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(54) Method for processing a black & white silver halide light-sensitive material.

(57) There is disclosed a processing method for a silver halide light-sensitive material, in which a nitrogen-containing compound is not contained in a fixing solution in order to reduce a nitrogen content in a washing water and a fixing speed is fast even in the case where a replenishing amount is decreased in order to reduce the amount of waste solution. The method is characterized by:

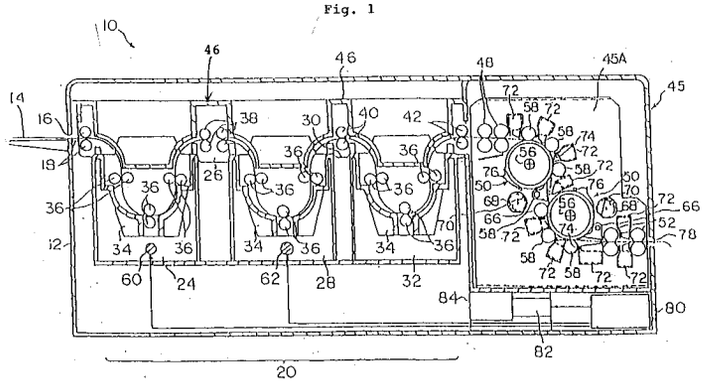
1) a developing solution having a potassium ion concentration of 0.1 mole/liter or less,

2) a fixing solution containing 0.5 to 2.5 mole/liter of sodium thiosulfate and having an ammonium ion concentration of 0.1 mole/liter or less and a water soluble aluminum compound concentration of 0.01 mole/liter or less,

3) a replenishing amount of the fixing solution at 250 ml/m^2 or less.

In certain embodiments of the present invention, the photographic material may be dried using the apparatus described in the specification.

Fig. 1



10	Automatic Developing Machine	56	Heat Source
14	Light-sensitive Material	68	Blowing Pipe (Chamber)
45	Drying Unit (Drying Apparatus for drying light-sensitive material)	70, 74	Slit
50	Heat Roller (1st and 2nd Heat Roller)	82	Fan (Drying air supply means)
		84	Heater (")

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FIELD OF THE INVENTION

The present invention relates to a method for processing a black & white silver halide light-sensitive material with an automatic developing machine, specifically to a processing method in which the replenishing amount of the fixing solution and the amount of the waste solution thereof can be reduced, the impact of washing water on environmental pollution can be lowered, and the impact on the environment generally is small.

BACKGROUND OF THE INVENTION

In general, a black and white silver halide light-sensitive material is processed by the steps of developing-fixing-washing-drying, after exposing. Most such materials are processed with an automatic developing machine in the fields of photographic plate making and X-ray photography. In these fields, attention has been given to reduction of the waste solution amount and lowering environmental pollution caused by washing water from the viewpoint of environmental protection in recent years.

The decrease in the replenishing amount of a fixing solution is effective for lowering the waste solution amount of the fixing solution. However, the reduction of the replenishing solution of the fixing solution containing a water soluble aluminum compound which acts as a hardener presents the problem that the aluminum compound is deposited, and accordingly the reduction of the replenishing amount is limited. Further, the reduction of the replenishing amount of the fixing solution delays fixing speed in a fatigued fixing solution and an inadequate replenishing amount causes inferior fixing. The method in which the amount of a fixing agent is increased for the purpose of increasing fixing speed is publicly known, but it is not preferred since it increases COD in washing water and therefore a large environmental pollution problem results from throwing away the washing water. Raising fixing temperature is effective as well for increasing fixing speed. However, it is not preferred in a practical use since it increases the generation of odor and gas from the fixing solution.

The nitrogen content in washing water is regulated from the viewpoint of the eutrophication of rivers. Ammonium thiosulfate is used as a fixing agent for a conventional fixing solution. Ammonium thiosulfate contains an elementary nitrogen and therefore the carrying over of the fixing solution in to the washing water increases the nitrogen content in the washing water. Accordingly, it is desired to replace ammonium thiosulfate with the other fixing agents. The method in which sodium thiosulfate is used as the fixing agent is described in JP-A-4-11250 (the term "JP-A" as used herein means an unexamined published Japanese patent application) and JP-A-4-11251. However, the fixing solution to which amine is added is used in these inventions and therefore the nitrogen content in the washing water can not be lowered.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a processing method for a silver halide light-sensitive material, in which a nitrogen-containing compound is not contained in the fixing solution in order to reduce the nitrogen content in a washing water and in which fixing speed is fast even where the replenishing amount is decreased in order to reduce the amount of waste solution to provide a processing method compatible with the environment.

This and other objects of the present invention can be achieved by a method for subjecting a black & white silver halide light-sensitive material to the the steps of developing, fixing and rinsing in an automatic developing machine, characterized by:

1) a developing solution having a potassium ion concentration of 0.1 mole/liter or less,

2) a fixing solution containing 0.5 to 2.5 mole/liter of sodium thiosulfate and having an ammonium ion concentration of 0.1 mole/liter or less and a water soluble aluminum compound concentration of 0.01 mole/liter or less, and

3) the replenishing amount of the fixing solution at 250 ml/m^2 or less.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a schematic view of an automatic developing machine used in the present invention.

Fig. 2 shows a schematic view of a drying unit used in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Ammonium thiosulfate has so far been used as a fixing agent for a fixing solution. Sodium thiosulfate is inferior in fixing speed to ammonium thiosulfate in the case of a fresh solution. However, the fixing speed of sodium thiosulfate is close to that of ammonium thiosulfate in the case of a fatigued solution after continuous processing with a low replenishing amount, and in the case of an even lower replenishing amount, the fixing speeds are reversed. Further, where sodium thiosulfate is used as the fixing agent, nitrogen content in a washing water is sharply decreased.

In order to decrease the replenishing amount of the fixing solution, it is necessary to accelerate the fixing speed of the fatigued fixing solution. In processing with an automatic developing machine, the developing solution is carried over to the fixing solution with the light-sensitive material. The fixing speed of the fatigued fixing solution can be accelerated by lowering the potassium ion concentration in the developing solution.

The present invention is explained below in detail.

First, the developing solution used for a development processing in the present invention is described. The combination of dihydroxybenzenes and 1-phenyl-3-pyrazolidones, or the combination of dihydroxybenzenes and p-aminophenols, is used as a developing agent for the developing solution, to readily obtain good performance.

The dihydroxybenzene developing agent used in the invention includes hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, methylhydroquinone, 2,3-dibromohydroquinone, and 2,5-dimethylhydroquinone. Of them, hydroquinone is particularly preferred.

Ascorbic acids may be used in place of hydroquinones.

The p-aminophenol developing agent used in the present invention includes N-methyl-p-aminophenol, p-aminophenol, N-(β-hydroxyethyl)-p-aminophenol, N-(4-hydroxyphenyl)glycine, 2-methyl-p-aminophenol, and p-benzylaminophenol. Among them, N-methyl-p-aminophenol is preferred.

The 3-pyrazolidone series developing agent used in the invention includes 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone, 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-p-aminophenyl-4,4-dimethyl-3-pyrazolidone, 1-p-tolyl-4,4-dimethyl-3-pyrazolidone, and 1-p-tolyl-4-methyl-4-hydroxymethyl-3-pyrazolidone.

Usually, the developing agent is used preferably in the amount of 0.001 to 1.2 mole/liter.

The sulfites used as the preservative for the developing solution in a development step in the present invention include sodium sulfite, lithium sulfite, ammonium sulfite, and sodium bisulfite. Sulfites are added preferably in the amount of 0.2 mole/liter or more, particularly preferably 0.4 mole/liter or more. The upper limit thereof is preferably 2.5 mole/liter.

The pH value of the developing solution used for the development step in the present invention falls preferably within the range of 8.5 to 13, more preferably 9 to 12.

An alkali agent used for setting pH includes a pH controlling agent such as sodium hydroxide, sodium carbonate, and sodium tertiary phosphate.

There may be used the buffer agents described in JP-A-62-186259 (borate) and JP-A-60-93433 (for example, sucrose, acetoxime, 5-sulfosalicylic acid, phosphate, and carbonate).

A potassium ion may be present in the develping solution. The amount thereof is 0 to 0.1 mole/liter, preferably 0 to 0.05 mole/liter, and more preferably 0 to 0.01 mole/liter. The potassium ion includes potassium sulfite, potassium hydroxide, and potassium carbonate.

A hardener may be used in the above developing solution.

A disaldehyde series hardener or the bisulfite adduct thereof is preferably used as the hardener. To enumerate the concrete example thereof, it is glutaraldehyde or the bisulfite adduct thereof.

There may be used as additives in the developing solution, other than those mentioned above, a development inhibitor such as sodium bromide, potassium bromide, sodium iodide, and potassium iodide; an organic solvent such as ethylene glycol, diethylene glycol, triethylene glycol, dimethylformamide, methyl cellosolve, hexylene glycol, ethanol, and methanol; and an anti-fogging agent such as a mercapto series compound including 1-phenyl-5-mercaptotetrazole and sodium 2-mercaptobenzimidazole-5-sulfonate, an indazole series compound including 5-nitroindazole, and a benzotriazole series compound including 5-methylbenzotriazole. There may be used the development accelerators described in Research Disclosure, vol. 176, No. 17643, p. 21 (December 1978), and further according to necessity, a color toning agent, a surface active agent, a defoaming agent, a softening agent, and the amino compounds described in JP-A-56-106244.

An anti-silver stain agent (for example, the compounds described in JP-A-56-24347) can be used in the developing solution.

There can be used in the developing solution, an amino compound such as the alkanolamines described in JP-A-56-106244 and European Patent Publication 0136582.

In addition thereto, there may be used the compounds described in Photographic Processing Chemistry by L.F.A. Mason, pp. 226 to 229, published by Focal Press Co., Ltd. (1966), U.S. Patents 2,193,015 and 2,592,364, and JP-A-48-64933.

Next, the fixing solution used in the fixing step in the processing method of the present invention is explained. In general, a condensate is diluted to a use solution to prepare a fixing solution. The fixing solution contains sulfite, and the concentration of sulfite in the condensate is 0.05 to 0.8 mole/liter, preferably 0.1 to 0.6 mole/liter. The condensate has pH of 5.0 or more, preferably 5.1 to 7.0, and more preferably 5.2 to 6.0, because pH of 5.0 or more causes less generation of sulfite gas and is preferred for the working environment. In diluting the condensate, the ratio of the condensate to water (condensate/water) is required to be 2 or less, preferably 0.3 to 1.4, and more preferably 0.8 to 1.2.

The fixing solution contains thiosulfate as the fixing agent, and sodium thiosulfate is mainly used as thiosulfuric acid salts. The use amount thereof in the form of a use solution is 0.5 to 2.5 mole/liter, preferably 0.8 to 1.8 mole/liter, and more preferably 1.0 to 1.5 mole/liter. Further, ammonium thiosulfate may be used. The use amount thereof in the form of the use solution does not exceed 0.1 mole/liter, preferably 0.01 mole/liter, in terms of an ammonium ion concentration.

A water soluble aluminum salt may be used in the fixing solution. The use amount thereof in the form of a use solution does not exceed 0.01 mole/liter, preferably 0.005 mole/liter.

The water soluble aluminum salt is used as a hardener in many cases. It generates a precipitate of aluminum hydroxide in the fixing solution and results in a white precipitate in the washing water. Therefore it is preferably not used for an automatic developing machine having a sufficient drying performance and transporting performance.

Further, the fixing solution can contain a preservative (for example, sulfite and bisulfite), a pH buffer agent (for example, acetic acid and boric acid), a pH controlling agent (for example, sulfuric acid), a chelating agent having a softening ability, and the compounds described in JP-A-62-78551 according to necessity.

Further, tartaric acid, citric acid, gluconic acid, malic acid, glycolic acid, and the derivatives thereof can be used in the fixing solution singly or in combination of two or more. It is particularly effective to use these compounds in the amount of 0.01 to 0.3 mole/liter in the fixing solution in the form of a use solution.

The temperature and time in the developing and fixing steps individually are preferably about 20 to 50 °C and 5 seconds to 1 minute, more preferably about 30 to 40 °C and 8 to 40 seconds. The replenishing amount of the developing solution is preferably 250 ml/m^2 or less, particularly preferably 170 ml/m^2 or less. The replenishing amount of the fixing solution is preferably 250 ml/m^2 or less, particularly preferably 200 ml/m^2 or less.

The light-sensitive material after the developing and fixing steps have been finished is then subjected to a washing or stabilizing step.

The washing or stabilizing step can be carried out at a replenishing amount of 3 liter or less (including zero, that is, washing without replenishing) per m^2 of the silver halide light-sensitive material. That is, not only does a water saving processing become possible, but also piping for settling an automatic developing machine is not necessitated.

In the case where washing is carried out with a small amount of washing water, there is more preferably provided a washing bath with a squeeze roller and a crossover roller described in JP-A-63-18350 and JP-A-62-287252. The addition of various oxidizing agents and filtration with a filter may be combined in order to reduce the effect of environmental pollution which is a problem in washng with the small amount of water.

Further, a part or all of the overflow solution effluent from the washing or stabilizing bath, which is generated by the replenishing water provided with an anti-mold treatment to the washing or stabilizing bath of the present invention, can also be utilized for a processing solution having a fixing function, which is the preceding bath thereof, as described in JP-A-60-255133.

Further, in order to avoid water spots which are likely to generate when washing with a small amount of washing water and/or to prevent a processing agent component stuck on a squeeze roller from being transferred to a processed film, a water soluble surface active agent and a defoaming agent may be added.

For the purpose of preventing a stain by a dye eluted from a light-sensitive material, a dye-adsorbing agent described in JP-A-63-163456 may be provided in the washing bath.

A stabilization step is carried out following the above washing step in some cases, and as an example thereof, there may be used for a final bath, the bath containing the compounds described in JP-A-2-201357, JP-A-2-132435, JP-A-1-102553, and JP-A-46-44446.

There can be added as well to this stabilizing bath according to necessity, an ammonium compound, a metal compound of Bi and Al, a fluorescent whitening agent, various chelating agents, a membrane pH controlling agent, a hardener, a fungicide, an anti-mold agent, alkanolamine, and a surface active agent. Preferably used as water used in a washing or stabilizing step are water subjected to a deionization processing and water sterilized with a UV bactericidal lamp and various oxidizing agents (ozone, hydrogen peroxide, and perchlorate) as well as tap water. Further, there may be used a washing water containing the compounds described in JP-A-2-147076.

According to the method of the present invention, a photographic light-sensitive material subjected to developing, fixing and washing (or stabilizing) is squeezed to remove washing water therefrom, that is, it is dried through a squeeze roller. Drying is carried out at about 40 to about 100 °C and a drying time is suitably changed according to the surrounding conditions.

Next, the automatic developing machine used in the present invention is described. The automatic developing machine used in the present invention is equipped with at least a developing unit, a fixing unit, a washing unit, and a drying unit. A rinsing unit may be provided between the developing unit and the fixing unit and/or between the fixing unit and the washing unit. The transporting means for a light-sensitive material in the automatic developing machine is preferably a roller transporting system. The transporting speed (the line speed) of the light-sensitive material can arbitrarily be set. It is preferably set at 1000 mm/minute or more, particularly preferably 1500 mm/minute or more for rapid processing.

Conventional units can be used as the developing unit, fixing unit and washing unit. The important characteristics of the automatic developing machine used in the present invention lie in the drying unit. The drying unit is explained below in detail.

The drying unit in the automatic developing machine used in the present invention is a unit for drying the light-sensitive material which is transported along a transporting path. It is characterized by the fact that the surface and back face of the light-sensitive material are each alternatively rolled on a plurality of heat rollers which are heated on the circumferences thereof with a heat source. The light-sensitive material is heated with a quantity of heat based on the temperature of the circumference of the heat roller and a contact time with the heat roller to evaporate water from the light-sensitive material face while it does not contact the heat roller.

Further, a dry wind can be blown on the light-sensitive material face which does not contact the heat roller to accelerate the evaporation of water. The circumferential temperature of the above heat roller is 80 °C or lower and the contact time of the heat roller to the light-sensitive material is 1.5 to 5 seconds.

The drying unit in the present invention is a light-sensitive material drying equipment for drying the light-sensitive material which is transported along a transporting path. It comprises, (i) first heat roller and second heat roller which have built-in heat source respectively and on which the above light-sensitive material is rolled so that one face thereof contacts a part of the circumference of the heat rollers, (ii) a chamber which has a built-in heat source and in which there are formed slits disposed along the lateral direction of the above light-sensitive material opposite to one face or another of the light-sensitive material which is transported while it is rolled on a part of the circumference of the above first heat roller and a second heat roller, and (iii) a dry wind supplying means for supplying a dry wind to the inside of the above chamber.

The temperature of the heat roller in the drying unit of the present invention and/or the temperature of a dry wind blown on the face which does not contact the heat roller can be set based on the temperature and humidity conditions of the place where the automatic developing machine is installed to carry out the drying at the necessary minimum temperatures of the heat roller and/or the dry wind blown on the face of the material which does not contact the heat roller.

According to the drying unit of the present invention, the amount of heat provided to a light-sensitive material with the heat roller is based on the temperature of the circumference of this heat roller and the contact time of the light-sensitive material to the heat roller. That is, the drying ability is determined by the product of the surface temperature of the heat roller and the contact time. Therefore, an increase in the rolling amount on the heat roller can extend the contact time without delaying the transporting speed and carry out a good drying even with a lowered temperature of the circumference of the heat roller. This can prevent superheating because of the lowered temperature on the circumference of the heat roller, even if paper clogging and film clogging occur and the light-sensitive material is stagnated in the vicinity of the heat roller. As a result, damage such as crinkling and deformation can be prevented. In heating one face with the heat roller, water is evaporated from the other face, wherein a dry wind can be blown to this other face to accelerate this evaporation and carry out drying in a short time.

In the drying unit of the present invention, the contact time of the light-sensitive material to the heat roller is as short as 1.5 to 5 seconds and therefore drying can be carried out in a total drying time of 6 to 20

seconds. Further, because the surface temperature of the heat roller is controlled to 80 °C or lower, drying with a good dimensional stability can be carried out without damaging image quality.

According to the drying unit of the present invention, the emulsion face of the light-sensitive material is heated with the first heat roller. This initiates evaporation on the back face, and the evaporation is accelerated by a dry wind supplied to a chamber with a dry wind supplying means.

Further, heating the back face of the light-sensitive material with the second heat roller initiates evaporation on the emulsion face and the evaporation is accelerated by the dry wind.

The light-sensitive material is rolled on the first heat roller and the second heat roller, and it is therefore heated for a time corresponding to this rolling amount. Accordingly, the lowered temperatures of the first heat roller and the second heat roller can be compensated for by extension of the time when the light-sensitive material contacts the first and second heat rollers, to carry out an optimum heating processing.

This can prevent crinkling due to local heating even if clogging of the light-sensitive material occurs and the light-sensitive material is stopped while in contact with the first and second heat rollers, and the quality thereof can be maintained.

Further, the temperature of the drying unit of the present invention is quite low compared with that (100 to 150 °C) of the heat roller of a conventional linear transport nipping type drying unit, and therefore its maintenance operating performance can be improved without impairing the safety of the operator during maintenance.

One embodiment of the apparatus used in the present invention is explained below with reference to the attached diagrams.

Fig. 1 is a schematic diagram of the automatic developing machine which is used in one embodiment of the present invention.

Film A with the size of 51 × 61 cm was subjected to a development processing with the automatic developing machine shown in above mentioned Fig. 1 under the environmental conditions of 27 °C and 70% RH to determine the shortest drying time during which the sample immediately after the processing becomes dry. In the experiments, after 20 sheets of the sample with the above size were continuously processed, the shortest drying time was checked. Washing was carried out with stocked water and the nitrogen content of the washing water after the processing was checked. The generating degree of a sulfur dioxide gas was checked in a fixing tank with a gas detecting tube during the processing.

There was used as the reference, FG-680A (a drying temperature: 50 °C, manufactured by Fuji Photo Film Co., Ltd.) in which there was used a hot wind blowing method in which a heat roller was not used. Both automatic developing machines were remodeled so that the trans-porting speed could be changed.

The schematic structural diagram of the automatic developing machine 10 which is a light-sensitive material processing equipment is shown in Fig. 1.

In the automatic developing machine 10, the inserting port 16 through which the light-sensitive material 14 is inserted is provided at the left side (i.e., the up stream end) of the casing 12 in Fig. 1. A pair of rollers 18 was installed at the inside of the inserting port 16 and designed to rotate with a driving means which is not illustrated. This allows the light-sensitive material 14 which is inserted through the inserting port 16 to be guided to the processing unit 20 installed in the automatic developing machine 10 with the driving power of a pair of the rollers 18.

The developing bath 24, the rinsing bath 26, the fixing bath 28, the rinsing bath 30, and the washing bath 32 are disposed in this order from the left side of Fig. 1 in the processing unit 20. A developing solution, a fixing solution and a washing water are stored in the developing bath 24, the fixing bath 26 and the washing bath 32 (hereinafter generically referred to as "the processing bath"), respectively. There are supplied a rinsing water (for example, water or an acetic acid aqueous solution) to the rinsing bath 26 and a rinsing water (for example, water) to the rinsing bath from respective stock tanks not illustrated through duct lines via pumps. Surplus rinsing water is designed to overflow from the rinsing baths 26, 30 to an overflowing bath which is not illustrated. In the case where the rinsing water is water, the duct lines may be provided directly to the rinsing baths 26 and 30 from a water supply via a solenoid valve without using a stock tank to supply tap water to the rinsing baths 26, 30, respectively.

The racks 34 are installed in the processing baths 24, 28 and 32, respectively and there are provided a plurality of pairs of rollers 36 with which the light-sensitive material 14 is nipped and transported along a prescribed transporting path. The crossover racks 46 equipped with the rinsing racks are disposed over the respective processing baths. In these crossover racks 46, the rollers 38, 40 are disposed over the rinsing baths 26, 30 to nip the light-sensitive material 14 and remove any processing solution stuck on the light-sensitive material 14 as well as quiding it to an adjacent processing bath.

The heaters 60, 62 are installed in the developing bath 24 and the fixing bath 28, respectively. These heaters 60, 62 are composed of a cylinder made of a stainless steel (for example, SUS 316) and a coil type

heater body (not illustrated) built in this cylinder as a heat source and are inserted in the processing baths 24, 28 from the side walls of the respective processing baths 24, 28 for installation. The developing solution and the fixing solution are heated with these heaters 60, 62. In starting up the operation of the automatic developing machine 10, the temperatures are set at those at which the light-sensitive material can be processed and after starting up, the temperatures are maintained at those at which the light-sensitive material can be processed.

The light-sensitive material 14 washed in the washing bath 32 is transported to the drying unit 45 adjacent to the processing unit 20 with a pair of the transporting rollers 42. In this drying unit 45, the light-sensitive material 14 after having been subjected to a washing processing with a washing water is subjected to a drying processing.

As shown in Fig. 2, the light-sensitive material 14 is inserted into the drying room 45A of the drying unit 45 from the drying room inserting port 44. The squeezing rollers 48, the two heat rollers 50, 50, and the discharging rollers 52 are installed in the drying room 45A along the transporting path for the light-sensitive material 14 and are fixed between a pair of side panels at the axes. These squeezing rollers 48, heat rollers 50 and discharging rollers 52 are designed so that the driving power of a driving means, not illustrated, is transmitted to them and the light-sensitive material 14 is transported at a fixed speed.

The light-sensitive material 14, which has water adhered to the surface thereof, is squeezed while it is nipped and transported with the squeezing rollers 48 and is guided to the circumference of one of the heat rollers 50 with the guide 74 provided at the downstream side of these squeezing rollers 48.

The two heat rollers 50 are almost vertically disposed and roll the light-sensitive material 14 on the circumference thereof to transport it.

Fig. 2 is the schematic diagram of the drying unit which shows an embodiment of the apparatus of the present invention.

As shown in Fig. 1, the rolling angle of the light-sensitive material 14 on the heat roller 50, that is, the angle from the rolling starting point (i.e., points B and D in Fig. 2) of the light-sensitive material 14 to the rolling finishing point (i.e., points C and E in Fig. 2) is about 90°.

This angle θ is set so that a prescribed contact time to the heat roller 50 can be obtained based on the major diameter of the heat roller 50 and the transporting speed of the light-sensitive material. The value based on this contact time and the peripheral temperature of the heat roller 50 is the quantity of heat given to the light-sensitive material 14. Accordingly, as shown in Fig. 2, setting the angle θ at not much more than 90° as is the case with the example of the present invention and setting the circumferential temperature of the heat roller 50 at 70°C can provide an optimum heating processing.

These heat rollers 50 are cylidrical and the heat source 56 composed of a halogen lamp heating the circumference of the heat roller 50 is coaxially disposed at each of the axis center portions. The circumference of the heat roller 50 is heated by this heat source 56.

A plurality of the nipping rollers 58 are disposed at the surroundins of the heat roller 50 and are designed to nip the light-sensitive material 14 rolled on the heat roller 50 with the circumferential face of the heat roller 50. The light-sensitive material 14 contacts the circumferential face of the heat roller 50 heated by the heat source 56 and is heated by a heat conduction from the heat roller 50.

The separating guide 66, one edge of which contacts the circumferential face of the heat roller 50 and the other edge of which is fixed at the side panel 64, is disposed in the transporting direction of the light-sensitive material 14 at the downstream side of the heat roller 50 and is designed to separate the light-sensitive material 14 rolled on the heat roller 50 from the circumferential face of the heat roller 50 at a prescribed position. The intermediate portion of the separating guide is projected toward the downstream side in the transporting direction of the light-sensitive material 14 and guides the light-sensitive material 14 separated from the heat roller 50 to the downstream side in the transporting direction.

The guides 72 are disposed at the downstream side of each of the heat rollers 50, 50 and between the discharging rollers 52. The light-sensitive material 14 sent via the squeezing roller 48, the heat roller 50 and the discharging roller 52 is guided to each of the downstream sides thereof by the guide 72.

The guide body 86 of the guide 72 is a cylinder with an almost rectangular section, in which one edge in a longitudinal direction is opened to form an aperture and the another edge is closed, the inside thereof being hollow. It constitutes the chamber. The guide 72 is disposed so that the longitudinal direction of the guide body 86 becomes the lateral direction of the light-sensitive material 14 (a perpendicular direction to a paper face in Fig. 2) and is fixed at the side panel of the drying room (not illustrated). There are disposed on the guide body 86, a plurality of ribs 90 parallel to the transporting direction of the light-sensitive material at the transporting path side thereof, and the slit 74 along the longitudinal direction of the guide body (in the lateral direction of the light-sensitive material 14).

As shown in Fig. 2, the blowing pipes 68 the insides of which are hollow are installed in the drying room 54A at the opposite side of the side on which the light-sensitive material is rolled. The slits 70 connected to the inside of the blowing pipes 68 are formed at the light-sensitive material transporting path side of the blowing pipes 68 along the lateral direction of the light-sensitive material 14. A dry wind is designed to be supplied to these blowing pipes from the dry wind supplying means as well as the above mentioned guides 72.

Accordingly, the dry winds supplied to the blowing pipes 68 and the guides 72 are blown toward the surface of the light-sensitive material 14 from the slits 70, 74. Air containing a lot of water in the vicinity of the surface of the light-sensitive material 14 heated with the heat roller 50 is removed by these dry winds.

The fan 82 and the heater 84 which are the dry wind supplying means are installed under the drying room 45A and are designed to generate a dry wind and supply it to the above mentioned blowing pipes 68 and the guide bodies 86 of the guides 72 via a duct which is not illustrated.

The environmental temperature and humidity-detecting sensor is provided at the outside of the automatic developing machine 10 to detect the environmental temperature and humidity at the place where the automatic developing machine is set and to control the temperature of the heat roller based on the conditions thereof.

The temperature sensors 76 are disposed in the vicinity of the circumferences of the respective heat rollers 50 in this drying room 45A. The surface temperature at the circumference of each of the heat rollers 50, that is, the heating temperature of the light-sensitive material, is measured with these temperature sensors 76.

The light-sensitive material 14 subjected to a drying processing in the drying room 45A is discharged from the exhaust port 78 to the external of the automatic developing machine.

The silver halide emulsion used in the present invention is prepared by dispersing silver halide such as silver chloride, silver iodide, silver bromide, silver bromochloride, silver bromoiodide, and silver bromochloroiodide in a hydrophilic colloid.

The silver halide emulsion is prepared by mixing a water soluble silver salt, a water soluble halide and water in the presence of a hydrophilic colloid by the methods well known in the art (for example, a single jet process, a double jet process, and a controlled double jet process) and subjecting it to physical ripening and chemical ripening such as a gold sensitization and/or a sulfur sensitization. The grain form of silver halide used in the present invention is not specifically limited, and there can be used cube, octahedron, sphere, of tabular silver halide grains with a high aspect ratio described in Research Disclosure 22534 (January 1983).

In case of an X-ray sensitive material, a tabular silver halide emulsion is preferably used. In this case, silver bromide or silver bromoiodide is preferred and the silver iodide content is preferably 10 mole% or less, particularly preferably 0 to 5 mole%. This emulsion can provide a high sensitivity and is suited to rapid processing.

The preferred grain form of the tabular silver halide grains has an aspect ratio of 4 or more and less than 20, more preferably 5 or more and less than 10. Further, the thickness of the grain is preferably 0.3 μm or less, particularly preferably 0.2 μm or less. The aspect ratio of the tabular silver halide grains is given by the ratio of the average value of the diameters of the circles each having the same area as the projected area of each of the tabular grains to the average value of the grain thicknesses of the respective tabular grains.

The tabular grains are present preferably in the proportion of 80 weight % or more, more preferably 90 weight % or more, based on all the grains contained in the tabular silver halide emulsion.

The use of a tabular silver halide emulsion can further increase the stability of photographic performance in the running processing according to the present invention. Further, because the coated silver amount can be reduced, the load particularly in a fixing process and a drying process can be decreased and a rapid processing becomes possible as well from this point.

The tabular silver halide emulsion is described in Cugnac and Chateau "Evolution of the Morphology of Silver Bromide Crystals During Physical Ripening", Science et Industrie Photographie, vol. 33, No. 2 (1962), pp. 121 to 125, Photographic Emulsion Chemistry by Duffin, published by Focal Press Co., Ltd., New York, 1966, pp. 66 to 72, and P.H. Tribvlli, W.F. Smith, Photographic Journal, vol. 80, p. 285 (1940). It can readily be prepared by referring to the methods described in JP-A-58-127921, JP-A-58-113927, and JP-A-58-113928.

Further, the tabular silver halide emulsion can be obtained by forming seed crystals in which the tabular grains are present in an amount of 40% or more by weight in an atmosphere of as relatively low a pBr value as 1.3 or less and growing the seed crystals by simultaneously adding a silver salt aqueous solution and a halide aqueous solution while maintaining the pBr value at the same level as that described above.

In this grain growth process, the silver salt aqueous solution and the halide aqueous solution are added desirably so that a new crystal nucleus is not generated.

The size of the silver halide grains can be controlled by adjusting the temperature, selecting the kind and amount of the solvent and controlling the silver salt used in growing the grains and the adding speed of halide.

The silver halide emulsion used in the present invention may be either a polydispersed emulsion or a monodispersed emulsion having a uniform grain size distribution. In particular, the monodispersed emulsion in which the fluctuation coefficient showing the grain distribution is 20% or less. The monodispersed emulsion is a silver halide emulsion having a grain size distribution with a fluctuation coefficient of 20% or less, particularly preferably 15% or less, wherein the fluctuation coefficient is defined by the equation:

$$\text{Fluctuation coefficient (\%)} = (\text{standard deviation}/\text{average value of grain size}) \times 100$$

The silver halide grains may be either of a composition in which the inside and the surface are even or a composition in which they are different. There may be used a silver halide emulsion prepared by mixing two or more kinds of silver halide emulsions separately prepared.

The silver halide emulsion may be of grains in which a latent image is formed mainly on the grain surface or grains in which the latent image is formed mainly in the inside of the grains. Further, it may be of grains the surface of which is fogged in advance.

A cadmium salt, a sulfite, a lead salt, a thallium salt, a rhodium salt or a complex salt thereof, and an iridium salt or a complex salt thereof may be coexistent in the silver halide emulsion used in the present invention during the process of formation of the silver halide grains or during physical ripening. In the case where a hard gradation and an improvement in reciprocity law failure characteristic are the objects, silver halide is prepared preferably in the presence of the iridium salt of 10^{-8} to 10^{-3} mole per mole of silver halide.

The silver halide emulsion used in the present invention may be an emulsion containing at least one of an iron compound, a rhenium compound, and an osmium compound. The addition amount thereof is 10^{-3} mole or less, preferably 10^{-6} to 10^{-4} mole, per mole of silver.

The silver halide emulsion used in the present invention may or may not be chemically sensitized. The known methods such as sulfur sensitization, reduction sensitization, and gold sensitization can be used as the chemical sensitiza-tion. They can be used singly or in combination thereof. The preferred chemical sensitizing method is the sulfur sensitization.

There can be used as the sulfur sensitizer, various sulfur compounds, for example, thiosulfates, thioureas, thiazoles, and rhodanines as well as the sulfur compounds contained in gelatin. Concrete examples thereof are those described in U.S. Patents 1,574,944, 2,278,947, 2,410,689, 2,728,668, 3,501,313, and 3,656,955. The preferred sulfur compounds are thiosulfate and a thiourea compound, and the pAg in the chemical sensitization falls preferably within the range of 8.3 or less, more preferably 7.3 to 8.0.

Further, as reported in Moisar, Klein Gelatine. Proc. Symp. 2nd, 301 to 309 (1976), the method in which polyvinyl pyrrolidone and thiosulfate are used in combination gives a good result as well.

Among the noble metal sensitizing methods, the gold sensitizing process is a typical one and a gold compound, mainly a gold complex salt, is used. There may be contained as well the noble metals other than gold, for example, the complex salts of platinum, palladium, and iridium. Concrete examples thereof are described in U.S Patent 2,448,060 and British Patent 618,061.

There can be used as a reduction sensitizer, stannous salts, amines, sulfinformamidine, dialkylaminoborane, and a silane compound. Concrete examples thereof are described in U.S. Patents 2,487,850, 2,518,698, 2,983,609, 2,983,610, and 2,694,637.

The silver halide grains used in the present invention are preferably subjected to a spectral sensitization with a sensitizing dye.

There may be included with the dye used, a cyanine dye, a merocycnine dye, a composite cyanine dye, a composite merocyanine dye, a holopolarcyanine dye, a hemicyanine dye, a styryl dye, or a hemioxonol dye. The particularly useful dyes are a cyanine dye, a merocynine dye, and a composite merocyanine dye. Any of the nuclei usually utilized for the cyanine dyes as a base heterocyclic nucleus can be applied to these dyes.

In particular, a carbocyanine series sensitizing dye is preferred.

To be concrete, there can be used the compounds described in Research Disclosure vol. 170, RD-17643 (December 1978), p. 23, and U.S. Patents 4,425,425 and 4,425,426.

In general, the timing for adding the sensitizing dye used in the present invention to an emulsion is before coating the emulsion on a suitable support. It may be during a chemical ripening process or a silver halide grain formation process.

A polymer and an emulsion such as an alkyl acrylate latex and a surfactant such as polyols including trimethylolpropane can be incorporated into the emulsion layer of the light-sensitive material of the present invention in order to improve its pressure characteristic.

The photographic emulsion layers and other hydrophilic colloid layers of the light-sensitive material prepared according to the present invention may contain various surface active agents for various purposes such as aiding coating, the prevention of electrification, the improvement in a sliding performance, the promotion of emulsification-dispersion, the prevention of sticking, and the improvement of the photographic characteristics (for example, development acceleration, harder gradation and sensitization).

There can be used, for example, the nonionic surface active agents such as saponin (a steroid series), an alkylene oxide derivative (for example, polyethylene glycol, a polyethylene glycol/polypropylene glycol condensation product (polyethylene glycol alkyl ethers, polyethylene glycol alkyl aryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or amides, and polyethylene oxide adducts of silicon), a glycidol derivative (for example, alkenylsuccinic acid polyglyceride and alkylphenol polyglyceride), fatty acid esters of polyhydric alcohol, and alkyl esters of sucrose; the anionic surface active agents having acid groups including a carboxy group, a sulfo group, a phospho group, a sulfuric acid ester group and a phosphoric acid ester group, such as an alkylcarbonic acid salt, an alkylsulfonic acid salt, an alkylbenzenesulfonic acid salt, an alkylnaphthalenesulfonic acid salt, alkylsulfuric acid esters, alkyl phosphoric acid esters, N-acyl-N-alkyltaurines, sulfosuccinic acid esters, sulfoalkyl polyoxyethylenealkylphenyl ethers, and polyoxyethylene alkylphosphoric acid esters; the amphoteric surface active agents such as amino acids, aminoalkylsulfonic acids, aminoalkylsulfonic acid or phosphoric acid esters, alkylbetains, and amine oxides; and the cationic surface active agents such as alkylamine salts, aliphatic or aromatic quaternary ammonium salts, pyridinium, heterocyclic quaternary ammonium salts such as imidazolium, and aliphatic or heterocycle-containing phosphonium or sulfonium salts.

The silver halide light-sensitive material used in the present invention comprises at least one silver halide emulsion layer on a support. In the case of a direct medical X-ray sensitive material, a light-sensitive material having at least one silver halide emulsion layer on both sides of the support is preferred as described in JP-A-58-127921, JP-A-59-90841, JP-A-58-111934, and JP-A-61-201235.

In addition to the above, the light-sensitive material according to the present invention can have an intermediate layer, a filter layer, and an anti-halation layer according to necessity.

The coated silver amount in the light-sensitive material used in the present invention is preferably 0.5 to 5 g/m^2 (one side), more preferably 1 to 4 g/m^2 (one side).

It preferably does not exceed 5 g/m^2 for rapid processing suitability. It is preferably 0.5 g/m^2 or more, in order to obtain a constant image density and contrast.

Gelatin is advantageously used as a binder or protective colloid for a photographic emulsion. In addition to gelatin, the other hydrophilic colloids can be used as well. There can be used, for example, proteins such as a gelatin derivative, a graft polymer of gelatin and the other polymers, albumin, and casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfuric acid esters; sucrose derivatives such as sodium alginate and a starch derivative; and various synthetic hydrophilic high molecular materials such as homopolymers or copolymers of vinyl alcohol, partially-acetalized vinyl alcohol, N-vinyl-pyrrolidone, acrylic acid, methacrylic acid, acrylamide, vinylimidazole, and vinylpyrazole.

In addition to lime-treated gelatin, acid-treated gelatin may be used as gelatin, and a gelatin hydrolysis product and a gelatin enzyme-decomposed product can be used as well.

An organic material which will be effluent in a development processing process is preferably incorporated into an emulsion layer or the other hydrophilic colloid layers particularly in an X-ray sensitive material. In the case where the effluent material is gelatin, a gelatin of the kind which is not subject to a crosslinking reaction of gelatin with a hardener is preferred. For example, acetalized gelatin and phthalized gelatin correspond to this. Those having a small molecular weight are preferred.

Meanwhile, there can be effectively used as a high molecular material other than gelatin, a hydrophilic polymer such as polyacrylamide described in U.S. Patent 3,271,158, polyvinyl alcohol, and polyvinylpyrrolidone, and sugars such as dextran, sucrose, and pulran are effective as well. Among them, polyacrylamide and dextran are preferred and polyacrylamide is the particularly preferred material. The average molecular weight of these materials is preferably 20,000 or less, more preferably 10,000 or less. The effluent amount thereof during a processing is effectively 10% or more and 50% or less, preferably 15% or more and 30% or less, based on the total weight of the coated organic materials excluding the silver halide grains.

The layer containing the organic material which is effluent in the processing according to the present invention may be either an emulsion layer or a surface protective layer. In the case where the total coated amount of the organic material is fixed, it is incorporated preferably into both of the surface protective layer and the emulsion layer, rather than only into the emulsion layer. Further, it is more preferably incorporated only into the surface protective layer. In the light-sensitive material in which the emulsion layer is of a multi-layer structure, a greater amount of the organic material is incorporated preferably into the emulsion layer closer to the surface protective layer in the case where the total coated amount of the organic material is fixed.

In the present invention, there can be used as a matting agent, the fine particles of an organic compound such as a homopolymer of polymethyl methacrylate or a copolymer of methyl methacrylate and methacrylic acid as described in U.S. Patents 2,992,101, 2,701,245, 4,142,894, and 4,396,706, and starch, and an inorganic compound such as silica, titanium dioxide, strontium sulfate, and barium sulfate. The particle size thereof is preferably 1.0 to 10 μm, particularly preferably 2 to 5 μm.

In the silver halide light-sensitive material according to the present invention, a photographic emulsion layer or the other layers may be colored with a dye for the purpose of absorbing rays with a specific wavelength, that is, for the purposes of preventing halation and irradiation and providing a filter layer to control the spectral composition of the rays incident upon the photographic emulsion layer. In a duplicated film such as a direct medical Roentgen film, the layer which is aimed at crossover cutting may be provided under the emulsion layer. There can be mentioned as such a dye, an oxonol dye having a pyrazolone nucleus and a barbituric acid nucleus, an azo dye, an azomethine dye, an anthraquinone dye, an allylidene dye, a styryl dye, a triarylmethane dye, a merocyanine dye, and a cyanine dye.

In using these dyes, it is an effective technique to mordant an anionic dye to a specific layer in the light-sensitive material with a polymer having a cationic site. In this case, the dye which is irreversibly decolored in the developing-fixing-washing processes is preferably applied. The layer to which the dye is mordanted with the polymer having the cationic site may be an emulsion layer, a surface protective layer, or the opposite side of the emulsion layer on a support. It is preferably between the emulsion layer and the support. In particular, the dye is mordanted ideally to a subbing layer for the purpose of the crossover cutting of an X-ray duplicated film for medical use.

A nonionic surface active agent of an ethylene oxide series can be used as a coating aid for the subbing layer preferably in combination with a polymer having a cationic site.

An anion-converted polymer is preferred as the polymer providing the cationic site.

The various known quaternary ammonium salt (or a phosphonium salt) polymers can be used as the anion-converted polymer. The quaternary ammonium salt (or a phosphonium salt) polymers are widely known as a mordant polymer and an antistatic polymer in the publications mentioned below.

There can be mentioned the water-dispersed latexes described in JP-A-59-166940, U.S. Patent 3,958,995, and JP-A-55-142339, JP-A-54-126027, JP-A-54-155835, JP-A-53-30328, and JP-A-54-92274; the polyvinyl-pyridinium salts described in U.S. Patents 2,548,564, 3,148,061, and 3,756,814; the water soluble quaternary ammonium salt polymers described in U.S. Patent 3,709,690; and the water insoluble quaternary ammonium salt polymers described in U.S. Patent 3,898,088.

Further, in order to prevent transferring from a prescribed layer to the other layers or a processing solution and there exerting a photographically undesirable affect, an aqueous polymer latex prepared by copolymerizing a monomer having at least two or more (preferably 2 to 4) ethylenically unsaturated groups and crosslinking the copolymer is particularly preferably used.

The solid matter dispersing method described in JP-A-55-155350 and WO88/0479 is also effective as a fixing method for a dye.

The light-sensitive material used in the present invention may be designed so that a super hard gradation photographic characteristic is shown with a hydrazine nucleus-forming agent. This system and the hydrazine nucleus-forming agent to be used are described in the following literature references. In particular, this system is suitably used for in graphic arts: Research Disclosure Item 23516 (November 1983, p. 346) and the publications cited therein, and in addition, U.S. Patents 4,080,207, 4,269,929, 4,276,364, 4,278,748, 4,385,108, 4,459,347, 4,560,638, and 4,478,928, British Patent 2,011,391B, JP-A-60-179734, JP-A-62-270948, JP-A-63-29751, JP-A-61-170733, JP-A-61-270744, and JP-A-62-948, EP 217,310, JP-A-63-32538, JP-A-63-104047, JP-A-63-121838, JP-A-63-129337, JP-A-63-234245, JP-A-63-234246, JP-A-63-223744, JP-A-63-294552, JP-A-63-306438, and JP-A-64-10233, U.S. Patent 4,686,167, and JP-A-62-178246, JP-A-63-234244, JP-A-64-90439, JP-A-1-276128, JP-A-1-283548, JP-A-1-280747, JP-A-1-283549, JP-A-1-285940, JP-A-2-2541, JP-A-2-139538, JP-A-2-177057, JP-A-2-198440, JP-A-2-198441, JP-A-2-198442, JP-A-2-196234, JP-A-2-196235, JP-A-2-220042, JP-A-2-221953, and JP-A-2-221954.

When the hydrazine nucleus-forming agent is incorporated into a photographic light-sensitive material, it is incorporated preferably into a silver halide emulsion layer, but it may be incorporated into a different non-light-sensitive hydrophilic colloid layer (for example, a protective layer, an intermediate layer, a filter layer, and an anti-halation layer). The addition amount of the hydrazine nucleus-forming agent falls preferably within the range of 1×10^{-6} to 5×10^{-2} mole, particularly preferably 1×10^{-5} to 2×10^{-2} mole, per mole of silver halide.

Various compounds containing an N or S atom in addition to the compounds shown in JP-A-53-77616, JP-A-54-37732, JP-A-53-137133, JP-A-60-140340, and JP-A-60-14959 are effective as a development accelerator suitable for use in this super hard gradation system or as an accelerator for a nucleus-forming infectious development.

These accelerators are different with respect to their optimum addition amount according to the kind of compound. They are used desirably in the range of 1.0×10^{-3} to 0.5 g/m^2, preferably 5.0×10^{-3} to 0.1 g/m^2.

Further, in the super hard gradation system, a redox compound releasing a development inhibitor can be used in combination. There can be used as this redox compound, the compounds described in JP-A-2-293736, JP-A-2-308239, JP-A-1-154060, and JP-A-1-205885. The use amount thereof falls preferably within the range of 1×10^{-6} to 5×10^{-2} mole, particularly preferably 1×10^{-5} to 1×10^{-2} mole, per mole of silver halide.

Various compounds can be incorporated into the light-sensitive material according to the present invention for the purpose of preventing fog during manufacturing, during the storage or during the photographic processing of the light-sensitive material, or for stabilizing a photographic performance. That is, there can be added many compounds known as an anti-fogging agent and a stabilizer, such as azoles, for example, a benzothiazolium salt, nitroindazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptotetrazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptothiadiazoles, aminotriazoles, benzothiazoles, and nitrobenzotriazoles; mercaptotriazines; a thioketo compound such as, for example, oxazolinethione; azaindenes, for example, triazaindenes, tetraazaindenes (paricularly 4-hydroxysubstituted (1,3,3a,7)tetraazaindenes), and pentaazaindenes; benzenethiosulfonic acid, benzenesulfinic acid, and benzeneosulfonic amide. Among these compounds, preferred are benzotriazoles (for example, 5-methylbenzotriazole) and nitroindazoles (for example, 5-nitroindazole). These compounds may be contained in a processing solution. Further, the compounds releasing an inhibitor during processing described in JP-A-6230243 can be incorporated working as a stabilizer or preventing a black speck.

A developing agent such as a hydroquinone derivative and a phenidone derivative can be incorporated into the light-sensitive material according to the present invention to function as a stabilizer or an accelerator.

An inorganic or organic hardener may be incorporated into a photographic emulsion layer and the other hydrophilic colloid layers in the light-sensitive material according to the present invention. There can be used singly or in combination, for example, a chromium salt (chromium alum and chromium acetate), aldehydes (formaldehyde and glutaraldehyde), an N-methylol compound (dimethylolurea), a dioxane derivative, an active vinyl compound (1,3,5-triacryloyl-hexahydro-s-triazine and 1,3-vinylsulfonyl-2-propanol), an active halogen compound (2,4-dichloro-6-hydroxy-s-triazine), and mucohalogenic acids (mucochloric acid).

There may be incorporated into the light-sensitive material according to the present invention, a hydroquinone derivative (a so-called DIR-hydroquinone) releasing a development inhibitor to a photographic emulsion layer and the other hydrophilic colloid layers according to the density of the image during developing.

Concrete examples thereof include, the compounds described in U.S. Patents 3,379,529, 3,620,746, 4,377,634, and 4,332,878, and JP-A-49-129536, JP-A-54-67419, JP-A-56-153336, JP-A-56-153342, JP-A-59-278853, JP-A-59-90435, JP-A-59-90436, and JP-A-59-138808.

A dispersion of a water insoluble or slightly soluble synthetic polymer can be incorporated into the light-sensitive material according to the present invention for the purpose of dimensional stability. There can be used, for example, a polymer in which the monomer component thereof comprises a single component or a combination of alkyl (meth)acrylate, alkoxyalkyl (meth)acrylate, and glycidyl (meth)acrylate, or a combination of acrylic acid and methacrylic acid therewith.

A compound having an acid group is preferably incorporated into the silver halide emulsion layer and the other layers of the light-sensitive material according to the present invention. There can be mentioned as the compound having the acid group, an organic acid such as salicylic acid, acetic acid, and ascorbic acid, and a polymer or a copolymer having an acid monomer such as acrylic acid, maleic acid and phthalic acid as a repetitive unit. These compounds are described in JP-A-61-223834, JP-A-61-228437, JP-A-62-25745, and JP-A-62-55642. Of these compounds, particularly preferred are ascorbic acid as a low molecular compound and an aqueous dispersible latex of the copolymer consisting of an acid monomer such as

acrylic acid and a crosslinkable monomer having two or more unsaturated groups such as divinylbenzene as a high molecular compound.

The silver halide emulsion thus prepared is coated on the support of a cellulose acetate film and a polyethylene terephthalate film by a dipping method, an air knife method, a bead method, an extrusion doctor method, and a duplex coating method.

Various photographic additives capable of being used in the present invention are described in, for example, above mentioned Research Disclosures pp. 23 to 28 of No. 17643 and pp. 648 to 651 of No. 18716. These additives and the passages describing them are shown below.

Kind of Additive	RD 17643	RD 18716
1. Chemical sensitizer	p.23	p. 648, right colmn.
2. Sensitivity improver	-	p. 648, right colmn.
3. Spectral sensitizer & supersensitizer	pp. 23 to 24	p. 648, right colmn. to p. 649, right colmn.
4. Whitening agent	p. 24	-
5. Anti-foggant & stabilizer	pp. 24 to 25	p. 649, right colmn.
6. Light absorber, filter dye, & UV absorber	pp. 25 to 26	p. 649, right colmn. to p. 650, left colmn.
7. Anti-stain agent	p. 25, right colmn.	p. 650, left colmn. to right colmn.
8. Dye image stabilizer	p. 25	-
9. Hardener	p. 26	p. 651, left colmn.
10. Binder	p. 26	p. 651, left colmn.

The present invention is concretely explained below with reference to examples.

EXAMPLE 1

(1) Preparation of Emulsions

Preparation of Emulsion A

Solution 1:	
Water	1.0 liter
Gelatin	20 g
Sodium chloride	20 g
1,3-Dimethylimidazolidine-2-thione	20 mg
Sodium benzenethiosulfonate	8 mg

Solution 2:	
Water	400 ml
Silver nitrate	100 g

Solution 3:	
Water	400 ml
Sodium chloride	27.1 g
Potassium bromide	21 g
Potassium hexachloroiridate (III) (0.001% aqueous solution)	15 ml
Potassium hexabromorhodate (III) (0.001% aqueous solution)	1.5 ml

Solution 2 and Solution 3 were simultaneously added to Solution 1 maintained at 38 °C and pH 4.5 over a period of 10 minutes while stirring to form a nuclear grain of 0.16 μm. Subsequently, the following

Solution 4 and Solution 5 were added over a period of 10 minutes. Further, potassium iodide 0.15 g was added to finish the grain formation.

Solution 4:	
Water	400 ml
Silver nitrate	100 g

Solution 5:	
Water	400 ml
Sodium chloride	27.1 g
Potassium bromide	21 g
Potassium hexacyanoferrate (III) (0.1% aqueous solution)	5 ml

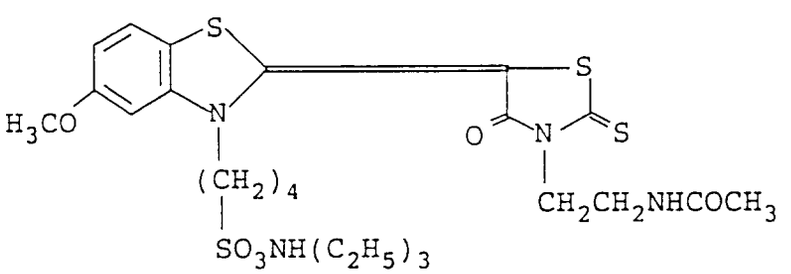
Subsequently, the emulsion thus prepared was washed by a conventional flocculation method and gelatin 30 g was added.

The emulsion was adjusted to pH 5.3 and to pAg 7.5, and sodium thiosulfate (2.6 mg), triphenylphosphine selenide (1.0 mg), and chlorauric acid (6.2 mg) were added thereto. Further, sodium benzenethiosulfonate (4 mg) and sodium benzenethiosulfinate (1 mg) were added, whereby the emulsion was subjected to chemical sensitization so that an optimum sensitivity could be obtained at 55 °C.

There were added 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (200 mg) as a stabilizer and phenoxyethanol as an antiseptic agent, whereby there was obtained a silver bromochloroiodide cubic grain emulsion finally containing silver chloride of 70 mole% and having an average grain size of 0.2 μm (fluctuation coefficient: 9%).

(2) Preparation of the Coated Sample

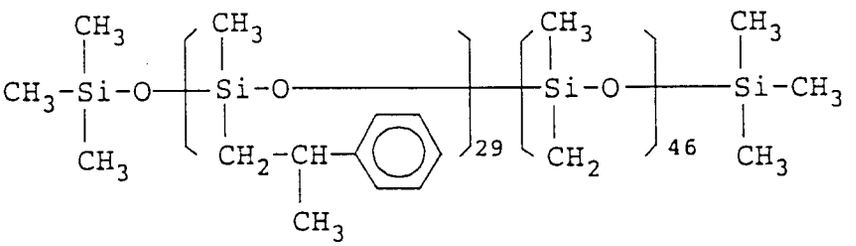
An ortho sensitizing dye (the following compound) was added to the above emulsion in the amount of 5×10^{-4} mole/mole Ag to subject it to ortho sensitization. There were added hydroquinone and 1-phenyl-5-mercaptotetrazole as an anti-fogging agent in the amounts of 2.5 g and 50 mg per mole of Ag, respectively, a polyethyl acrylate latex as a plasticizer in the ratio of 25% based on the amount of gelatin binder, 2-bis-(vinylsulfonylacetoamide)ethane as a hardener, and further colloidal silica in the ratio of 40% based on the amount of gelatin binder. The coating solution thus prepared was applied on a polyester support to Ag 3.0 g/m^2 and gelatin 1.0 g/m^2. A lower protective layer and an upper protective layer each having the following composition were coated thereon.



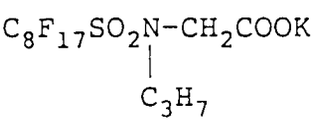
Lower protective layer:	
Gelatin	0.25 g/m^2
Sodium benzenethiosulfonate	4 mg/m^2
1,5-Dihydroxy-2-benzaldoxime	25 mg/m^2
Polyethyl acrylate latex	125 mg/m^2

Upper protective layer:	
Gelatin	0.25 g/m^2
Silica matting agent with the average particle size of 2.5 μm	50 mg/m^2
Compound (1) (gelatin dispersion) Colloidal silica with a particle size of 10 to 20 μm	30 mg/m^2
Compound (2)	5 mg/m^2
Sodium dodecylbenzenesulfonate	22 mg/m^2

Compound (1)



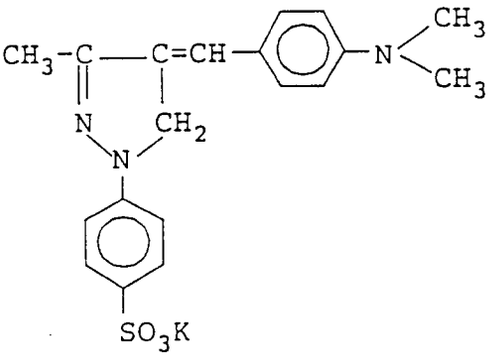
Compound (2)



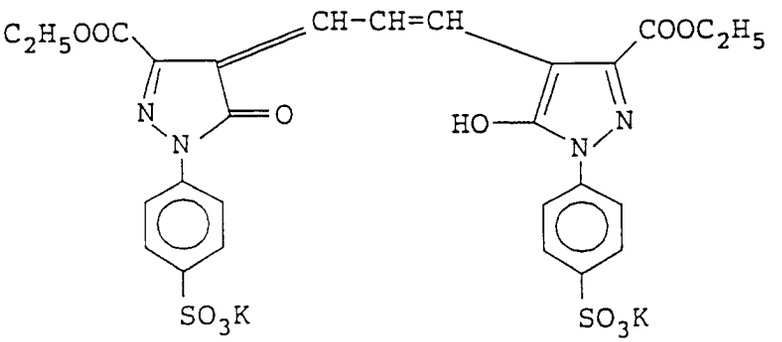
The support used in the present examples had a back layer and a back protective layer each having the following composition:

Back layer:	
Sodium dodecylbenzenesulfonate	80 mg/m^2
Compound (3)	70 mg/m^2
Compound (4)	85 mg/m^2
Compound (5)	90 mg/m^2
1,3-Divinylsulfonyl-2-propanol	60 mg/m^2

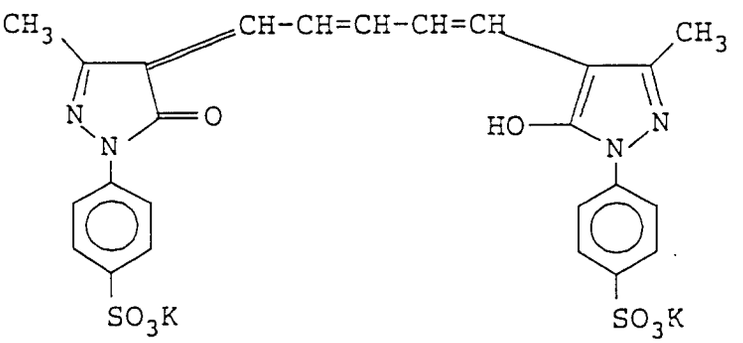
Compound (3)



Compound (4)



Compound (5)



Back protective layer:	
Gelatin	0.5 g/m^2
Polymethyl methacrylate (grain size: 4.7 μm)	30 mg/m^2
Sodium dodecylbenzenesulfonate	20 mg/m^2
Above compound (2)	2 mg/m^2
Above compound (1) (gelatin dispersion)	100 mg/m^2

Developing solution:		
	Developing Solution-A	Developing Solution-B
Diethylenetriaminepentacetic acid	2.0 g	2.0 g
Sodium carbonate	5.0 g	5.0 g
Boric acid	10.0 g	10.0 g
2,3,5,6,7,8-hexahydro-2-thioxo-4-(1H)-quinazolinone	0.1 g	0.1 g
Potassium sulfite	85.0 g	-
Sodium sulfite	-	67.7 g
Sodium bromide	6.0 g	6.0 g
Diethylene glycol	40.0 g	40.0 g
5-Methylbenzotriazole	0.2 g	0.2 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	0.3 g	0.3 g
Hydroquinone	30.0 g	30.0 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	1.6 g	1.6 g
Water was added to (after adjusting pH)	1 liter	1 liter
pH (adjusted with potassium hydroxide and sodium hydroxide)	10.7	10.7

Fixing solution:	
Sodium thiosulfate pentahydrate	refer to Table 1
Ammonium thiosulfate (70 weight%/volume)	refer to Table 1
Disodium ethylenediaminetetraacetate	0.025 g
Sodium sulfite	7.0 g
Sodium metabisulfite	20.0 g
Aluminum sulfate	refer to Table 1
Water was added to	1 liter
pH	5.6

The sample thus obtained was subjected to a running test with the automatic developing machine FG-680A manufactured by Fuji Photo Film Co., Ltd. at the following conditions.

Step	Temparature	Time
Developing	38 °C	20 seconds
Fixing	37 °C	18.9 seconds
Washing	26 °C	18.3 seconds
Drying	55 °C	24.0 seconds
Total		85.4 seconds

In the running test, a film of the size of 50.8 cm × 61.0 cm was processed by 450 sheets per day and the running was carried out for 2 days. The replenishing amount of a developing solution was 50 ml per film and the replenishing amount per film of a fixing solution is shown on Table 1. A washing water flowed in the amount of 2 liter per minute. The automatic developing machine FG-680A was remodeled so that it could be operated at a high speed up to a developing time of 8 seconds.

After the running was finished, the fixing time was changed while passing the sample of the above size. The fixing time was determined by the time when a fixing drop failure was generated (the partial generation was judged as the fixing drop failure).

The status of the fixing solution was checked observing the precipitate in the rack after the running was finished.

The nitrogen content in a washing water was determined by analyzing the washing water after the running was finished.

The composition of the fixing solution and the running results are shown in Table 1.

TABLE 1

Experiment No.	Fixing solution: Sodium thiosulfate (mole/ℓ)	Fixing solution: Ammonium thiosulfate (mole/ℓ)	Fixing solution: Aluminum sulfate (g/ℓ)	Fixing solution: Replenishing amount (ml/Dz)	Developing solution	Fixing time (sec.)	Status of fixing solution	Nitrogen content* (ppm)
1 (Comp.)	0.3	-	-	60	Solution B	>40	Clear	7
2 (Inv.)	1.0	-	-	60	Solution B	11.0	Clear	9
3 (Inv.)	1.2	-	-	60	Solution B	9.2	Clear	9
4 (Inv.)	1.5	-	-	60	Solution B	7.3	Clear	8
5 (Inv.)	1.8	-	-	60	Solution B	9.7	Clear	7
6 (Comp.)	2.3	-	-	60	Solution B	15.0	Clear	5
7 (Comp.)	1.2	-	15	60	Solution B	10.5	Cloudy	7
8 (Comp.)	-	1.2	-	60	Solution B	9.3	Clear	93
9 (Comp.)	-	1.2	15	60	Solution B	10.7	Cloudy	85
10 (Comp.)	1.2	-	-	60	Solution A	16.2	Clear	7
11 (Comp.)	1.5	-	-	60	Solution A	14.2	Clear	8
12 (Comp.)	1.8	-	-	60	Solution A	16.7	Clear	7
13 (Comp.)	2.3	-	-	60	Solution A	22.4	Clear	9
14 (Inv.)	1.2	-	2	60	Solution B	9.5	Clear	6
15 (Inv.)	1.2	0.05	-	60	Solution B	9.3	Clear	12

TABLE 1 (continued)

Experiment No.	Fixing solution: Sodium thiosulfate (mole/ℓ)	Fixing solution: Ammonium thiosulfate (mole/ℓ)	Fixing solution: Aluminum sulfate (g/ℓ)	Replenishing amount (ml/Dz)	Developing solution	Fixing time (sec.)	Status of fixing solution	Nitrogen content* (ppm)
16 (Comp.)	1.2	0.20	-	60	Solution B	8.5	Clear	35
17 (Inv.)	1.5	-	-	40	Solution B	9.3	Clear	8
18 (Comp.)	1.5	-	-	40	Solution A	19.5	Clear	7
19 (Inv.)	1.5	-	-	20	Solution B	12.3	Clear	5
20 (Comp.)	1.5	-	-	20	Solution A	23.4	Clear	9
21 (Comp.)	-	1.5	-	40	Solution B	8.7	Clear	100
22 (Comp.)	-	1.5	-	40	Solution A	22.6	Clear	87
23 (Comp.)	-	1.5	-	20	Solution B	11.9	Clear	88
24 (Comp.)	-	1.5	-	20	Solution A	25.9	Clear	97

* in washing water

As apparent from the results shown in Table 1, it can be found that while the fixing time is slightly delayed in case of Solution B containing no potassium ion in the developing solution, the fixing time is delayed to a large extent in case of Solution A containing the potassium ion. In a low replenishing region in which the replenishing amount of the fixing solution falls within this range, the fixing solution in finishing the running gets cloudy in the case where aluminum sulfate is contained as a hardener. Further, in the case where ammonium thiosulfate is used as a fixing agent, the nitrogen content in the fixing solution is high,

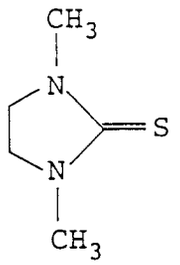
which is not preferable from the viewpoint of environmental pollution. It can be found that the replenishing amount of the fixing solution is small in the present invention and that the present invention provides a processing method in which the environmental pollution in the washing water is low.

EXAMPLE 2

(1) Preparation of the silver halide emulsion

Gelatin (40 g) was dissolved in water (1 liter) and sodium chloride (6 g), potassium bromide (0.4 g), and Compound [1]:

Compound [I]



Sixty mg of this solution were put in a vessel heated at 53 °C. Then, an aqueous solution (600 ml) containing silver nitrate (100 g) and an aqueous solution (600 ml) containing potassium bromide (56 g) and sodium chloride (7 g) were added by a double jet method to form a core portion containing 20 mole% silver chloride. Subsequently, an aqueous solution (500 ml) containing silver nitrate (100 g) and an aqueous solution (500 ml) containing potassium bromide (40 g), sodium chloride (14 g) and potassium hexachloroiridate (III) (10^{-7} mole/mole silver) were added by a double jet method to form a shell portion containing 40 mole% silver chloride, whereby so-called core/shell type cubic monodispersed silver bromochloride grains having an average grain size of 0.35 μm were prepared.

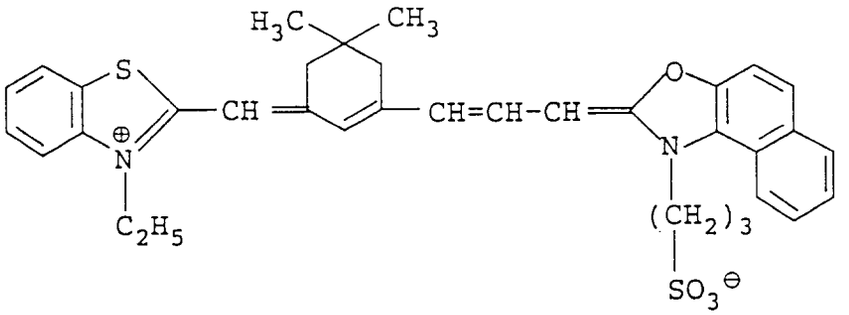
After this emulsion was subjected to a desalting processing, gelatin (40 g) was added, and pH and pAg were adjusted to 6.0 and 8.5, respectively, followed by adding triethyl thiourea (2 mg), chlorauric acid (4 mg), and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (0.2 g) to thereby provide a chemical sensitization at 60 °C.

(2) Preparation of the emulsion layer coating solutions

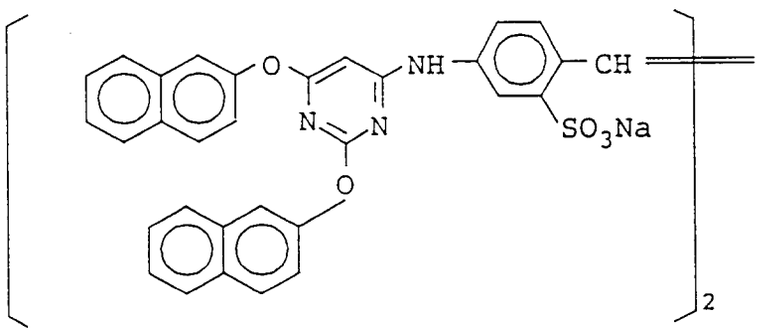
The vessel in which the emulsion (850 g) was put and weighed was heated to 40 °C and the additives were added in the manner shown below to prepare the emulsion layer coating solution.

Composition of the emulsion layer coating Solution A:	
Emulsion	850 g
Spectral Sensitizing Dye [II]	1.2×10^{-4} mole
Supersensitizer [III]	0.8×10^{-3} mole
Preservativity Improver [IV]	1×10^{-3} mole
Polyacrylamide (molecular weight: 40,000)	7.5 g
Trimethylolpropane	1.6 g
Poly(sodium styrenesulfonate)	2.4 g
Poly(ethyl acrylate/methacrylic acid) latex	16 g
N,N'-ethylenebis-(vinylsulfonacetoamide)	1.2 g

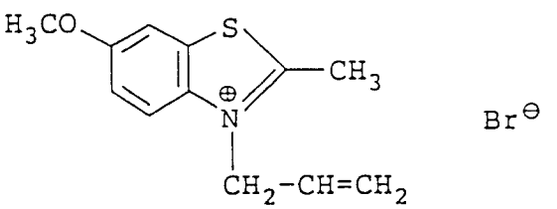
Spectral Sensitizing Dye [II]



Supersensitizer [III]



Preservativity Improver [IV]



(3) Preparation of the surface protective layer coating solution for the emulsion layer

A vessel was heated to 40 °C and the additives were added in the manner shown below to prepare the coating solution.

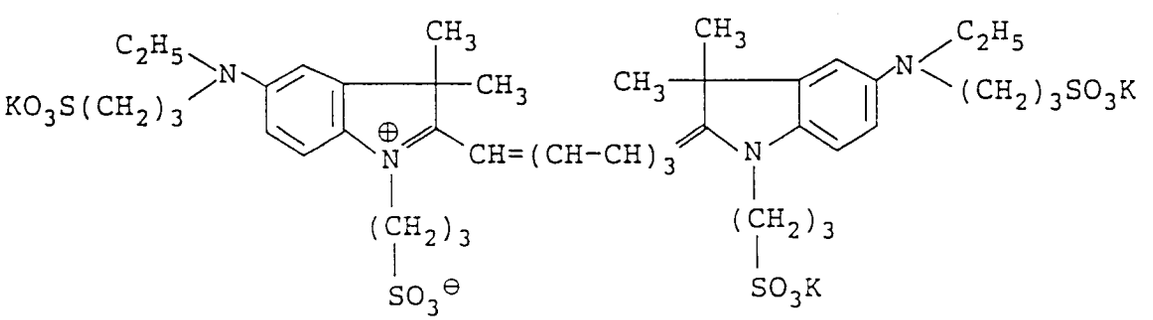
Composition of the surface protective layer coating solution for the emulsion layer:	
Gelatin	100 g
Polyacrylamide (molecular weight: 40,000)	10 g
Poly(sodium styrenesulfonate) (molecular weight: 600,000)	0.6 g
N,N'-ethylenenebis-(vinylsulfonacetoamide)	1.5 g
Polymethyl methacrylate fine grains (average grain size: 2.0 μm)	2.2 g
Sodium t-octylphenoxyethoxyethanesulfonate	1.2 g
$C_{16}H_{33}O$-$(CH_2CH_2O)_{10}$-H	2.7 g
Poly(sodium acrylate)	4 g
$C_8F_{17}SO_3K$	70 mg
$C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_4(CH_2)_4$-$SO_3Na$	70 mg
NaOH (1N)	4 ml
Methanol	60 ml

(4) Preparation of the back layer coating solution

A vessel was heated to 40 °C and the additives were added in the manner shown below to prepare the back layer coating solution.

Composition of the back layer coating solution:	
Gelatin	80 g
Dye [V]	3.1 g
Poly(sodium styrenesulfonate)	0.6 g
Poly(ethyl acrylate/methacrylic acid) latex	15 g
N,N'-ethylenenebis-(vinylsulfonacetoamide)	4.3 g

Dye [V]



(5) Preparation of the surface protective layer coating solution for the back layer

A vessel was heated to 40 °C and the additives were added in the manner shown below to prepare the coating solution.

Composition of the surface protective layer coating solution for the back layer:	
Gelatin	80 g
Poly(sodium styrenesulfonate)	0.3 g
N,N'-ethylenebis-(vinyl-sulfonacetoamide)	1.7 g
Polymethyl methacrylate fine grains (average grain size: 4.0 μm)	4 g
Sodium t-octylphenoxyethoxyethanesulfonate	3.6 g
NaOH (1N)	6 ml
Poly(sodium acrylate)	2 g
$C_{16}H_{33}O$-$(CH_2CH_2O)_{10}$-H	3.6 g
$C_8F_{17}SO_3K$	50 mg
$C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_4(CH_2)_4$-$SO_3Na$	50 mg
Methanol	130 ml

(6) Preparation of the coated sample

The above mentioned back layer coating solution was coated on a polyethylene terephthalate support together with the surface protective layer coating solution for the back layer so that the total gelatin coating amount was 3 g/m^2. Subsequently, the above mentioned emulsion layer coating solution and surface protective layer coating solution were applied on the opposite side of the support so that the coated Ag amount and the gelatin coating amount of the surface protective layer were 2.5 g/m^2 and 1 g/m^2, respectively

Next, the composition of the developing condensate is shown below:

Developing condensate (concentrated by 2.5 times)		
	Solution A	Solution B
Potassium hydroxide	43 g	-
Sodium hydroxide	-	31 g
Sodium sulfite	100 g	200 g
Potassium sulfite	126 g	-
Diethylenetriaminepentaacetic acid	5 g	5 g
Boric acid	20 g	20 g
Hydroquinone	85 g	85 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	15 g	15 g
Diethylene glycol	30 g	30 g
5-Methylbenzotriazole	0.2 g	0.2 g
Potassium bromide	10 g	-
Sodium bromide	-	9 g
Water was added to make the total quantity 1 liter (pH was adjusted to 10.65) (pH was adjusted with potassium hydroxide in Solution A and with sodium hydroxide in Solution B)		

The above condensate was diluted in the following manner to prepare a use solution:
Developing condensate 400 ml + water 600 ml = use solution (pH was adjusted to 10.35)

Fixing solution:	
Sodium thiosulfate pentahydrate	refer to Table 2
Ammonium thiosulfate (70 weight%/volume)	refer to Table 2
Disodium ethylenediaminetetraacetate	0.025 g
Sodium sulfite	7.0 g
Sodium metabisulfite	20.0 g
Aluminum sulfate	refer to Table 2
Water was added to	1 liter
pH	5.6

Next, a roller transporting type automatic developing machine FPM-2000 (manufactured by Fuji Photo Film Co., Ltd.) was remodeled so that a 30 seconds processing (Dry to Dry) could be carried out. The above mentioned samples were used to carry out running. In the running test, a half-exposed film with a size of 10 × 12 inch was processed by 1800 sheets per day and the running was carried out for 2 days. The replenishing amount of the developing solution was 15 ml per sheet and the replenishing amount per sheet of the fixing solution is shown in Table 2. Washing water was flowed in the amount of 2 liter per minute.

After the running was finished, a fixing time was changed while passing the sample of the above size. The fixing time was determined by the time when a fixing drop failure was generated (the partial generation was judged as the fixing drop failure).

The status of the fixing solution was checked observing the precipitate in the rack after the running was finished.

The nitrogen content in the washing water was determined by analyzing the washing water after the running was finished.

The composition of the fixing solution and the running results are shown in Table 2.

TABLE 2

Experiment No.	Fixing solution: Sodium thiosulfate (mole/ℓ)	Fixing solution: Ammonium thiosulfate (mole/ℓ)	Fixing solution: Aluminum sulfate (g/ℓ)	Replenishing amount (ml/Dz)	Developing solution	Fixing time (sec.)	Status of fixing solution	Nitrogen content* (ppm)
1 (Comp.)	0.3	–	–	180	Solution B	>40	Clear	9
2 (Inv.)	1.0	–	–	180	Solution B	9.8	Clear	6
3 (Inv.)	1.2	–	–	180	Solution B	8.4	Clear	7
4 (Inv.)	1.5	–	–	180	Solution B	6.3	Clear	9
5 (Inv.)	1.8	–	–	180	Solution B	8.7	Clear	7
6 (Comp.)	2.3	–	–	180	Solution B	13.5	Clear	8
7 (Comp.)	1.2	–	15	180	Solution B	9.5	Cloudy	7
8 (Comp.)	–	1.2	–	180	Solution B	8.4	Clear	103
9 (Comp.)	–	1.2	15	180	Solution B	9.6	Cloudy	78
10 (Comp.)	1.2	–	–	180	Solution A	15.7	Clear	7
11 (Comp.)	1.5	–	–	180	Solution A	13.1	Clear	9
12 (Comp.)	1.8	–	–	180	Solution A	15.2	Clear	10
13 (Comp.)	2.3	–	–	180	Solution A	20.9	Clear	8

* in washing water

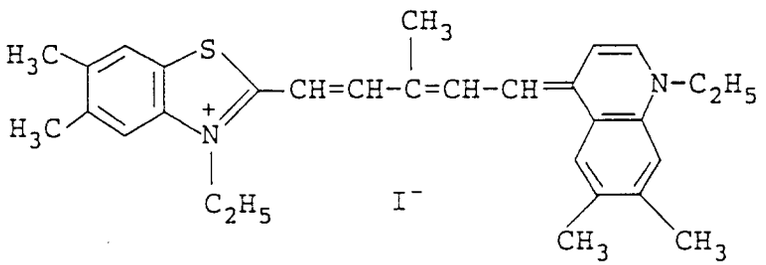
As with Example 1, the results show that the replenishing amount of the fixing solution is small in the present invention and that the present invention provides a processing method in which the environmental pollution in the washing water is low.

EXAMPLE 3

An aqueous solution of $AgNO_3$ (1 kg) and the aqueous solution of KBr (161 g) and NaCl (205 g) were simultaneously added to an aqueous solution containing gelatin (72 g) and NaCl (16 g) at a fixed speed for 32 minutes (Br = 23 mole%), wherein rhodium chloride and K_3IrCl_6 were added each at 5×10^{-7} mole/mole Ag for 10 minutes from the starting. Then, the soluble salts were removed and gelatin was added. The solution was adjusted to pH 6.0 and pAg 7.5 and then chlorauric acid and hypo were added to thereby provide chemical sensitization at 60 °C. In the chemical sensitization, the time when the highest sensitivity was given was selected. There were added to this emulsion, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene as a stabilizer and phenoxyethanol as an antiseptic.

A 0.05% aqueous solution (110 ml) of Sensitizing Dye (I) was added to the emulsion (1 kg) thus obtained and then there were added hydroquinone (100 mg/m^2), a polyethyl acrylate latex as a plasticizer in the ratio of 25% based on the amount of gelatin binder, and 2-bis(vinylsulfonylacetoamide)ethane (85 mg/m^2) as a hardener. The coating solution thus prepared was applied on a polyester support to Ag 3.7 g/m^2. The coated amount of gelatin was 2.0 g/m^2.

Sensitizing Dye (I)



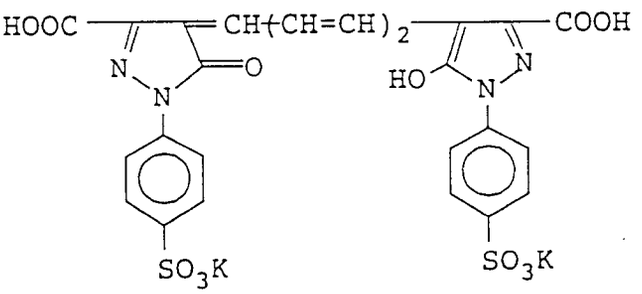
There were coated thereon as a protective layer, gelatin (0.8 g/m^2), polymethyl methacrylate having an average particle size of 2.5 μm (40 mg/m^2) as a matting agent, colloidal silica having an average particle size of 4 μm (30 mg/m^2), silicon oil (80 mg/m^2), sodium benzenesulfonate (80 mg/m^2) as a coating aid, Surface Active Agent (1) having the following structural formula in back protective layer, a polyethyl acrylate latex (150 mg/m^2), and potassium 1,1'-disulfobutyl-3,3,3',3'-tetramethyl-5,5'-disulfoindo-tri-carbocyanine (6 mg/m^2).

A back layer and a back protective layer each having the following composition are provided on the opposite side of a polyester support in these samples:

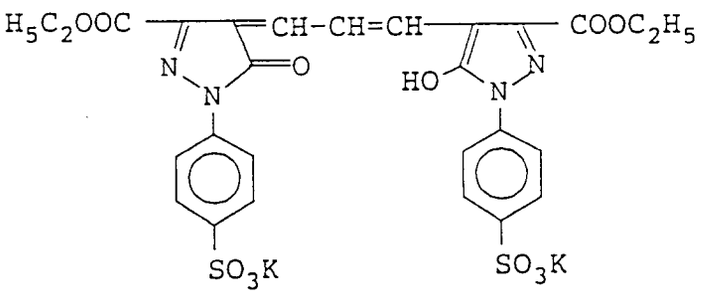
Back layer:	
Gelatin	2.4 g/m^2
Sodium dodecylbenzenesulfonate	60 mg/m^2
Dye (2)	80 mg/m^2
Dye (3)	30 mg/m^2
Potassium 1,1'-disulfobutyl-3,3,3',3'-tetramethyl-5,5'-disulfoindotricarbocyanine	80 mg/m^2
1,3-Divinylsulfonyl-2-propanol	60 mg/m^2
Poly(sodium vinylbenzenesulfonate)	30 mg/m^2

Back protective layer:	
Gelatin	0.75 g/m^2
Polymethyl methacrylate (average particle size: 3.5 μm)	40 mg/m^2
Sodium dodecylbenzenesulfonate	20 mg/m^2
Surface Active Agent $C_8F_{17}SO_2N(C_3H_7)$-CH_2COOK	2 mg/m^2
Silicon oil	100 mg/m^2

Dye (2)



Dye (3)



The sample thus obtained was subjected to a scanning exposure by half of the film with a semiconductor laser having an emission at 780 nm. Then, the sample was subjected to the same running test as in Example 1 in the developing Solutions A and B used in Example 1 and the fixing solution used in Experiment No. 3 at a replenishing amount per sheet of 25 ml each for the developing solution and the fixing solution. The running test was carried out at the processed sheet number of 450 sheets per day for 7 days.

In the case where Solution A was used for the developing solution, a fixing drop failure was seen on the fifth day and therefore the running test was stopped. Meanwhile, in Solution B, the running for 7 days did not cause a fixing drop failure. It was found that in the processing method according to the present invention, even low replenishing does not cause a fixing drop failure.

EXAMPLE 4

Emulsions A and B were prepared by the following method.

A 0.5 M silver nitrate aqueous solution and a halide aqueous solution containing 0.1 M potassium bromide, 0.44 M sodium chloride, potassium hexachloroiridate (III), and ammonium hexabromorhodate (III) were added to a gelatin aqueous solution containing sodium chloride, 1,3-dimethylimidazolidine-2-thione and benzenethiosulfonic acid and having its pH adjusted to 4.0 by a double jet method at 38 °C for 10 minutes while stirring, whereby the silver bromochloride grains having an average grain size of 0.16 μm and

a silver chloride content of 70 mole% were obtained to thereby form the nuclei. Subsequently, a 0.5 M silver nitrate aqueous solution and a halide aqueous solution containing 0.1 M potassium bromide, 0.44 M sodium chloride, and potassium ferrocyanide were similarly added by a double jet method for 10 minutes to finish the grain formation. The grains thus obtained were silver bromochloride cubic grains having an average grain size of 0.2 μm and a silver chloride content of 70 mole% and containing Ir of 3.8×10^{-7} mole per mole of silver, Rh of 6.1×10^{-8} mole per mole of silver and Fe of 2.3×10^{-5} mole per mole of silver (fluctuation coefficient: 10%). Then, the emulsion was washed by a conventional flocculation method and gelatin (30 g) was added thereto. This emulsion was divided to two equal parts to prepare Emulsions A and B in the following manner.

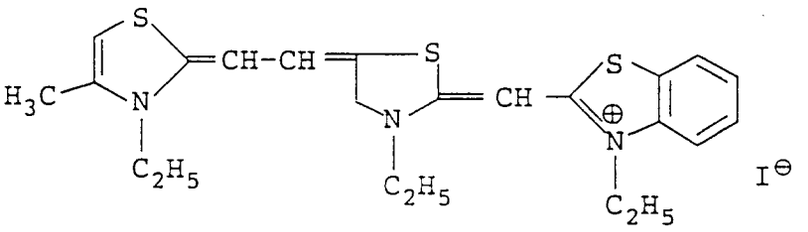
Emulsion A: the emulsion was adjusted to pH 5.6 and pAg 7.5, and sodium thiosulfate (3.2 mg) and chlorauric acid (4.3 mg) were added to thereby provide a chemical sensitization processing at 65 °C so that the optimum sensitivity could be obtained, followed by adding 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (75 mg) as a stabilizer.

Emulsion B: the emulsion was adjusted to pH 5.1 and pAg 7.5, and sodium thiosulfate (2.2 mg) , N,N-dimethylselenourea (0.85 mg), sodium benzenesulfonate (3.4 mg), sodium benzenesulfinate (0.85 mg), and chlorauric acid (4.3 mg) were added to provide an after-ripening at 55 °C. Then, a chemical sensitization was provided and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (75 mg) was added as a stabilizer.

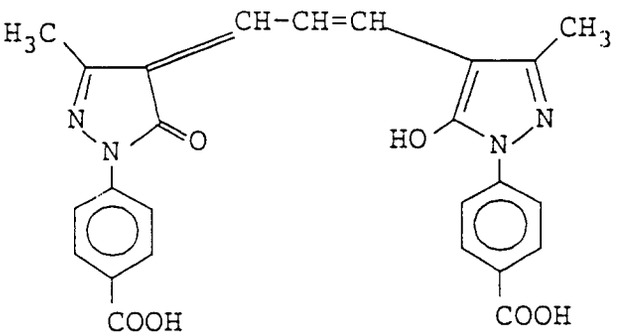
A pigment (4.2 mg/m^2) having the following structure was added to Emulsions A and B thus obtained. Further, there were added disodium 4,4'-bis(4,6-dinaphthoxypyrimidine-2-ylamino)stilbenedisulfonate (234 mg) and 1-phenyl-5-mercaptotetrazole (25 mg) each per mole of silver.

Further, there were added hydroquinone (150 mg/m^2), a polyethyl acrylate latex in the ratio of 30% based on the amount of gelatin binder, colloidal silica of 0.01 μm in the ratio of 30% based on the amount of gelatin binder, and 2-bis(vinylsulfonyl-acetoamide)ethane (70 mg/m^2) as a hardener. The coating solution thus prepared was applied on a polyester support to Ag 3.2 g/m^2 and a coated gelatin amount 1.4 g/m^2. A protective layer coating solution was prepared by adding gelatin (0.5 g/m^2), the dye having the following structure (70 mg/m^2), polymethyl methacrylate having a particle size of 2.5 μm (60 mg/m^2) as a matting agent, colloidal silica having a particle size of 10 μm (70 mg/m^2), sodium dodecylbenzenesulfonate as a coating aid and a fluorine-containing surface active agent having the following structure (1.5 mg/m^2) as a coating aid, and the following chelating agent (20 mg/m^2). The coating solution was adjusted to pH 5.5 and then coated on an emulsion layer simultaneously with the emulsion layer.

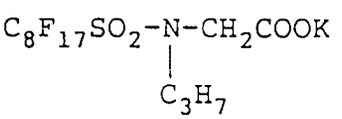
Pigment



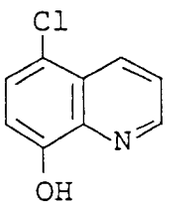
Dye



Surface Active Agent



Chelating Agent

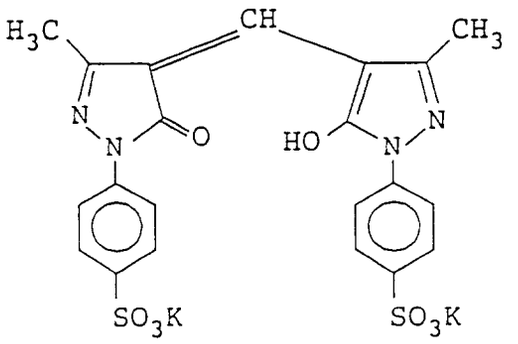


The support used in the present examples had a back layer and a back protective layer each having the following composition:

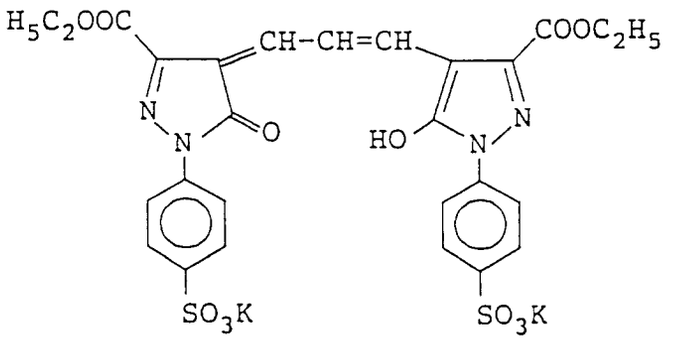
Back layer:

Gelatin 2.0 g/m^2

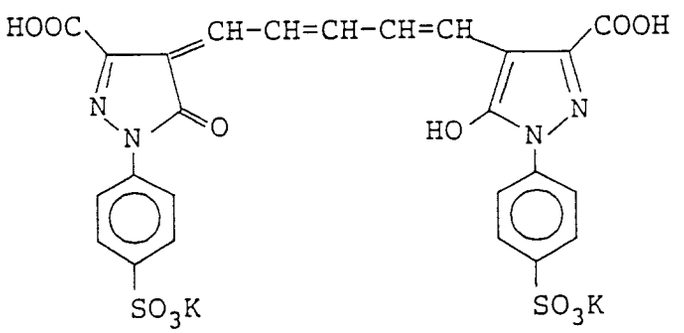
Sodium dodecylbenzenesulfonate 80 mg/m^2



160 mg/m^2



40 mg/m^2



120 mg/m^2

1,3-Divinylsulfonyl-2-propanol 60 mg/m^2

Back protective layer:	
Gelatin	0.5 g/m^2
Polymethyl methacrylate (particle size: 4.7 μm)	30 mg/m^2
Sodium dodecylbenzenesulfonate	20 mg/m^2
Fluorine-containing surface active agent (shown above)	2 mg/m^2
Silicon oil	100 mg/m^2

The sample thus obtained was exposed by half of the film to a xenon flash light at an emitting time of 10^{-5} second via an interference filter having a peak at 633 nm. The same running test as in Example 3 was carried out. The results of the running test were the same as those in Example 1, and it was found that even a low replenishing does not generate a fixing drop failure in the processing method of the present invention.

EXAMPLE 5

(1) Preparation of the emulsions

Preparation of Emulsion A

Solution 1':	
Water	1.0 liter
Gelatin	20 g
Sodium chloride	20 g
1,3-Dimethylimidazolidine-2-thione	20 mg
Sodium benzenethiosulfonate	8 mg

Solution 2':	
Water	400 ml
Silver nitrate	100 g

Solution 3':	
Water	400 ml
Sodium chloride	27.1 g
Potassium bromide	21 g
Potassium hexachloroiridate (III) (0.001% aqueous solution)	15 ml
Potassium hexabromorhodate (III) (0.001% aqueous solution)	1.5 ml

Solution 2' and Solution 3' were simultaneously added to Solution 1' maintained at 38°C and pH 4.5 over a period of 10 minutes while stirring to form nuclear grains of 0.16 μm. Subsequently, the following Solution 4' and Solution 5' were added over a period of 10 minutes. Further, potassium iodide (0.15 g) was added to finish grain formation.

Solution 4':	
Water	400 ml
Silver nitrate	100 g

Solution 5':	
Water	400 ml
Sodium chloride	27.1 g
Potassium bromide	21 g
Potassium hexacyanoferrate (III) (0.1% aqueous solution)	5 ml

Subsequently, the emulsion thus prepared was washed by a conventional flocculation method and gelatin (30 g) was added.

The emulsion was adjusted pH 5.3 and pAg 7.5, and sodium thiosulfate (2.6 mg), triphenylphosphine selenide (1.0 mg), and chlorauric acid (6.2 mg) were added thereto. Further, sodium benzenethiosulfonate (4 mg) and sodium benzenethiosulfinate (1 mg) were added, whereby the emulsion was subjected to chemical sensitization so that an optimum sensitivity could be obtained at 55 °C.

There were added 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (200 mg) as a stabilizer and phenoxyethanol as an antiseptic agent, whereby there was obtained a silver bromochloroiodide cubic grain emulsion finally containing silver chloride of 70 mole% and having an average grain size of 0.2 μm (fluctuation coefficient: 9%).

Preparation of the coated sample

An ortho sensitizing dye (the compound used in coated sample in Example 1) was added to the above emulsion in the amount of 5×10^{-4} mole/mole Ag to subject it to an ortho sensitization. There were added hydroquinone and 1-phenyl-5-mercaptotetrazole as an anti-fogging agent in the amounts of 2.5 g and 50 mg per mole of Ag, respectively, a polyethyl acrylate latex as a plasticizer in the ratio of 25% based on the amount of gelatin binder, 2-bis(vinylsulfonylacetoamide)ethane as a hardener, and further colloidal silica in the ratio of 40% based on the amount of gelatin binder. The coating solution thus prepared was applied on a polyester support to Ag 3.0 g/m^2. A lower protective layer and an upper protective layer each having the following composition were coated thereon.

Lower protective layer:	
Gelatin	0.25 g/m^2
Sodium benzenethiosulfonate	4 mg/m^2
1,5-Dihydroxy-2-benzaldoxime	25 mg/m^2
Polyethyl acrylate latex	125 mg/m^2

Upper protective layer:	
Gelatin	0.25 g/m^2
Silica matting agent with an average particle size of 2.5 μm	50 mg/m^2
Compound (1) used in Example 1 (gelatin dispersion)	30 mg/m^2
Colloidal silica with the particle size of 10 to 20 μm	
Compound (2) used in Example 1	5 mg/m^2
Sodium dodecylbenzenesulfonate	22 mg/m^2

The support used in the present examples had a back layer and a back protective layer each having the following composition:

Back layer:	
Sodium dodecylbenzenesulfonate	80 mg/m^2
Compound (3) used in Example 1	70 mg/m^2
Compound (4) "	85 mg/m^2
Compound (5) "	90 mg/m^2
1,3-Divinylsulfonyl-2-propanol	60 mg/m^2

Back protective layer:	
Gelatin	0.5 g/m^2
Polymethyl methacrylate (grain size: 4.7 μm)	30 mg/m^2
Sodium dodecylbenzenesulfonate	20 mg/m^2
Compound (2)	2 mg/m^2
Compound (1) (gelatin dispersion)	100 mg/m^2

The coated sample thus prepared was designated as Film A and the sample which was prepared in the same manner except that triphenylphosphine selenide was replaced with triphenylphosphine telluride was 4 designated as Film B.

Developing solution:	
Diethylenetriaminepentaacetic acid	2.0 g
Sodium carbonate	10.0 g
2,3,5,6,7,8-hexahydro-2-thioxo-4-(1H)-quinazoline	0.1 g
Potassium sulfite	85.0 g
Sodium bromide	6.0 g
Diethylene glycol	40.0 g
5-Methylbenzotriazole	0.2 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	0.3 g
Hydroquinone	30.0 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	1.6 g
Water was added to (after adjusting pH)	1 liter
pH (adjusted with potassium hydroxide and sodium hydroxide)	10.7

Fixing solution:	
Sodium thiosulfate	described in Table 3
Ammonium thiosulfate	described in Table 3
Disodium ethylenediaminetetraacetate	0.025 g
Sodium sulfite	7.0 g
Sodium metabisulfite	20.0 g
Aluminum sulfate	described in Table 3
Water was added to	1 liter
pH	described in Table 3

The compositions of the fixing solutions are described in Table 3. The experiments were carried out for five kinds of fixing solutions.

TABLE 3

	Fixing Solution A	Fixing Solution B	Fixing Solution C	Fixing Solution D	Fixing Solution E
Sodium thiosulfate (M)	1.2 M	1.2 M	1.2 M	1.2 M	-
Ammonium thiosulfate (M)	-	-	-	-	1.2 M
Aluminum sulfate (g/ℓ)	15	-	15	-	-
pH	5.6	5.6	4.2	4.2	5.2

All of the developing, fixing and washing tanks in the automatic developing machine shown in Fig. 1 have a tank capacity of 15 liter. The results of the experiments carried out with Film A are summarized in Table 4.

TABLE 4

Fixing solution	Drying time	Automatic developing machine	Nitrogen content in washingwater	Sulfur dioxide gas
A* (Comparison)	10 sec.	shown in Fig. 1	7 ppm	5 ppm
B (Invention)	12 sec.	shown in Fig. 1	8 ppm	4 ppm
C (Comparison)	10 sec.	shown in Fig. 1	7 ppm	23 ppm
D (Comparison)	12 sec.	shown in Fig. 1	6 ppm	27 ppm
E (Invention)	13 sec.	shown in Fig. 1	85 ppm	7 ppm
A (Comparison)	15 sec.	FG-680A	8 ppm	5 ppm
B (Comparison)	20 sec.	FG-680A	9 ppm	5 ppm

* Leaving the fixing solution after the experiment to stand for one night generated a white precipitate.

As is apparent from the results summarized in Table 4, it can be found that the generation of odor and gas from the fixing solution can be reduced by the present invention and that the present invention provides a processing method having a good drying performance and an excellent rapid processing suitability. Further, using sodium thiosulfate as a fixing agent for a fixing solution in place of ammonium thiosulfate can reduce the nitrogen content in a washing water and can decrease the impact of a washing waste solution on

the environment.

The same experiments were carried out with Film B in place of Film A. The results of a running test were the same as those with Film A and it could be confirmed that the present invention provided the processing method having a good drying performance and a short fixing time.

EXAMPLE 6

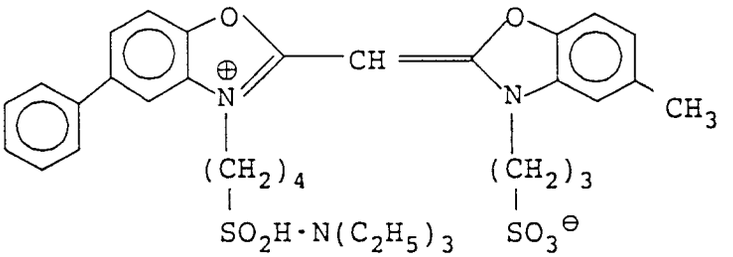
First light-sensitive emulsion layer:

A 0.37 M silver nitrate aqueous solution and a halide aqueous solution containing $(NH_4)_3RhCl_6$ corresponding to 5×10^{-7} mole and K_3IrCl_6 5×10^{-7} mole each per mole of silver, 0.11 M potassium bromide, and 0.27 M sodium chloride were added to a gelatin aqueous solution containing sodium chloride and 1,3-dimethyl-2-imidazolidinethione by a double jet method at 45 °C for 12 minutes while stirring, whereby silver bromochloride grains having an average grain size of 0.02 μm and a silver chloride content of 70 mole% were obtained to thereby form nuclei. Subsequently, a 0.63 M silver nitrate aqueous solution and a halide aqueous solution containing 0.19 M potassium bromide and 0.47 M sodium chloride were similarly added by a double jet method over a period of 20 minutes. Then, a KI solution of 1×10^{-3} mole was added to carry out a conversion and washing was carried out by a flocculation method according to a conventional method, followed by adding gelatin (40 g) and adjusting pH and pAg to 6.5 and 7.5, respectively. Further, there were added sodium thiosulfate (5 mg), chlorauric acid (8 mg), and sodium benzenesulfonate (7 mg) each per mole of silver and heating was applied at 60 °C for 45 minutes to provide a chemical sensitization, followed by adding 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (150 mg) as a stabilizer, Proxel and phenoxyethanol. The grains thus obtained were silver bromochloride cubic grains having an average grain size of 0.28 μm and a silver chloride content of 70 mole% (fluctuation coefficient: 9%).

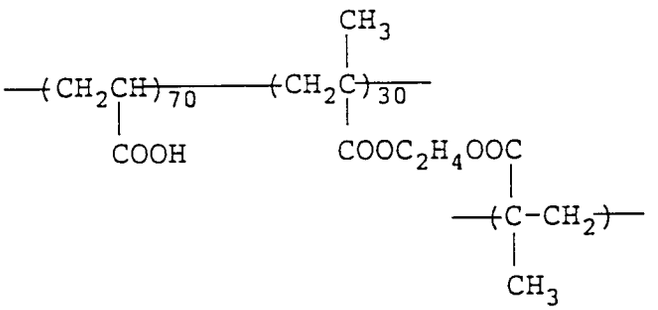
Coating of the first light-sensitive emulsion layer:

These emulsions were divided and there was added as a sensitizing dye, 1×10^{-3} mole of potassium 5-[3-(4-sulfobutyl)-5-chloro-2-benzoxazolidilidene]-1-hydroxy ethoxyethyl-3-(2-pylidyl)-2-thiohydantoin. Further added were 2×10^{-4} mole of 1-phenyl-5-mercapto-tetrazole, 5×10^{-4} mole of a short wave cyanine dye of Compound (a) represented by the following structural formula and a polymer of Compound (b) (200 mg/m^2), hydroquinone (50 mg/m^2), a dispersion of polyethyl acrylate (200 mg/m^2), 1,3-bis(vinylsulfonyl)-2-propanol (200 mg/m^2), and the following Hydrazine Compound (c). The coating solution thus prepared was applied to a coated silver amount of 3.6 g/m^2 and a gelatin amount of 2.0 g/m^2.

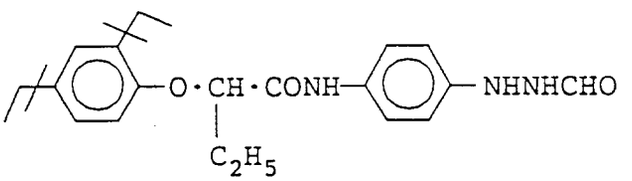
Compound (a)



Compound (b)



Hydrazine Compound (c)



2.8×10^{-5} mole/m^2

Coating of an intermediate layer:

Gelatin	1.0 g/m^2
1,3-Bis(vinylsulfonyl)-2-propanol	4.0 wt% based on gelatin

Coating of the second light-sensitive emulsion layer Preparation of the light-sensitive Emulsion B:

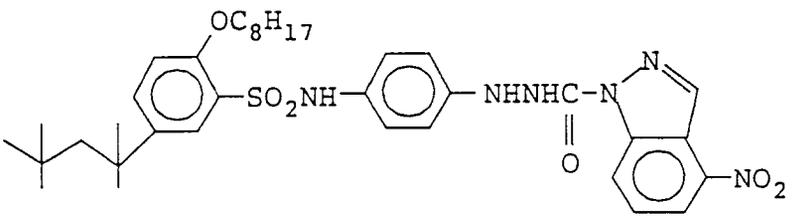
A 1.0 M silver nitrate aqueous solution and a halide aqueous solution containing $(NH_4)_3RhCl_6$ of 3×10^{-7} mole per mole of silver, 0.3 M potassium bromide, and 0.74 M sodium chloride were added to a gelatin aqueous solution containing sodium chloride and 1,3-dimethyl-2-imidazolidinethione by a double jet method at 45 °C for 30 minutes while stirring, whereby silver bromochloride grains having an average grain size of 0.28 μm and a silver chloride content of 70 mole% were obtained. Then, the emulsion was washed by a flocculation method according to a conventional method and gelatin (40 g) was added, followed by adjusting pH and pAg to 6.5 and 7.5, respectively. Further added were sodium thiosulfate (5 mg) and chlorauric acid

(8 mg) each per mole of silver and heating was applied at 60 °C for 60 minutes to provide a chemical sensitization, followed by adding 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (150 mg) as a stabilizer, Proxel and phenoxyethanol. The grains thus obtained were silver bromochloride cubic grains having an average grain size of 0.28 μm and a silver chloride content of 70 mole% (fluctuation coefficient: 10%).

Coating of the second light-sensitive emulsion layer:

Light-sensitive Emulsion B was dissolved once again and there were added 1×10^{-3} mole of potassium 5-[3-(4-sulfobutyl)-5-chloro-2-benzoxazolidilidene]-1-hydroxy ethoxyethyl-3-(2-pylidyl)2-thiohydantoin as a sensitizing dye, and 1.0×10^{-3} mole of a KI solution each per mole of silver. Further added were 2×10^{-4} mole of 1-phenyl-5-mercaptotetrazole, a dispersion of polyethyl acrylate (50 mg/m^2), 1,3-bis(vinylsulfonyl)-2-propanol (4.0 wt% based on the amount of gelatin) as a hardener, and the following Redox Compound (1.0×10^{-4} mole/m^2). The coating solution thus prepared was applied so that the coated silver amount and the gelatin amount were 0.2 g/m^2 and 0.3 g/m^2, respectively.

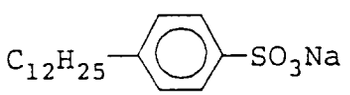
Redox Compound



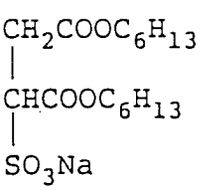
Coating of a protective layer:

There were coated thereon gelatin (1.0 g/m^2) and the polymethyl methacrylate grains (average grain size: 2.5 μm) (0.3 g/m^2) by means of the following surface active agents.

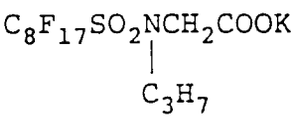
Surface Active Agents



37 mg/m^2



37 mg/m^2

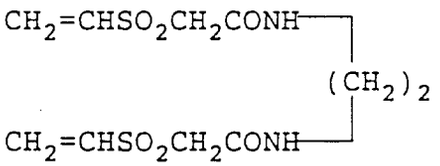


2.5 mg/m^2

A back layer and a back protective layer each having the following composition were coated.

Composition of the back layer:

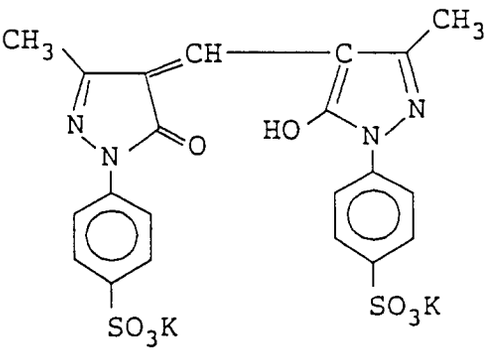
Gelatin	3 g/m^2
Polyethyl acrylate latex	2 g/m^2
Surface active agent (sodium p-dodecyl-benzenesulfonate)	40 mg/m^2
Gelatin hardener shown below	110 mg/m^2



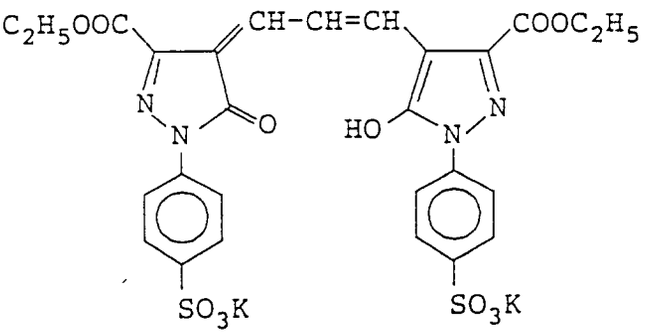
Mixture of the following Dye (a), Dye (b) and Dye (c)

Dye (a)	50 mg/m^2
Dye (b)	100 mg/m^2
Dye (c)	50 mg/m^2

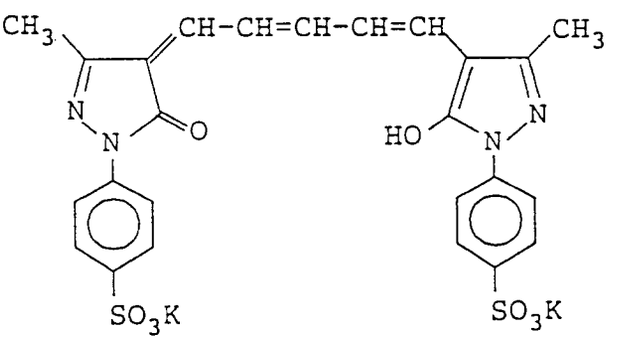
Dye (a)



Dye (b)

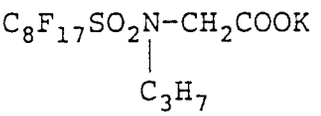


Dye (c)



Composition of the back protective layer:

Gelatin	0.8 g/m^2
Polymethyl methacrylate fine* particles (average particle size: 4.5 μm)	30 mg/m^2
Sodium dihexyl-α-sulfosuccinate	15 mg/m^2
Sodium dodecylbenzenesulfonate	15 mg/m^2
Sodium acetate	40 mg/m^2
Fluorinated surface active agent shown below:	5 mg/m^2



There were simultaneously coated on a polyester film (100 μm), the first light-sensitive emulsion layer as the lowest layer, the second light-sensitive emulsion layer containing the redox compound via an intermediate layer and provided thereon a protective layer, whereby Sample C (Film C) was prepared. Sample C comprises a support thereon, a under coat layer, the first light-sensitive emulsion layer, the intermediate layer and the second light-sensitive layer and the protective layer, in these orders.

The composition of the developing solution is shown below.

Developing solution:	
Hydroquinone	50 g
N-methyl-p-aminophenol	0.3 g
Sodium hydroxide	18 g
5-Sulfosalicylic acid	45 g
Boric acid	10 g
Potassium sulfite	110 g
Disodium ethylenediaminetetraacete	1.0 g
Potassium bromide	10.0 g
5-Methylbenzotriazole	0.4 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	0.3 g
3-(5-Mercaptotetrazole)benzenesulfonic acid	0.2 g
Sodium p-toluenesulfonate	8.0 g
N-n-butyldiethanolamine	15.0 g
Water was added to	1 liter
pH was adjusted to (by adding potassium hydroxide)	11.6

GR-FI and SR-FI (each manufactured by Fuji Photo film Co., Ltd.) were used as a fixing solution. GR-FI contains aluminum sulfate of 0.01 mole/liter or more and SR-FI contains aluminum sulfate of 0.01 mole/liter or less. Film C with a size of 51 × 61 cm was subjected to a development processing with the same automatic developing machine of Fig. 1 as that used in Example 5 under the environmental conditions of 27°C and 70% RH to determine the shortest drying time when the sample was completely dried immediately after the processing. In the experiments, the shortest drying time was found after continuously passing 20 sheets of the sample having the above size. Washing was carried out with stocked water and a nitrogen content in washing water after the processing was checked. The degree of sulfur dioxide gas generation was checked with a gas detecting tube on a fixing tank during processing. There was used as a reference, FG-680A (used at the drying temperature of 50°C, manufactured by Fuji Photo Film Co., Ltd.) in which a hot wind blow-drying method which is not a heat roller drying method was used. Both of the automatic developing machines were remodeled so that the transporting speed could be changed. The results of the experiments are shown in Table 5.

TABLE 5

Fixing solution	Automatic developing machine	Drying time	Nitrogen content in washing water	Sulfur dioxide gas
SR-F1 (Invention)	shown in Fig. 1	13 sec.	8 ppm	3 ppm
GR-F1 (Comparison)	shown in Fig. 1	10 sec.	90 ppm	15 ppm
SR-F1 (Comparison)	FG-680A	20 sec.	9 ppm	4 ppm
GR-F1 (Comparison)	FG-680A	15 sec.	83 ppm	14 ppm

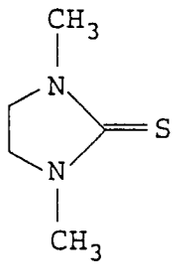
It can be found from the results shown in Table 5 that the generation of odor and gas is small in the processing according to the present invention with the automatic developing machine in which a heat roller drying is used and that the present invention provides the processing method having less load on washing water and a good drying performance.

EXAMPLE 7

(1) Preparation of the silver halide emulsion

Gelatin (40 g) was dissolved in water 1 liter and sodium chloride (6 g), potassium bromide (0.4 g), and Compound [I]:

Compound [I]



Sixty mg of the solution were put in a vessel heated at 53 °C. Then, an aqueous solution (600 ml) containing silver nitrate (100 g) and an aqueous solution (600 ml) containing potassium bromide (56 g) and sodium chloride (7 g) were added by a double jet method to form a core portion containing 20 mole% of silver chloride. Subsequently, the aqueous solution (500 ml) containing silver nitrate (100 g) and the aqueous solution (500 ml) containing potassium bromide (40 g), sodium chloride (14 g) and potassium chloroiridate (III) (10^{-7} mole/mole silver) were added by a double jet method to form a shell portion containing 40 mole% of silver chloride, whereby so-called core/shell type cubic monodispersed silver bromochloride grains having an average grain size of 0.35 μm were prepared.

After this emulsion was subjected to a desalting processing, gelatin (40 g) was added and pH and pAg were adjusted to 6.0 and 8.5, respectively, followed by adding triethylthiourea (2 mg), chlorauric acid (4 mg) and 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (0.2 g) to thereby provide a chemical sensitization at 60 °C.

(2) Preparation of the emulsion layer coating solutions

The vessel in which the emulsion (850 g) was put and weiged was heated to 40 °C and additives were added in the manner shown below to prepare the emulsion layer coating solution.

Composition of the emulsion layer coating solution A:	
Emulsion	850 g
Spectral Sensitizing Dye [II] (used in Example 2)	1.2×10^{-4} mole
Supersensitizer [III] (used in Example 2)	0.8×10^{-3} mole
Preservativity Improver [IV] (used in Example 2)	1×10^{-3} mole
Polyacrylamide (molecular weight: 40,000)	7.5 g
Trimethylolpropane	1.6 g
Poly(sodium styrenesulfonate)	2.4 g
Poly(ethyl acrylate/methacrylic acid) latex	16 g
N,N'-ethylenebis-(vinylsulfonacetoamide)	1.2 g

(3) Preparation of the surface protective layer coating solution for the emulsion layer

A vessel was heated to 40 °C and the additives were added in the manner shown below to prepare the coating solution.

Composition of the surface protective layer coating solution for the emulsion layer:

Gelatin	100 g
Polyacrylamide (molecular weight: 40,000)	10 g
Poly(sodium styrenesulfonate) (molecular weight: 600,000)	0.6 g
N,N'-ethylenenebis-(vinylsulfonacetoamide)	1.5 g
Polymethyl metacrylate fine grains (average grain size: 2.0 μm)	2.2 g
Sodium t-octylphenoxyethoxyethanesulfonate	1.2 g
$C_{16}H_{33}O-(CH_2CH_2O)_{10}-H$	2.7 g
Poly(sodium acrylate)	4 g
$C_8F_{17}SO_3K$	70 mg
$C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_4(CH_2)_4-SO_3Na$	70 mg
NaOH (1N)	4 ml
Methanol	60 ml

(4) Preparation of the back layer coating solution

A vessel was heated to 40 °C and the additives were added in the manner shown below to prepare the back layer coating solution.

Composition of the back layer coating solution:	
Gelatin	80 g
Dye [V] (used in Example 2)	3.1 g
Poly(sodium styrenesulfonate)	0.6 g
Poly(ethyl acrylate/metacrylic acid) latex	15 g
N,N'-ethylenebis-(vinylsulfonacetoamide)	4.3 g

(5) Preparation of the surface protective layer coating solution for the back layer

A vessel was heated to 40 °C and the additives were added in the manner shown below to prepare the coating solution.

Composition of the surface protective layer coating solution for the back layer:

Gelatin	80 g
Poly(sodium styrenesulfonate)	0.3 g
N,N'-ethylenebis-(vinyl-sulfonacetoamide)	1.7 g
Polymethyl methacrylate fine grains (average grain size: 4.0 μm)	4 g
Sodium t-octylphenoxyethoxyethane-sulfonate	3.6 g
NaOH (1N)	6 ml
Poly(sodium acrylate)	2 g
$C_{16}H_{33}O-(CH_2CH_2O)_{10}-H$	3.6 g
$C_8F_{17}SO_3K$	50 mg
$C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_4(CH_2)_4-SO_3Na$	50 mg
Methanol	130 ml

(6) Preparation of the coated material

The above mentioned back layer coating solution was applied on a polyethylene terephthalate support together with the surface protective layer coating solution for the back layer so that the total gelatin coating amount was 3 g/m^2. Subsequently, the above mentioned emulsion layer coating solution and the surface protective layer coating solution were applied on the opposite side of the support so that the coated Ag amount and the gelatin coating amount of the surface protective layer were 2.5 g/m^2 and 1 g/m^2, respectively

The composition of the developing solution is shown below:

Developing solution	
Potassium hydroxide	17 g
Sodium sulfite	40 g
Potassium sulfite	50.4 g
Diethylenetriaminepentaacetic acid	2 g
Boric acid	8 g
Hydroquinone	34 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	6 g
Diethylene glycol	12 g
5-Methylbenzotriazole	0.08 g
Potassium bromide	4 g
Water was added to make the total quantity 1 liter (pH was adjusted to 10.35)	

RF-10 (manufactured by Fuji Photo Film Co., Ltd.) was used as a fixing solution. RF-10 is the fixing solution containing no aluminum hydroxide and having a pH of 5. While the shortest drying time during which the sample was completely dried after processing was 18 seconds when the roller transporting type automatic developimg machine FPM-2000 (manufactured by Fuji Photo Film Co., Ltd.), the use of the automatic developing machine shown in Fig. 1 provided the shortest drying time of 12 seconds. The use of a non-hardening fixing solution could provide a good drying performance and gave a processing method having a good rapid processing suitability.

EXAMPLE 8

Sample A prepared in Example 5 was used.

Developing solution:		
	Developing Solution-A	Developing Solution-B
Diethylenetrriaminepentacetic acid	2.0 g	2.0 g
Sodium carbonate	5.0 g	5.0 g
Boric acid	10.0 g	10.0 g
2,3,5,6,7,8-hexahydro-2-thioxo-4-(1H)-quinazolinone	0.1 g	0.1 g
Potassium sulfite	85.0 g	-
Sodium sulfite	-	67.7 g
Sodium bromide	6.0 g	6.0 g
Diethylene glycol	40.0 g	40.0 g
5-Methylbenzotriazole	0.2 g	0.2 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	0.3 g	0.3 g
Hydroquinone	30.0 g	30.0 g
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	1.6 g	1.6 g
Water was added to (after adjusting pH)	1 liter	1 liter
pH (adjusted with potassium hydroxide and sodium hydroxide)	10.7	10.7

Fixing solution:	
Sodium thiosulfate pentahydrate	refer to Table 6
Ammonium thiosulfate (70 weight %/volume)	refer to Table 6
Disodium ethylenediaminetetraacetate	0.025 g
Sodium sulfite	7.0 g
Sodium metabisulfite	20.0 g
Aluminum sulfate	refer to Table 6
Water was added to	1 liter
pH	5.6

There were used the automatic developing machine of Fig. 1 used in Example 5 and FG-680A which was remodeled so that it could be operated at a high speed.

The drying time and the nitrogen content in the washing water were measured in the same manner as in Example 5. Further, the running test was carried out at a developing temperature of 38 °C, a fixing temperature of 37 °C and a developing time of 20 seconds. In the running test, a film with a size of 50.8 cm × 61.0 cm was processed by 450 sheets per day and the running was carried out for 2 days. After the running was finished, a fixing time was changed while passing the above non-developed sample of the above size and the fixing time was determined by the time when a fixing drop failure was generated after the processing (the partial generation was judged as the fixing drop failure). Washing water flowed in the amount of 2 liter per minute during the running test. The experimental results and the compositions of the fixing solutions are shown in Table 6.

TABLE 6

Experiment No.	Fixing solution: Sodium thiosulfate (mol/ℓ)	Fixing solution: Ammonium thiosulfate (mol/ℓ)	Fixing solution: Aluminum sulfate (g/ℓ)	Fixing solution: Replenishing amount (ml/Dz)	Developing solution	Automatic developing machine	Drying time (sec.)	Nitrogen * content (ppm)	Fixing time (sec.)	Status of fixing solution**
1 (Inv.)	1.2	-	-	60	Sol B	Fig. 1	11	8	10.8	Clear
2 (Inv.)	-	1.2	-	60	Sol B	Fig. 1	12	100	9.8	Clear
3 (Comp.)	1.2	-	15	60	Sol B	Fig. 1	8	9	11.5	A little cloudy
4 (Inv.)	1.2	-	-	60	Sol A	Fig. 1	11	7	15.9	Clear
5 (Comp.)	1.2	-	-	60	Sol B	FG-680A	20	11	10.9	Clear
6 (Comp.)	1.2	-	-	60	Sol A	FG-680A	19	8	16.2	Clear
7 (Comp.)	1.2	-	15	60	Sol B	FG-680A	15	7	11.5	A little cloudy
8 (Inv.)	1.2	-	-	25	Sol B	Fig. 1	12	10	15.3	Clear
9 (Inv.)	-	1.2	-	25	Sol B	Fig. 1	13	92	17.2	Clear
10 (Comp.)	1.2	-	15	25	Sol B	Fig. 1	10	9	16.2	Cloudy
11 (Inv.)	1.2	-	-	25	Sol A	Fig. 1	12	7	28.4	Clear
12 (Comp.)	1.2	-	-	25	Sol B	FG-680A	21	11	15.2	Clear
13 (Comp.)	1.2	-	-	25	Sol A	FG-680A	21	9	26.9	Clear
14 (Comp.)	1.2	-	15	25	Sol B	FG-680A	16	8	16.4	Cloudy

* in washing water. ** after running.

It can be found from the results summarized in Table 6 that the use of an automatic developing machine according to the present invention in combination with a fixing solution according to the present invention can provide a processing method in which drying performance is good and the load of washing waste solution is small. In the case where the developing solution does not contain a potassium ion, a processing method having a short fixing time can be provided even when with a lower replenishing amount of the fixing solution.

Film B in Example 5 was used to carry out the same experiments. The results of the running test were the same as those with Film A and it could be confirmed that the processing method having a good drying performance and a short fixing time could be provided.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A method for processing an image-wise exposed black and white silver halide light-sensitive material with an automatic developing machine, comprising the steps of,

developing the exposed material with a developing solution having a potassium ion concentration of 0.1 mole/liter or less,

fixing the developed material with a fixing solution containing 0.5 to 2.5 mole/liter of sodium thiosulfate, an ammonium concentration of 0.1 mole/liter or less, and a water soluble aluminum compound concentration of 0.01 mole/liter or less, and

washing the fixed material,

wherein the fixing solution has a replenishing amount of 250 ml/m^2 or less.

2. The method of claim 1, wherein the developing solution has a replenishing amount of 250 ml/m^2 or less.

3. The method of claim 1, further comprising the step of drying the washed material in a drying unit which comprises a plurality of heat rollers having circumferences heated by heat sources and which is contained in the automatic developing machine, wherein a surface and a back face of the washed material are rolled alternatively over the respective rollers, and wherein the material is heated in an amount based upon the temperature of the circumference of the heat rollers and the contact time between the rollers and the material, to evaporate water from the side of the material while that side is not in contact with the rollers.

4. The method of claim 1, wherein the developing solution contains a dihydroxybenzene and either a 1-phenyl-3-pyrazolidone or a p-aminophenol.

5. The method of claim 1, wherein the sodium thiosulfate concentration of the fixing solution is 0.8 to 1.8 mole/liter.

6. The method of claim 1, wherein the sodium thiosulfate concentration of the fixing solution is 1.0 to 1.5 mole/liter.

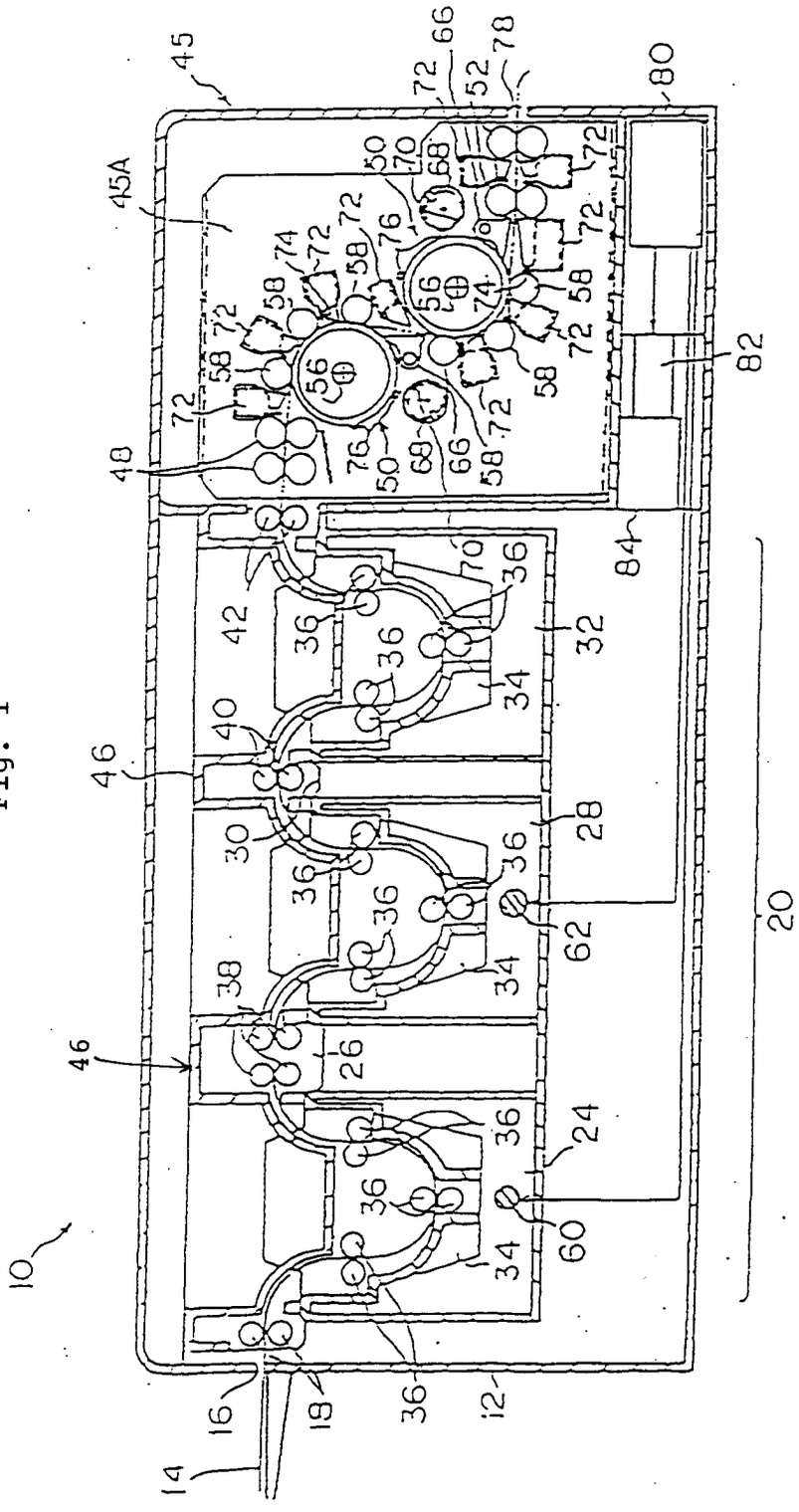
7. The method of claim 1, wherein the ammonium ion concentration of the fixing solution is 0.01 mole/liter or less.

8. The method of claim 1, wherein the water soluble aluminum concentration of the fixing solution is 0.005 mole/liter or less.

9. The method of claim 1, wherein the fixing solution has a replenishing amount of 200 ml/m^2 or less.

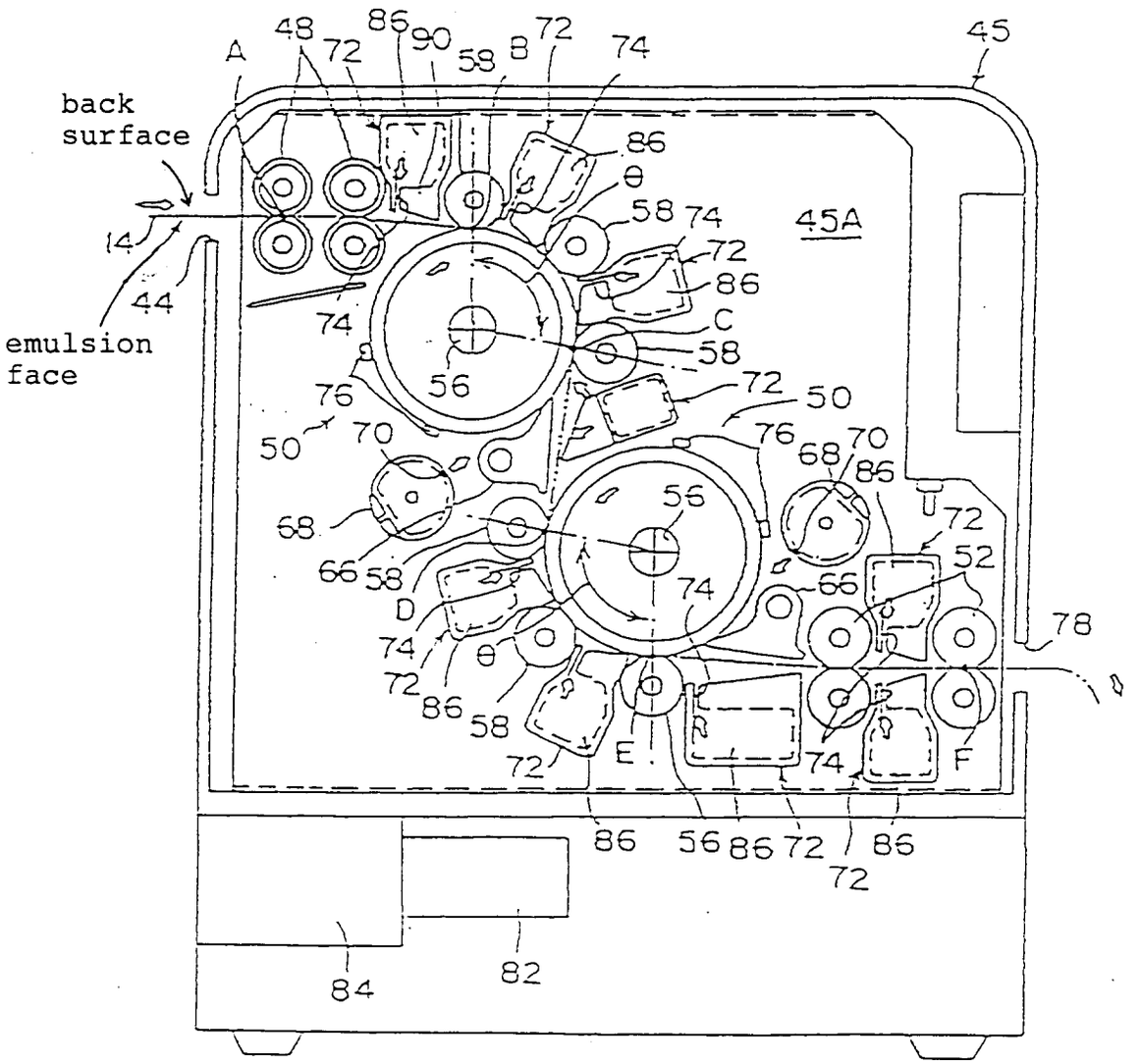
10. The method of claim 3, further comprising the step of blowing a dry wind, during the drying step, onto the face of the material while it is not in contact with the rollers.

Fig. 1



10 Automatic Developing Machine
14 Light-sensitive Material
45 Drying Unit (Drying Apparatus for drying light-sensitive material)
50 Heat Roller (1st and 2nd Heat Roller)
56 Heat Source
68 Blowing Pipe (Chamber)
70, 74 Slit
82 Fan (Drying air supply means)
84 Heater (")

Fig. 2



86 Guide Body (Chamber)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 5377

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	GB-A-1 045 044 (KODAK) * page 2; examples 1,2 * ---	1-10	G03C5/26 G03D15/02
Y	JP-A-63 118 744 (FUJI) * abstract * * page 8, left column, line 2 - right column, line 3 * * page 10, left column, line 6 - line 11 * ---	1-10	
Y	PATENT ABSTRACTS OF JAPAN vol. 15, no. 347 (P-1246)3 September 1991 & JP-A-03 131 852 (FUJI) 5 June 1991 * abstract * -----	3,10	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

G03C
G03D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 December 1993	Magrizos, S

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