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(54) Light-sensitive silver halide photographic material.

(57) A light-sensitive silver halide photographic material suitable for super rapid processing is disclosed. The photographic material comprisses a support and, provided on at least one side thereof, a light-sensitive silver halide emulsion layer containing a silver halide emulsion obtained by a method comprising steps of
adding an aqueous solution of water-soluble silver salt and an aqueous solution of a water soluble halide into an aqueous solution containing a protective colloid to precipitate silver halide grains,
coagulating said silver halide grains together with said protective colloid by the use of a polymer coagulant, and removing a supernatant liquid containing dissolved metrials.

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a light-sensitive silver halide photographic material capable of fast processing and which also has a high speed and high image quality. The present invention can be utilized as a lightsensitive material that is resistant to roller marks and hence can obtain an image of high quality even when, for example, the material is subjected to fast processing in an automatic processor.

BACKGROUND OF THE INVENTION

Light-sensitive silver halide photographic materials are demanded to be of high speed and high image quality, and on the other hand required to be processed in a short time. Particularly in recent years, it is strongly required for them to be rapidly processed in a short time, with an increase in the consumption of light-sensitive silver halide photographic materials. For example in the field of X-ray photographic materials as exemplified by X-ray films for medical use there is an increase in the number of X-ray photographs taken because of a rapid increase in the number of times for diagnosis or an increase in test items, and on the other hand it is necessary to notify as soon as possible the outcome of the diagnosis to those who have been diagnosed. Particularly in angiography, mid-operation photography etc., it is fundamentally necessary to view photographs in a time as short as possible.

With this background, various rapid processing techniques have been attempted. For example, in image-formation processing, it has been attempted to carry out development processing at a high pH and a high temperature (30 to 40 °C) to accelerate the processing. However, such a high pH and high temperature condition has brought about a deterioration of the photographic images obtained. In particular, in instances in which the processing is carried out with an automatic processor, it has sometimes occurred that the pressure resistance of light-sensitive materials is deteriorated to make so-called roller marks owing to the pressure of carrying rollers, thus causing a deterioration of image quality.

To solve this problem, various techniques have been proposed, but none of them have been sufficient.

On the other hand, it is effective to reduce the amount of binders (usually gelatin) for light-sensitive materials in order to achieve rapid processing, but the reduction of the amount of binders tends to more deteriorate the pressure resistance, to readily make the above roller marks or the like.

Such deterioration of images is not desirable and may possibly cause misdiagnosis in the case of X-ray light-sensitive materials.

SUMMARY OF THE INVENTION

The present invention was made on account of the above circumstances, and an object of the present invention is to provide a light-sensitive silver halide photographic material that can be free of any deterioration of images as exemplified by the deterioration of images owing to roller marks, can obtain an image of high quality and also can be of high speed, even when rapid fast processing is carried out.

The above object of the present invention was achieved by a light-sensitive silver halide photographic material comprising a support and, provided on at least one side thereof, a light-sensitive silver halide emulsion layer, containing a silver halide emulsion obtained by a method comprising the steps of
adding an aqueous solution of a water-soluble silver salt and an aqueous solution of a water-soluble halide into an aqueous solution containing a protective colloid to precipitate silver halide grains, and
coagulating said silver halide grains together with said protective colloid by the use of a polymer coagulant, and removing a supernatant liquid containing dissolved matters.

Namely, in the present invention, incorporation of the above specific emulsion made it possible to obtain a light-sensitive material that can be satisfactory in every respect of the rapid processing performance, speed and image quality.

Because of the superior rapid processing performance of the light-sensitive material of the present invention, the speed or image quality may not be deteriorated even when it is subjected to fast processing carried out in the total processing time of not less than 20 seconds and not more than 3 minutes 30 seconds, and the image quality deterioration due to roller marks may be substantially avoided even when it is processed with an automatic processor having rollers.

Thus, the present invention is suited to the fast processing carried out in the total processing time of not less than 20 seconds and not more than 3 minutes 30 seconds, but can also be more preferably used in the rapid processing carried out in the total processing time of not less than 20 seconds and not more than 90 seconds, and can be further preferably used in the ultra-rapid processing carried out in not less than 20 seconds and nor more than 60 seconds. For example, even when processing with an automatic processor is carried out in not less than 20 seconds and not more than 60 seconds, an excellent image can be obtained because of an improvement in the roller-mark-free performance.

DETAILED DESCRIPTION OF THE INVENTION

The total processing time mentioned here is meant to be the total time taken after the tip of a film is inserted to an automatic processor and before the tip of the film comes out of a drying section, passing through a developing tank, a carrying path, a fixing tank, a carrying path, a washing tank, a carrying path and the drying section [in other words, the quotient (sec.) obtained by dividing the whole length (m) of a processing line by the line conveyance velocity (m/sec). The reason why the time for passing the carrying paths is included here is, as well known in the present industrial field, that a solution for the processing swells gelatin films also on the carrying paths and hence the processing steps can be deemed to substantially proceed there.

The light-sensitive material of the present invention comprises a support having on one side thereof at least one light-sensitive silver halide emulsion layer.

More specifically, in the present invention, at least one light-sensitive silver halide emulsion layer may be provided on both sides of a support to give a both-sided light-sensitive material, or may be provided on one side thereof to give a one-sided light-sensitive material.

The light-sensitive silver halide photographic material of the present invention contains a silver halide emulsion obtained by bringing silver halide grains formed by adding an aqueous solution of a water-soluble silver salt and an aqueous solution of a water-soluble halide in an aqueous solution containing a protective colloid, into coagulation together with the protective colloid by use of a polymer coagulant followed by removal of dissolved matters (hereinafter referred to as "emulsion according to the present invention" or so).

The emulsion according to the present invention may be contained in at least one of any emulsion layers of the light-sensitive material of the present invention, but the emulsion according to the present invention may preferably be contained in many of the emulsion layers, and more preferably in all of the emulsion layers.

The emulsion according to the present invention is prepared by adding an aqueous solution of a water-soluble silver salt and an aqueous solution of a water-soluble halide in an aqueous solution containing a protective colloid, and obtained by bringing silver halide grains formed thereafter, into coagulation together with the protective colloid from the state of a suspension by use of a polymer coagulant, followed by removal of dissolved matters in the suspension.

Here, the aqueous solution containing a protective colloid refers to an aqueous solution in which protective colloid is formed by gelatin or other materials capable of constituting a hydrophilic colloid (e.g. materials capable of serving as a binder), and may preferably refer to an aqueous solution containing colloidal protective gelatin.

In instances in which gelatin is used as the above protective colloid in working the present invention, the gelatin may be either subjected to lime treatment or treated with use of an acid. Details of the preparation method for the gelatin are described in Arther Vice, The Macromolecular Chemistry of Gelatin, Academic Press, published 1964.

Hydrophilic colloids other than the gelatin that can be used as protective colloids include a variety of synthetic hydrophilic polymer materials as exemplified by proteins such as gelatin derivatives, graft polymers of gelatin with other polymers, albumin, and casein; sugar derivatives such as cellulose derivatives including hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfates, sodium alginate, and starch derivatives: homopolymers or copolymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl pyrrolidone, polyacrylate, polymethacrylate, polyacrylamide, polyvinyl imidazole, and polyvinyl pyrazole.

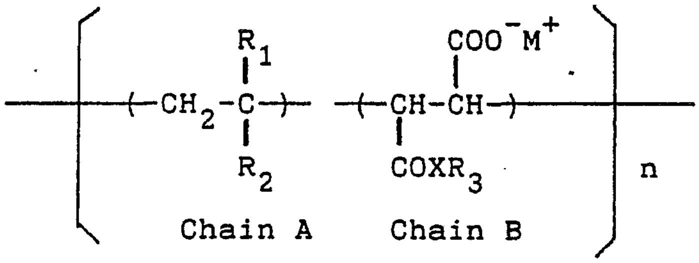
In the case of gelatin, the one having a jelly strength of 200 or more when measured by the PAGI method may preferably be used.

In the light-sensitive material of the present invention, it is advantageous to use gelatin as the hydrophilic colloid that can be used in photographic component layers such as protective layers, backing layers and intermediate layers that are optionally formed, but it is also possible to use the above hydrophilic colloids other than that alone or together with the gelatin.

The aqueous solution of a water-soluble silver salt and aqueous solution of a water-soluble halide refer to what are reacted to obtain a desired silver halide, and they are appropriately selected and combined depending on the desired composition of silver halides.

The polymer coagulant refers to a polymeric material capable of bringing silver halide grains into coagulation together with the protective colloid. Using such a polymer coagulant, the gelatin or the like, which is the protective colloid, is coagulated and formed into a gel, and then the step of removing dissolved matters such as soluble salts in the solution is carried out (the so-called desalting step).

In the present invention, various types of agents can be used as the polymer coagulant, but preferred ones may include a polymeric compound represented by Formula (I), comprising Chain A and Chain B as shown below. Formula (I)



$$\left[\underbrace{\left(CH_2-\overset{R_1}{\underset{R_2}{C}} \right)}_{\text{Chain A}} \underbrace{\left(\overset{COO^-M^+}{CH}-\underset{COXR_3}{CH} \right)}_{\text{Chain B}} \right]_n$$

wherein R_1 and R_2 each represent an aliphatic group which may be the same with or different from each other; R_3 represents a hydrogen atom, an aliphatic group, an aryl group or an aralkyl group: X represents -O- or NH- ; M^+ represents a cation; and n is an integer of from 10 to 10^4; provided that either one of two bonding arms in Chain B may be connected with the R_1 and R_2- bonded tertiary carbon atom in Chain A, and when X represents -NH- it may form a nitrogen-containing heterocyclic ring together with R_3.

Also preferably used is a modified gelatin in which 50 % or more of amino groups in gelatin molecules has been substituted (hereinafter referred to as an "coagulating gelatin agent). Examples of the substituents for the amino groups of gelatin are described in U.S. patents No. 2,91,582, No. 2,164,928 and No. 2,525,753.

Useful substituents may include;

(1) acyl groups such as alkylacyl, arylacyl, acetyl and substituted or unsubstituted benzoyl;

(2) carbamoyl groups such as alkylcarbamoyl and arylcarbamoyl;

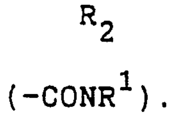
(3) sulfonyl groups such as alkylsulfonyl and arylsulfonyl;

(4) thiocarbamoyl groups such as alkylthiocarbamoyl and arylthiocarbamoyl;

(5) straight-chain or branched alkyl groups having 1 to 18 carbon atoms; and

(6) aryl groups such as substituted or unsubstituted phenyl or naphthyl and aromatic heterocyclic group such as pyridyl and furyl.

Among these preferred modified gelatin (coagulating gelatin agent) include those substituted with an acyl group (-COR¹) or a carbamoyl group



$$(-CO\overset{R_2}{N}R^1).$$

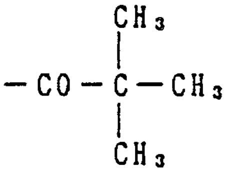
The above R^1 represents a substituted or unsubstituted aliphatic group as exemplified by an alkyl group having1 to 18 carbon atoms and an allyl group, or an aryl group or aralkyl group as exemplified by a phenethyl group, and R^2 represents a hydrogen atom, an aliphatic group, an aryl group or an aralkyl group.

Particularly preferred ones include instances in which R^1 is an aryl group and R^2 is a hydrogen atom.

Examples of the coagulating gelatin agent used as the polymer coagulant in the present invention are shown below as substituents for the amino group, but the present invention is by no means limited by these.

Exemplary coagulating gelatin agents (substituents for the amino group):

G - 1

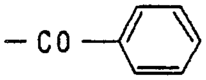


$-CO-C(CH_3)_2-CH_3$

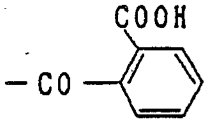
G - 2

$-COCH_3$

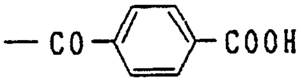
G - 3



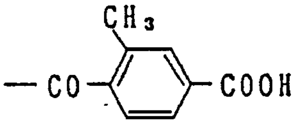
G - 4



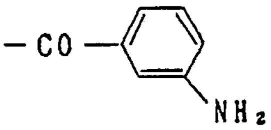
G - 5



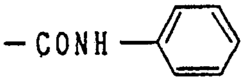
G - 6



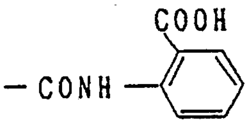
G - 7



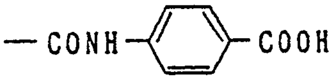
G - 8



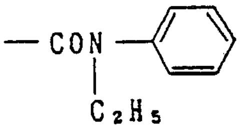
G - 9



G - 10



G - 11



G - 12

$-CONHCH_3$

In instances in which the coagulating gelatin agent is used in the step of removing dissolved matters (desalting), there is no particular limitation on the amount of the agent to be added, but it is appropriate for it to be added in an amount of from 0.3 to 10 times (by weight) that of the material (preferably gelatin) contained as a protective colloid at the time of the removing, and particularly preferably 1 to 5 times (by weight).

In the present invention, silver halide grains are brought into coagulation together with the protective colloid by use of the polymer coagulant, and, when the coagulating gelatin agent is used as the polymer coagulant, the pH may be adjusted after the addition of the coagulating gelatin agent to effect coagulation of a silver halide emulsion. The pH at which the coagulation is effected may preferably be 5.5 or less, and particularly preferably 4.5 to 2. There are no particular limitations on the acid used in the adjustment of the pH, but preferably used are organic acids such as acetic acid, citric acid and salicylic acid, and inorganic acids such as hydrochloric acid, nitric acid, sulfuric acid and phosphoric acid. For use in combination with the coagulating gelatin agent, heavy metal ions may be added as exemplified by magnesium ions, cadmium ions, lead ions and zirconium ions.

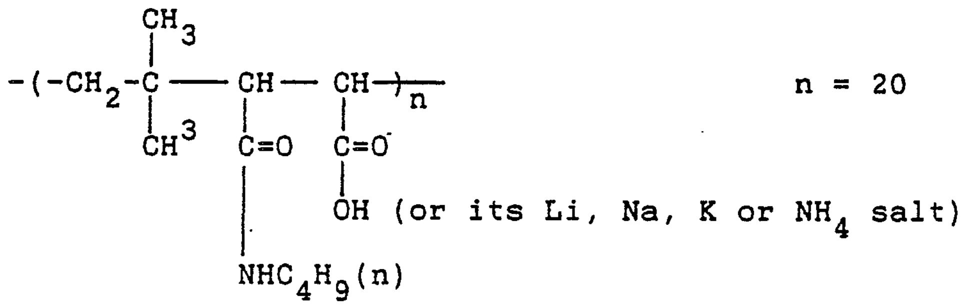
The removal of the dissolved matters (i.e., desalting) may be carried out once or may be repeated several times. In instances in which it is repeated several times, the coagulating gelatin agent may be added every time when the removal is carried out, but the coagulating gelatin agent may be added only at the beginning.

Next, description will be made on the instance where the polymeric compound represented by the above Formula (I) is used in the present invention as the polymer coagulant. This polymeric compound may preferably have a molecular weight of from 10^3 to 10^6 and more preferably from 3×10^3 to 2×10^5, and may be added in an amount of from 1/50 to 1/4, and more preferably from 1/40 to 1/10, in weight ratio, based on the protective colloid (preferably gelatin) contained in the emulsion. The method to use it may follow what has been described for the coagulating gelatin agent.

Examples of the polymeric compound represented by Formula (I) are set out below, but by no means limited to these.

Exemplary polymeric compound represented by Formula (I):

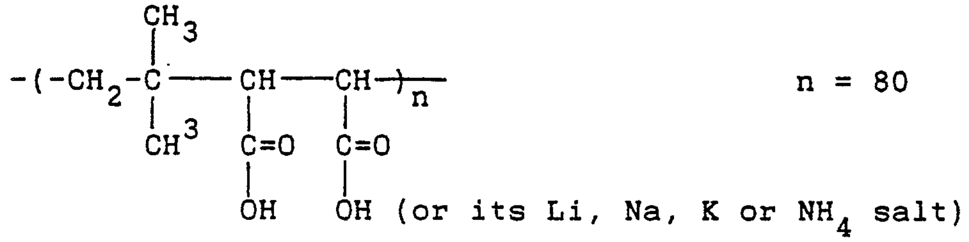
P-1



$$-(-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\underset{NHC_4H_9(n)}{C=O}}{CH}-\underset{\underset{OH}{C=O}}{CH}-)_n \quad n = 20$$

(or its Li, Na, K or NH_4 salt)

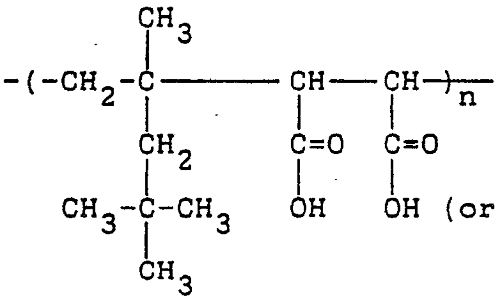
P-2



$$-(-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\underset{OH}{C=O}}{CH}-\underset{\underset{OH}{C=O}}{CH}-)_n \quad n = 80$$

(or its Li, Na, K or NH_4 salt)

P-3

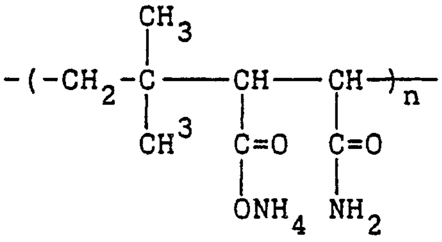


$$-(-CH_2-\underset{\underset{CH_3-\underset{CH_3}{C}-CH_3}{CH_2}}{\overset{CH_3}{C}}-\underset{\underset{OH}{C=O}}{CH}-\underset{\underset{OH}{C=O}}{CH}-)_n-$$

(or its Li, Na, K or NH_4 salt)

n = 35

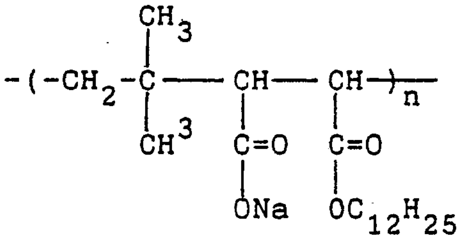
P-4



$$-(-CH_2-\underset{CH^3}{\overset{CH_3}{C}}-\underset{\underset{ONH_4}{C=O}}{CH}-\underset{\underset{NH_2}{C=O}}{CH}-)_n-$$

n = 60

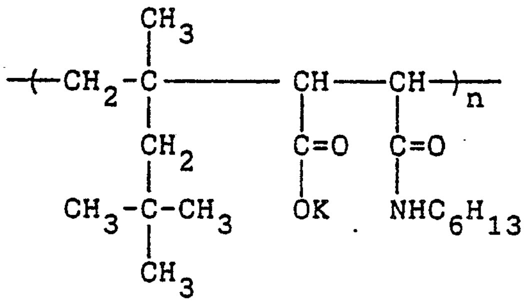
P-5



$$-(-CH_2-\underset{CH^3}{\overset{CH_3}{C}}-\underset{\underset{ONa}{C=O}}{CH}-\underset{\underset{OC_{12}H_{25}}{C=O}}{CH}-)_n-$$

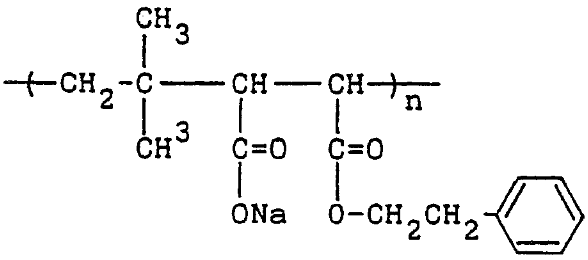
n = 8

P-6



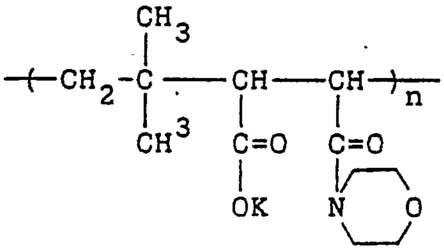
n = 20

P-7



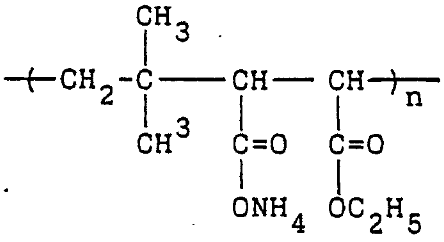
n = 20

P-8



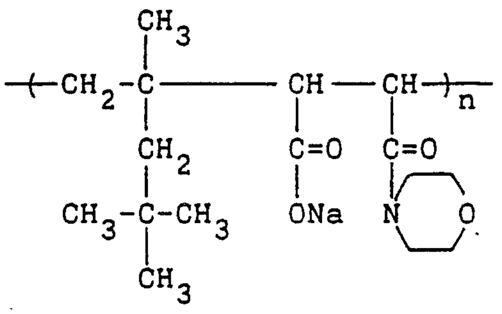
n = 16

P-9



n = 40

P-10



n = 15

The emulsion according to the present invention may be obtained by preparing an emulsion containing seed crystals and allowing grains to grow from the seed crystals. In the instance where the seed crystals are used and the emulsion itself containing the seed crystals is the emulsion according to the present invention in which the polymer coagulant is used, all the emulsions obtainable therefrom fall under the emulsion according to the present invention. However, a seed crystal emulsion for obtaining the emulsion according to the present invention may not necessarily be the emulsion according to the present invention. It is preferred that a seed crystal emulsion falling under the emulsion according to the present invention is used as the seed crystals and at the same time the emulsion according to the present invention, obtained by using the polymer coagulant in the present invention, is used also when the grains are made to grow therefrom.

The silver halides in the emulsion according to the present invention may be of any composition, and usable silver halides include any silver halides as exemplified by silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide, silver chloroiodide, silver chloroiodobromide and a mixture of any of these, but silver iodobromide is particularly preferably used. In the instance where the silver iodobromide is used, there is no particular limitation on the content of the silver iodide. However, an average silver iodide content in the whole silver halide grains may preferably be not more than 10 mol %, more preferably not more than 6 mol %, and still more preferably from 0.2 to 6 mol %.

In this instance, the silver iodide may desirably be concentrated in the inside.

Preferable silver halide grains contained in the emulsion according to the present invention may include silver halide grains having a multi-layer structure and plate-like grains.

The plate-like grains can be obtained by adding a certain type of agent as exemplified by thioethers in the course of the growth of grains. The plate-like grains are disclosed in, for example, Japanese Patent Publications Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publications) No. 113927/1983, No. 113928/1983, No. 105636/1984 (pages 252 to 253), and No. 147727/1985.

Here, the grains having a multi-layer structure refer to those provided on the outside of a core with a shell having any desired halogen composition, and the so-called core/shell grains can be used. The shell may comprise only one layer, or comprise layers laminated in two or more layers, e.g., three or four layers, and preferably not more than five layers.

Silver bromide, silver iodobromide or silver iodide may preferably be used as the silver halide in the core and shell, but a mixture with a small amount of silver chloride (specifically speaking, the one containing preferably about 10 mol % or less of silver chloride, and more preferably about 5 mol % or less, of silver chloride) may also be used.

It is preferred to use silver iodobromide grains in which the layer has been formed by making different the silver iodide content.

It is also preferred that the outermost layer substantially consists of silver bromide or substantially consists of silver iodobromide (10 % or less of silver iodide content), and it may also contain a small amount (less than several %) of chlorine atoms.

The emulsion according to the present invention is prepared by forming silver halide grains by adding an aqueous solution of a water-soluble silver salt and an aqueous solution of a water-soluble halide in an aqueous solution containing a protective colloid, and as a means for forming the silver halide grains here a variety of techniques can be used.

For example, there can be used a simultaneous mixing method; a double jet method; a method which is one form of the simultaneous mixing method, in which the pAg in the liquid phase where silver halides are produced is kept constant, i.e., the so-called controlled double jet method; and also a triple jet method as another form of the double jet method, in which soluble halogen salts each having different composition are independently added (as exemplified by soluble silver salts, soluble bromine salts and soluble iodine salts).

It is also possible to use a regular mixing method, and still also possible to use a method in which the grains are formed by use of excess silver ions (the so-called reverse mixing method).

According to the controlled double jet method, it is possible to obtain a silver halide emulsion comprising grains having a regular crystal form and an almost uniform grain size.

To obtain the regular silver halide grains like this, reaction conditions may be controlled when silver halide grains are made to grow by use of the simultaneous mixing method, but, in such a simultaneous mixing method, it is possible to use a means of preparing silver halide grains by adding an aqueous solution of a soluble silver salt as exemplified by silver nitrate and an aqueous solution of a halide in substantially equal amounts in an aqueous solution of a protective colloid with, in general, vigorous stirring.

There are no particular limitations on the grain size of the silver halide grains, but preferred grains are those having an average grain size of from 0.1 to 3 µm. More preferred are those of from 0.3 to 2 µm.

The emulsion according to he present invention may be either a monodisperse emulsion or a polydisperse emulsion, both of which can effectively exhibit the effect of the present invention.

The emulsion according to the present invention can be chemically sensitized.

Besides, additives can be appropriately contained in the emulsion according to the present invention or other emulsions optionally used to constitute the light-sensitive material of the present invention.

More specifically, the light-sensitive material that embodies the present invention may contain any desired additives, which are described in Research Disclosures Vol. 176, No. 17643 (December, 1978) and Vol. 187, No. 18716 (November, 1976). Corresponding passages thereof are summarized in the following table.

Photographic additives that can be used in preparing the emulsion in working the present invention described above are also described in the above two Research Disclosures. The following table shows where they are described.

Type of additives	RD 17643	RD 18716
1. Chemical sensitizer	p.23	p.648, right col. ff.
2. Speed-increasing agent		ditto
3. Spectral sensitizer Supersensitizer	pp.22-24	p.648, right col. to p.649, right col.
4. Brightening agent	p.24	
5. Antifoggant Stabilizer	pp.24-25	p.649, right col.
6. Colored coupler	p.25	p.649, right col.
7. Organic solvent	p.25	

8. Light-absorbent Filter dye Ultraviolet absorbent	pp.25-26	p.648, right col. to p.650, left col.
9. Stain preventive agent	p.25, right col.	p.650, left to right col.
10. Dye-image stabilizer	p.25	
11. Hardening agent	p.26	p.651, left col.
12. Binder	p.26	ditto
13. Plasticizer Lubricant	p.27	p.650, right col.
14. Coating auxiliary Surfactant	pp.26-27	ditto
15. Antistatic agent	p.27	ditto

The amount of the gelatin used to constitute the light-sensitive silver halide photographic material of the present invention may be arbitrarily selected, but the amount of gelatin may more desirably be as small as possible in view of the rapid processing. For example, the amount of gelatin per one side on the side having a light-sensitive emulsion layer of an undeveloped light-sensitive material (in the case of the both-sided light-sensitive material, the amount of gelatin when only one side is noted) may be controlled in the range of from 2.0 to 3.5 g/m^2 to preferably work the invention.

The present invention, which can remarkably exhibit the effect particularly when the amount of gelatin has been reduced so as to be adapted to rapid processing, can be said to be feasible for the rapid processing.

The support for the light-sensitive material may be made of any desired materials.

In the developing solution used in the processing of the light-sensitive material, a developing agent such as dihydroxybenzene as exemplified by hydroquinone, 3-pyrazolidones as exemplified by 1-phenyl-3-pyrazolidone, aminophenols as exemplified by N-methyl-p-aminophenol can be used alone or in combination.

Details thereof are described in L.F.A. Mason, Photographic Processing Chemistry, Forcal Press, 1975 and Research Disclosures Vol. 188, No. 18873 (December, 1979) and Vol. 204, No. 20405 (April, 1981).

EXAMPLES

Examples of the present invention will be described below in detail. As a matter of course, the present invention is by no means limited by the following Examples.

Example 1

In the present Example, two types of seed crystals T-1 and T-2 were prepared in the manner as shown below, and also prepared were Emulsion 1-1 (a comparative emulsion) and Emulsion 1-2 (an emulsion according to the present invention), obtained by effecting crystal growth from Seed Crystal T-1 (this seed crystal emulsion T-1 corresponds to a comparative emulsion), and Emulsion 1-3 (an emulsion according to the present invention) and Emulsion 1-4 (an emulsion according to the present invention), obtained by effecting crystal growth from Seed Crystal T-2 (this seed crystal emulsion T-2 correspond to an emulsion according to the present invention). Emulsion 1-5 (a comparative emulsion) and Emulsion 1-6 (an emulsion according to the present invention), which are monodisperse and do not use any seed crystals, were further obtained. Emulsion 1-7 (an emulsion according to the present invention) and Emulsion 1-8 (a comparative emulsion), which are polydisperse, were also obtained, and Emulsion 1-9 (a comparative emulsion) and Emulsion 1-10 (an emulsion according to the present invention), containing plate-like grains, were further obtained.

In describing below the present Example, descriptions are made by dividing them into (i) preparation of emulsions (preparation of the above emulsions 1-1 to 1-10) and (ii) preparation of and evaluation on samples (preparation of samples by use of the above emulsions 1-1 to 1-10, and evaluation thereon based on the processing of the samples and the results from various measurements).

(i) Preparation of emulsions:

(A) Preparation of Seed Crystals T-1 and T-2:

Monodisperse cubic grains of silver iodobromide containing 2 mol % of silver iodide and having an average grain size of 0.3 µm were prepared according to a double jet method while controlling the conditions to 60° C, pAg = 8 and pH = 2.0. A reaction mixture containing the resulting grains was divided into two portions, which were respectively subjected to the desalting as shown below to obtain two types of seed crystals (T-1 and T-2).

Desalting for T-1:

While keeping the temperature at 40° C, added to the reaction mixture obtained after the mixing was completed were 15 g/mol•AgX of a condensate (Compound I) of sodium naphthalenesulfonate with formalin and 60 g/mol•AgX of magnesium sulfate $MgSO_4$, and the resulting mixture was stirred for 3 minutes. The mixture was left to stand thereafter to remove excess salts by decantation. Thereafter, 2.1 ℓ/mol•AgX of pure water of 40° C was added thereto to effect dispersion, followed by addition of 30 g/mol•AgX of $MgSO_4$ and stirring for 3 minutes, and then the reaction mixture was left to stand to carry out decantation. Thereafter, so called post gelatin was added, and the mixture was kept to 55° C, stirred for 20 minutes and re-dispersed to obtain T-1.

Desalting of T-2 (corresponding to the means for removing dissolved matters to obtain the emulsion according to the present invention):

While keeping the temperature at 40° C, added to the reaction mixture obtained after the mixing was completed was 38 g of a modified gelatin of which 90 % of the amino groups has been substituted by the exemplary group G-8 shown above, and the resulting mixture was stirred for 3 minutes. Thereafter, 0.13 g/mol•AgX of potassium hydroxide KOH was added thereto to control the pH to 4.0, and the mixture was left to stand to carry out decantation. Thereafter, 2.1 ℓ/mol•AgX of pure water of 40° C was added thereto, followed by addition of 0.25 g/mol•AgX of KOH to control the pH to 5.8, and then stirring for 5 minutes. Thereafter, 1.5 cc/mol•AgX of nitric acid HNO_3 (1.7 N) was added thereto to control the pH to 4.3, and the mixture was left to stand to carry out decantation. Thereafter, post gelatin and 0.2 g/mol•AgX of KOH were added, and, with the pH controlled to 5.8, the mixture was re-dispersed to obtain T-2.

This seed crystal emulsion T-2 is an emulsion according to the present invention, and hence the emulsion obtained therefrom is the emulsion according to the present invention.

(B) Growth from seed crystals:

Using the above Seed Crystals T-1 and T-2, the grains were made to grow in the following manner: First, Seed Crystal T-1 was dissolved in 8.5 ℓ of an aqueous solution containing a protective colloid and optionally ammonia (corresponding to the aqueous solution containing a protective colloid), kept to 40° C, and the pH was adjusted by using acetic acid. Using the resulting solution as a mother solution, an aqueous solution of 3.2 N ammoniacal silver ions as the aqueous solution of water-soluble silver salt was added thereto according to a double jet method. Here, the pH and pAg were varied on occasion depending on the silver iodide content and crystal habit. More specifically, the pAg was controlled to 7.3, and the pH, to 9.7, thus forming a layer having a silver iodide content of 35 mol %. Next, the pH was varied to between 8 and 9 and the pAg was kept to 9.0 to make grains grow to the extent of about 95 % of the final grain size. Thereafter, an aqueous potassium bromide solution as the aqueous solution of a water-soluble halide was added over a period of 8 minutes through a nozzle, the pAg was dropped to 11.0, and the mixing was completed 3 minutes after the addition of the potassium bromide was completed. Next, the pH was dropped to 6.0 using acetic acid. The resulting emulsion was comprised of monodisperse grains having an average grain size of 0.53 µm and also having a silver iodide content of about 2 mol % in the whole grains. Subsequently, the resulting reaction mixture is divided into two portions, which were respectively subjected to removal of excess soluble salts (corresponding to the removal of dissolved matters) according to the two types of methods for the desalting methods (a) and (b) as shown below.

Desalting method (a):

1. While keeping the temperature to 40° C, added to the reaction mixture obtained after the mixing is completed are 5.5 g/mol•AgX of the previously mentioned Compound I (corresponding to a comparative compound with respect to the polymer coagulant used in the present invention) and 8.5 g/mol•AgX of $MgSO_4$, and the resulting mixture is stirred for 3 minutes, and then left to stand to carry out decantation.
2. After 1.8 ℓ/mol•AgX of pure water of 40° C is added to effect dispersion, 20 g/mol•AgX of $MgSO_4$ is added, and thereafter the mixture is stirred for 3 minutes and then left to stand to carry out decantation.
3. The step of the above 2. is repeated once more.
4. After 15 g/mol•AgX of post gelatin and water are added to make up the mixture to 450 cc/mol•AgX, the mixture is stirred at 55° C for 20 minutes to effect dispersion.

Emulsion 1-1 was obtained in this way.

Desalting method (b):

1. While keeping the temperature to 40° C, added to the reaction mixture obtained after the mixing is completed is 50 g/mol•AgX of a modified gelatin of which amino groups have been substituted by the exemplary group G-8 shown above, followed by addition of 110 cc/ of 56 wt.% acetic acid HAC to drop the pH to 5.0, and the resulting mixture is left to stand to carry out decantation.
2. After 1.8 ℓ/mol•AgX of pure water of 40° C is added, 6.8 g/mol•AgX of KOH is added to control the pH to 6.0, and dispersion is effected. After the dispersion was sufficiently effected, 70 cc/mol•AgX of 56 wt.% HAC is added to control the pH to 4.5, and the mixture is left to stand to carry out decantation.
3. The step of the above 2. is repeated once more.
4. Thereafter, 15 g/mol•AgX of post gelatin, 1 g/mol•AgX of KOH and water are added to make up the mixture to 450 cc/mol•AgX.

Emulsion 1-2 was obtained in this way. The above desalting method (b) corresponds to the means for removing dissolving matters to obtain the emulsion according to the present invention.

In the same manner as above, grains were made to grow using Seed Crystal T-2, and Emulsions 1-3 and 1-4 were obtained according to the above two types of desalting methods.

(C) Preparation of Emulsions 1-5 and 1-6 by preparing monodisperse grains without using any seed crystals:

In the same procedures as those for the seed crystals, i.e., under conditions of 60° C, pAg = 8 and pH = 2.0, an aqueous halogen salt solution and an aqueous silver salt solution were added according to the controlled double jet method to obtain grains having an average grain size of 0.53 µm and an average silver iodide content of 2 mol %. Emulsions containing such grains were desalted by the two types of methods in the same manner as for the seed, thus obtaining Emulsion 1-5 (a comparative emulsion) and Emulsion 1-6 (an emulsion according to the present invention).

(D) Preparation of polydisperse emulsions:

These were prepared using the following four types of solutions according to a regular mixing method:

Solution A	
Silver nitrate	100 g
Ammonia water (28%)	78 cc
By adding water, made up to	240 cc
Solution B:	
Ossein gelatin	8 g
Potassium bromide KBr	80 g
Potassium iodide KI	1.3 g
By adding water, made up to	550 cc
Solution C:	
Ammonia water	6 cc
Glacial acetic acid	10 cc
Water	34 cc
Solution D:	
Glacial acetic acid	226 cc
By adding water, made up to	400 cc

Solution B and Solution C were poured into a reaction vessel for use in preparing emulsions, which were stirred with a propeller type stirrer rotating at 300 rpm/min, while keeping the reaction temperature at 55 °C.

Next, Solution A was divided in the proportion of 1 part by volume : 2 parts by volume, and 80 mℓ, corresponding to 1 part by volume among them, of the solution was poured into the vessel taking a period of 1 minute. After stirring was continued for 10 minutes, 160 mℓ of the solution, corresponding to the remaining 2 parts by volume of Solution A, was poured into the vessel taking a period of 10 minutes. Stirring was further continued for 30 minutes. Then, Solution D was added and the pH of the solution in the reaction vessel was controlled to 6.0, where the reaction was stopped.

Thereafter, desalting was carried out using the two types of desalting methods (a) and (b), thus obtaining Emulsion 1-7 (a comparative emulsion and Emulsion 1-8 (an emulsion according to the present invention), respectively.

(E) Preparation of plate-like grains:

In 1 ℓ of water, 10 cc of an aqueous 0.5 wt.% solution of thioether [$HO(CH_2)_2S(CH_2)_2S(CH_2)_2S(CH_2)_2OH$] and 30 g of gelatin were added and dissolved, and the resulting solution was kept to 70 °C. In the solution, 30 mℓ of an aqueous 0.88 mol/ℓ solution of silver nitrate and 30 mℓ of an aqueous 0.88 mol/ℓ solution of potassium iodide and potassium bromide (in molar ratio of 3.5:96.5) were added with stirring according to a double jet method. After addition of this mixed solution, the temperature was dropped to 40 °C. Thereafter, the solution was divided into two portions, to one of which 24.6 g/mol•AgX each of Compound (I) and $MgSO_4$ was added, and the pH was dropped to 34.0 to carry out desalting, followed by addition of 15 g/mol•AgX of post gelatin, thus preparing Emulsion 1-9 (a comparative emulsion). The other portion was also subjected to desalting according to Steps 1 and 4 of the desalting method (b), thus obtaining Emulsion 1-10 (an emulsion according to the present invention).

Emulsions 1-1 to 1-10 were obtained as in the above, where, in respect of the grains in (A) to (E), the grains subjected to desalting by the means for obtaining the emulsion according to the present invention showed better re-dispersibility in all instances.

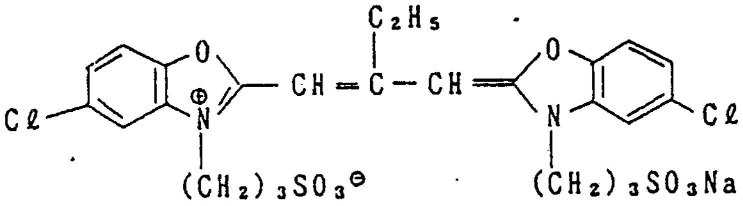
(ii) Preparation of samples and evaluation thereon:

(ii-1) Preparation of samples:

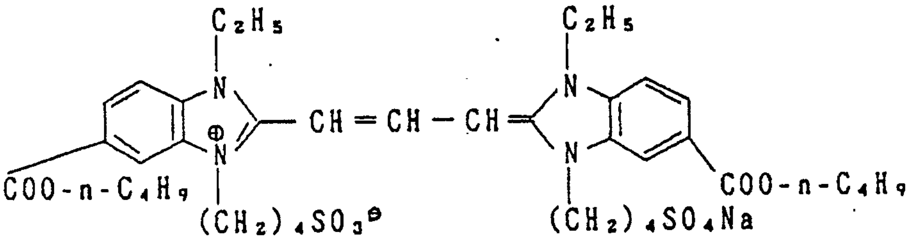
The ten types of emulsions obtained in the above (i) were chemically sensitized. More specifically, gold-sulfur sensitization was carried out by adding ammonium thiocyanate, chloroauric acid and hypo.

After this chemical sensitization was completed, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added. Thereafter, 150 mg/mol•AgX of potassium iodide, and 300 mg/mol•AgX and 15 mg/mol•AgX of spectral sensitizing dyes (1) and (2), respectively, were added to carry out spectral sensitization.

Spectral sensitizing dye (1)

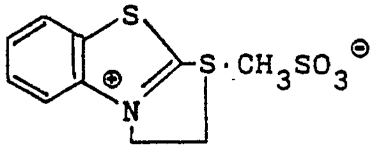
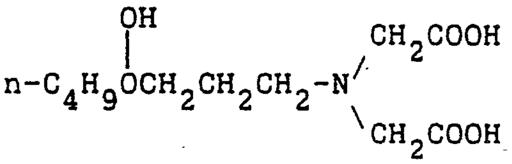


Spectral sensitizing dye (2)

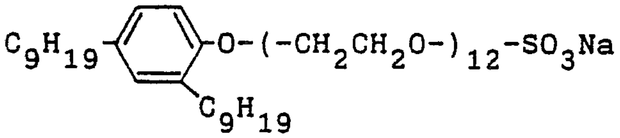
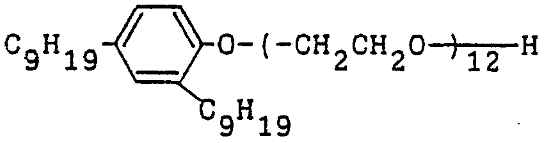
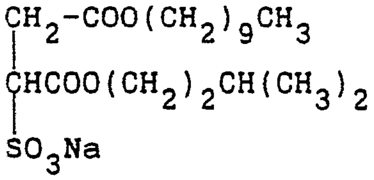


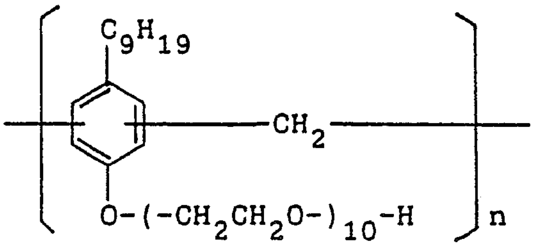
The coating solutions and protective layer coating solutions thus obtained were coated in layers on both sides of a polyester-film support having been subjected to subbing treatment, in such a way that two layers are simultaneously coated in the order of a silver halide emulsion layer and a protective layer from the support side, which were thereafter dried to prepare silver halide photographic films.

To the above emulsion layers, the following additives were added per mol of silver halide.

t-Butyl catechol	400 mg
Polyvinyl pyrrolidone (molecular weight: 10,000)	1.0 g
Styrene/maleic anhydride copolymer	2.5 g
Trimethylolpropane	10 g
Diethylene glycol	5 g
Nitrophenyl-triphenyl-phosphonium chloride	50 mg
Ammonium 1,3-dihydroxybenzene-4-sulfonate	4 g
Sodium 2-mercaptobenzimidazole-5-sulfonate	15 mg
	70 mg
 $n\text{-}C_4H_9\overset{\overset{OH}{\vert}}{O}CH_2CH_2CH_2\text{-}N\begin{matrix} CH_2COOH \\ CH_2COOH \end{matrix}$	1 g
1,1-Dimethylol-1-bromo-1-nitromethane	10 mg

To the protective layers, the following compounds were added per 1 g of gelatin.

	10 mg
	2 mg
 $\begin{array}{l} CH_2\text{-}COO(CH_2)_9CH_3 \\ \vert \\ CHCOO(CH_2)_2CH(CH_3)_2 \\ \vert \\ SO_3Na \end{array}$	7 mg
$C_9F_{19}\text{-}O\text{-}(\text{-}CH_2CH_2O\text{-})_{10}\text{-}CH_2CH_2OH$	2 mg
$C_8F_{17}SO_3K$	3 mg



15 mg

(n = 3)

Polymethyl methacrylate having an average particle size of 5 µm (a matting agent)	7 mg
Colloidal silica (average particle size: 0.013 µm)	70 mg
Aqueous 40 % $(CHO)_2$ solution	1.5 mℓ
35 % HCHO	2 mℓ
Aqueous 2 % sodium 2,4-dichloro-6-hydroxy-1,3,5-triazine	10 mℓ

The following was used as a subbing solution.

(Subbing solution)

A copolymer comprising three types of monomers, comprising 50 wt.% of glycidyl methacrylate, 10 wt.% of methyl methacrylate and 40 wt.% of butyl methacrylate was diluted to give its concentration of 10 wt.%, to obtain an aqueous copolymer dispersion, which was used as a subbing solution.

The amount of gelatin of an undeveloped film used here was 3.10 g/m^2 per one side. Samples 2-1 to 2-10 were thus obtained, corresponding to Emulsions 1-1 to 1-10 (See Table 1).

(ii-2) Evaluation of samples (Processing and measurement of samples):

The following measurement and evaluation were made on the samples.

Sensitometry measurement:

Using as a light source the standard light B as described on page 39 of "SHINPEN SHOMEI-NO-DETABUKKU (Data Book of Lighting, New Version)", edited by SHADANHOJIN SHOMEI GAKKAI (Lighting Society Corporation), 1st Edition, 2nd Issue, all the samples 2-1 to 1-10 as shown in Table 1 were subjected to the so-called white exposure, wherein non-filter exposure is carried out in an exposure time of 0.1 second and at 3.2 CMS (candle meter second). Here, this exposure was made from both side of a film so as to give the same amount of light on both sides of the film. The above samples were processed with a development processing solution XD-90 (a product of Konica Corporation), at 35° C for 90 seconds, using an automatic processor KX-800 manufactured by Konica Corporation, to determine the speed of each sample.

The speed was obtained by finding a reciprocal of the amount of light which is necessary for the blackening density to increase by 1.0 owing to the exposure. Provided that, in Table 1, the speed is indicated as relative speed assuming the speed of Sample 2-1 as 100.

Evaluation on roller marks:

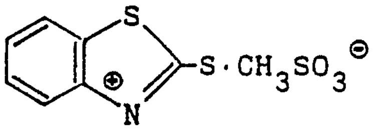
The pressure resistance in development processing (resistance to pressure marks, i.e. roller marks, made by rollers of the automatic processor) was evaluated in the following way: Samples, which were not exposed to light, were processed using an X-ray automatic processor that comprises strongly uneven particular rollers comprising opposing rollers and is capable of changing processing time in such a way that the processing can be carried out in the processing time as shown below. Here, the processing was carried out in three processing times: 3 minutes 30 seconds, 90 seconds, and 45 seconds. As to the processing temperature, it was 32° C for the processing in 3 minutes 30 seconds, 35° C for the processing in 90 minutes, and 37° C for the processing in 45 minutes. Results obtained are shown in Table 1.

Roller marks made at that time were evaluated by grouping into 5 ranks depending on their degree.

5 No roller mark was made.
4 Roller marks were very slightly made.
3 They were slightly made (tolerable to practical use.
2 Many roller marks were made (intolerable to practical use).
1 Very many roller marks were made.

The developing solution and fixing solution used in the processing each had the composition as shown below.

Developing solution :

Potassium sulfite	68.75 g
Sodium hydroxyethyl ethylenediaminetriacetate	8 g
1,4-Dihydroxybenzene	27 g
Boric acid	10 g
5-Methylbenzimidazole	0.035 g
1-Phenyl-5-mercaptotetrazole	0.015 g
Sodium metabisulfate	5.0 g
Acetic acid (90%)	12.8 g
Diethylene glycol	16.0 g
1-Phenyl-3-pyrazolidone	1.2 g
5-Nitroindazole	0.14 g
	0.001 g
Glutaldehyde	3.08 g
potassium bromide	4.0 g
5-Methylbenzotriazole	0.05 g

Made up to an aqueous 1 ℓ solution, and made to have the pH of 10.40 using potassium hydroxide.

Fixing solution :

Ammonium thiosulfate	140 g
Sodium sulfite	7.3 g
Sodium acetate	15.5 g

Aluminum sulfate·deca- to octadecahydrate	27.7 g
Sulfuric acid (50 wt.%)	6.0 g
Citric acid	0.9 g
Boric acid	7.0 g
Glacial acetic acid	5.1 g
Disodium ethylenediaminetetraacetate	5 g

Made up to an aqueous 1 ℓ solution, and made to have the pH of 4.3 using sulfuric acid (50 wt.%)

Table 1

Sample NO.	Emulsion NO.	Speed	Roller Marks			The present invention or not
			Processed for			
			3′30″	90″	45″	
2-1	1-1	100	1	1	2	No
2-2	1-2	95	4	4	5	Yes
2-3	1-3	100	3	4	4	Yes
2-4	1-4	95	5	5	5	Yes
2-5	1-5	90	1	1	2	No
2-6	1-6	80	3	4	4	Yes
2-7	1-7	80	1	1	2	No
2-8	1-8	80	3	4	4	Yes
2-9	1-9	100	2	2	2	No
2-10	1-10	95	4	4	4	Yes

As will be evident from Table 1, Samples Nos. 2-2 to 2-4, 2-6, 2-8 and 2-10, which are the samples according to the present invention, all can be said to have good speed and also good roller mark resistance, and have been improved in roller mark resistance when they were subjected to rapid processing. The effect of the present invention is also evident when samples containing grains of the same type are compared with each other, namely, when Comparative Sample 2-1 and Samples 2-2 to 2-4 according to the present invention are compared, and similarly when Sample 2-5 and Sample 2-6, Sample 2-7 and Sample 2-8, and Sample 2-9 and Sample 2-10 are compared, respectively.

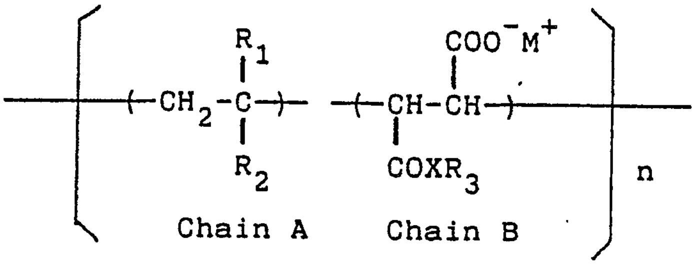
When the samples according to the present invention are compared with each other, Sample 2-4 in which the means for obtaining the emulsion according to the present invention has been employed in both the formation of seed crystals and the subsequent grain growth shows slightly better roller mark resistance than Sample 2-3 in which the same means has been employed only in respect of seed crystals. Other samples according to the present invention are seen to be all good as a whole and be able to obtain good results in any embodiments.

As described above, the present invention can provide a light-sensitive silver halide photographic material that can be free of any deterioration of images as exemplified by the deterioration of images owing to roller marks, can obtain an image of high quality and also can be of high speed, even when fast processing is carried out.

Claims

1. A light-sensitive silver halide photographic material comprising a support and, provided on at least one side thereof, a light-sensitive silver halide emulsion layer containing a silver halide emulsion obtained by a method comprising the steps of
adding an aqueous solution of water-soluble silver salt and an aqueous solution of a water soluble halide into an aqueous solution containing a protective colloid to precipitate silver halide grains, and
coagulating said silver halide grains together with said protective colloid by the use of a polymer coagulant, and removing a supernatant liquid containing dissolved materials.

2. The light-sensitive silver halide photographic material of claim 1, wherein said polymer coagulant is selected from the compounds represented by formula [I];



$$\left[\underbrace{-\!\left(CH_2-\underset{R_2}{\overset{R_1}{C}}\right)\!-}_{\text{Chain A}} \quad \underbrace{-\!\left(\underset{COXR_3}{CH}-\overset{COO^-M^+}{CH}\right)\!-}_{\text{Chain B}} \right]_n \qquad [I]$$

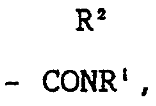
wherein R_1 and R_2 each represent an aliphatic group which may be the the same as or different from each other; R_3 represents a hydrogen atom, an aliphatic group, an aryl group or an aralkyl group; X represents - O - or - NH -; M^+ represents a cation; and n is an integer of 10 to 10^4 ; provided that either one of two bonding arms in chain B may be connected with the R_1- and R_2-bonded tertiary carbon atom in chain A, and when X is - NH -, it may form a nitrogen-containing ring together with R_3.

3. The light-sensitive silver halide photographic material of claim 1, wherein said polymer coagulant is a modified gelatin.

4. The light-sensitive silver halide photographic material of claim 3, wherein said polymer coagulant is a gelatin of which amino groups have been substituted by a group selected from an acyl group, a carbamoyl group, a sulfonyl group, a thiocarbamoyl group, an alkyl group having 1 to 18 carbon atoms, and an aryl group.

5. The light-sensitive silver halide photographic material of claim 3, wherein said polymer coagulant is a gelatin of which not less than 50 % of total amino groups contained therein has been substituted.

6. The light-sensitive silver halide photographic material of claim 5, wherein said polymer coagulant is a gelatin of which amino groups have been substituted by a group selected from an acyl group represented by - COR^1 or a carbamoyl group represented by by



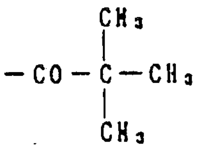
$$-\,CO\overset{R^2}{N}R^1\,,$$

wherein R^1 represents an aliphatic group, an aryl group or an aralkyl group, and R^2 represents a hydrogen atom, an aliphatic group, an aryl group or an aralkyl group.

7. The light-sensitive silver halide photographic material of claim 6, wherein said R^1 is an aryl group and R^2 is a hydrogen atom.

8. The light-sensitive silver halide photographic material of claim 5, wherein said polymer coagulant is a gelatin of which amino groups have been substituted by a group selected from the group consisting of G-1 to G-12;

G − 1

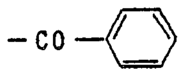


$-CO-C(CH_3)_2-CH_3$

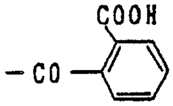
G − 2

$-COCH_3$

G − 3

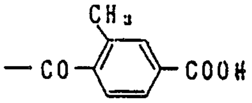


G − 4

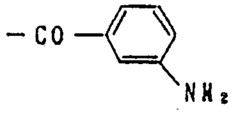


G − 5

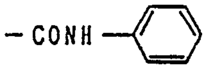
G − 6



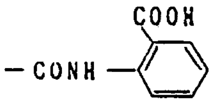
G − 7



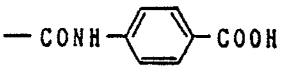
G − 8



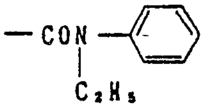
G − 9



G − 10



G − 11



G − 12

$-CONHCH_3$

9. The light-sensitive silver halide photographic material of claim 1, wherein said protective colloid is either a gelatin or another hydrophilic protective colloid.

10. The light-sensitive silver halide photographic material of claim 3, wherein said method further comprises a step of adjusting the pH of the solution after addition of the modified gelatin.

11. The light-sensitive silver halide photographic material of claim 10, wherein said pH is not more than 5.5.

12. The light-sensitive silver halide photographic material of claim 11, wherein said pH is between 2 and 4.5.

13. The light-sensitive silver halide photographic material of claim 1, wherein said silver halide grains essentially consist of a silver iodobromide containing silver iodide at a proportion of not more than 10 mol %.

14. The light-sensitive silver halide photographic material of claim 13, wherein said silver halide grain has higher silver iodide content in the inner portion thereof than the outer portion.

15. The light-sensitive silver halide photographic material of claim 1, wherein said water soluble silver salt is silver nitrate.

16. The light-sensitive silver halide photographic material of claim 1, wherein said material is to be processed after imagewise exposure in an automatic depeloping processor for a period of time ranging from 20 seconds to 3 minutes 30 seconds.

17. The light-sensitive silver halide photographic material of claim 16, wherein said period is from 20 seconds to 90 seconds.

18. The light-sensitive silver halide photographic material of claim 17, wherein said period is from 20 seconds to 60 seconds.

19. The light-sensitive silver halide photographic material of claim 1, wherein said material comprises said light-sensitive silver halide emulsion layer on both sides of the support.