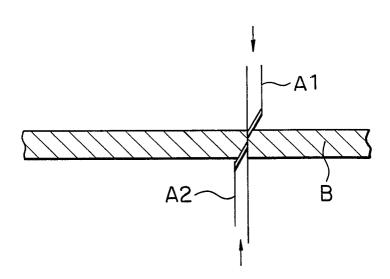
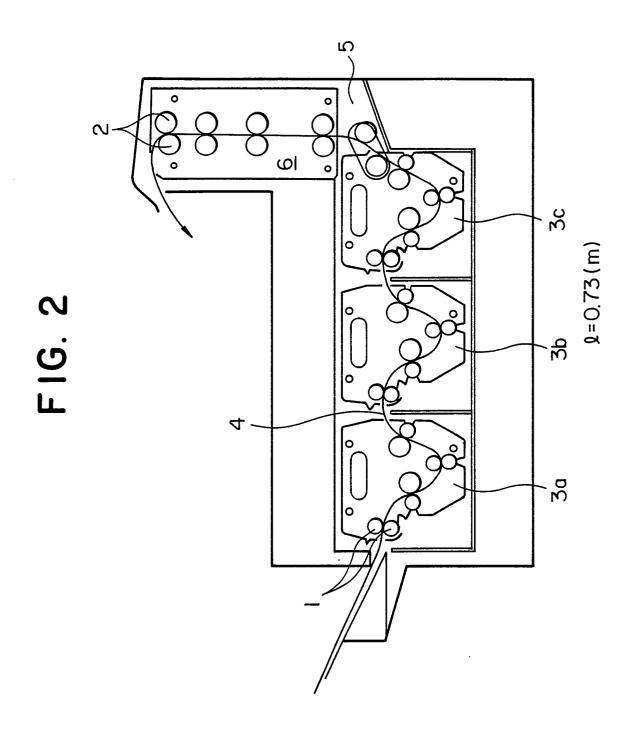


FIG. 3







# EUROPEAN SEARCH REPORT

EP 89 30 1610

				Eb 83 30 101
	DOCUMENTS CONSI	DERED TO BE RELEVA	NT	
Category	Citation of document with in of relevant pa	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)	
Y	PATENT ABSTRACTS OF 275 (P-321)[1712], & JP-A-59 142 543 (KOGYO K.K.) 15-08-14 * Abstract *	15th December 1984; KONISHIROKU SHASHIN	1-6	G 03 C 1/37 G 03 C 5/26
Y	PATENT ABSTRACTS OF 273 (P-401)[1996], JP-A-60 119 547 (KO KOGYO K.K.) 27-06-1 * Abstract *	30th October 1985; & NISHIROKU SHASHIN	1-6	
Y	GB-A-2 002 530 (FU * Claims *	JI)	1-6	
Y	AGFA-GEVAERT N.V., "Rapiline 95", no. 4 pages, Mortsel, B * Page 4: "Technisc	E	1	
Y	AGFA-GEVAERT N.V., "Scopix 12", no. MR 1981, 6 pages, Mort * Last page: "Trans	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)	
E,X	EP-A-0 308 212 (KO * Whole document * 	NICA)		
	The present search report has b	een drawn up for all claims		
<b></b> :	Place of search	Date of completion of the search	DUC	Examiner
TH	E HAGUE	09-06-1989	Busi	CHA A.J.
CATEGORY OF CITED DOCUMENTS  X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		E : earlier patent after the filin other D : document cit L : document cit	T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding	

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