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(54) Process for preparing silver halide photographic light-sensitive material for photo-mechanical process.

(57) A process for preparing a silver halide photographic light-sensitive material for photo-mechanical process is disclosed. The process involves coating a light-sensitive silver halide emulsion layer on a support and then coating a light-insensitive upper layer on the emulsion layer. The upper layer is comprised of a hydrophilic colloid and is coated on an upper portion of the emulsion layer. A composite solution is then coated on the light-insensitive upper layer. The composite solution is comprised of a solution which includes a non-diffusion polymeric hardener in a gelatin solution in an amount sufficient to make the melting time of the layer made by the gelatin solution larger than the melting time of the emulsion layer. The composite solution is coated in an amount such that the gelatin coating amount is in the range of 0.05 g/m^2 to 0.5 g/m^2. The resulting material has an improved aptitude for reduction treatment which is obtained without increasing the amount of silver coated on the support. The coating layers formed are excellent with respect to transparency.

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ACTORUM AG

PROCESS FOR PREPARING SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL FOR PHOTO-MECHANICAL PROCESS

FIELD OF THE INVENTION

This invention relates to a process for preparing a silver halide photographic light-sensitive material for photo-mechanical process (which is hereafter referred to as "light-sensitive material for photo-mechanical process") and particularly it relates to a process for preparing a light-sensitive material for photo-mechanical process which utilizes the selective hardening technique of the coating layers in order to improve aptitude for reduction treatment.

BACKGROUND OF THE INVENTION

Light-sensitive materials for photo-mechanical process are light-sensitive materials used in a photo-mechanical process step in the field of graphic art, such as for converting a continuous density image into a dot image or photographing a line drawing, etc.

When such light-sensitive materials for photo-mechanical process are used for making printing plates, a treatment called reduction treatment is frequently conducted. This treatment is performed in order to obtain delicate reproduction of tone or satisfy artistic expression of the images adapting to printing characteristics, by which fine correction of images is carried out partially or completely.

The corrections may include reduction of the area of dots or widening or narrowing of the width of a line drawing.

Therefore, aptitude for reduction treatment is a very important property in light-sensitive materials for photo-mechanical process.

When carrying out reduction treatment of light-sensitive materials for photo-mechanical process having dot images or line drawing images formed by exposure and development processing, it has been known to use a method which comprises contacting metal silver forming the dot images or line drawing images with a reducer. Various kinds of reducers are known. For example, reducers using a reducing component such as a permanganate, a ferric salt, a cerium (IV) salt, a ferricyanide, a bichromate or a persulfate, etc., are described in Mees, The Theory of the Photographic Process, pages 738-739 (1954, published by Macmillan Co.).

Since reduction treatment means a treatment comprising oxidizing silver images by a reducer to dissolve them, when dot images are subjected to reduction treatment, the decrease in area of dots is achieved accompanying with a decrease in black density of dots. Therefore, the extent to which dot images can be corrected by the reduction treatment is restricted by a degree of the decrease in black density of each dot which occurs together with the decrease in area of dots. In other words, a measure of the extent to which dot image can be corrected can be represented by a reduction of the area of dots while maintaining the black density of each dot at a specified value or more.

In the present specification, the term "reduction width" means a decrease in the area of dots from the area of dots before the reduction treatment when the black density of the dots is decreased by the reduction treatment to the lowest value necessary for the photo-mechanical process step. The term "reduction time" means the time necessary to accomplish the reduction treatment by which the black density of the dots is decreased to the lowest value necessary for the photo-mechanical process step. Thus, the wider the reduction width is, the higher the aptitude for reduction treatment is. The reduction time is necessary to be a proper length because when it is so much shorter or longer, the reduction operation is hard to carry out, and it is preferred to be several ten seconds to several minutes.

A method for improving aptitude for reduction treatment is described, for example, in Japanese Patent Application (OPI) No. 68419/77. A mercapto compound is used for the reduction treatment. However, the reducer is specific and difficult to use, because its reduction rate is different from that of conventionally used reducers. Further, it is possible to improve the aptitude for reduction treatment while increasing the covering power by softening the emulsion film, but the required film strength cannot be obtained by this method.

The most effective method for improving the aptitude for reduction treatment due to widening the reduction width is increasing the silver content for forming the images. This method is effective because the ability to correct images by the reduction treatment is generally increased when there is a greater amount of silver in the silver images per unit area, where, as described above, the reduction treatment comprises oxidizing silver images by a reducer to dissolve them. Therefore, the reduction width can be increased when a coating amount of silver halide per unit area in light-sensitive material for photo-mechanical process to be used is increased. However, since silver is very expensive and rare, as well known, increasing the coating amount of silver is not preferred in view of the cost of the light-sensitive material for photo-mechanical process and economy of resources.

Accordingly, it is an important subject in this field to produce a light-sensitive material for photo-mechanical process having the required properties while using silver in an amount as low as possible.

As a result of various investigation of methods for improving such subjects, the present inventors has found a technique for remarkably improving of the aptitude for reduction treatment by controlling the hardness of the light-insensitive upper layer and the hardness of the silver halide emulsion layer independently using a non-diffusion polymeric hardener for the light-insensitive upper layer (i.e., selective hardening technique of coating layers) and widening the reduction width by enlarging the hardness of the light-insensitive upper layer [Japanese Patent Application (OPI) No. 42039/83 (corresponding to British Patent 2,108,695A)]. In the process of progressing the further studies about this technique, however, it was found that when a polymeric hardener was used, a problem called increasing of viscosity of coating solution with the lapse of time easily occurred.

In this field, when the hardener is added to the gelatin solution, the coating thereof becomes difficult while the property of matter of the coating solution for a photographic layer deteriorates by forming the irreversible caking of gelatin or the coating surface quality are often aggravated due to a lump of insoluble substance mainly made of gelatin. This is believed to be ascribable to reacting a hardener with gelatin in a solution-preparing and solution-supplying system such as in a preparation tank, in a solution-supplying pipe or in an apparatus for supplying and for coating a coating solution for photographic layer on a support (e.g., a hopper) (hereafter referred to as "solution supplying apparatus") during time from preparation of the coating solution for photographic layer to coating the same (hereafter referred to as "dissolution time") and then gradually increasing a viscosity of the coating solution. This is the problem referred to an increasing of viscosity of coating solution with the lapse of time.

In the case of a diffusion low molecular hardener, for example, i) the occurrence of the increasing of viscosity of coating solution with the lapse of time can be previously prevented by adding the hardener continuously just before the formation step, as described in German Patent Application (OLS) No. 2,648,286, and the increasing of viscosity of coating solution with the lapse of time can also be prevented ii) by changing the pH of the coating solution or iii) by dividing the hardener to coating solutions of the layers other than the proposed layer. In case of the non-diffusion polymeric hardener, however, the above-mentioned first method is difficult to achieve a uniform hardening, the above-mentioned second method is also ineffective because the change of the hardening rate due to pH is small, and the third method described above cannot be adopted because of its nondiffusibility.

In the light-insensitive upper layer of the light-sensitive material for photo-mechanical process, fine particles which are referred to a matting agent are often added in order to improve slipping or adhesion resistance, but a problem that the opacity (referred to a haze) of the coating layer becomes large by adding the matting agent proved to be caused.

SUMMARY OF THE INVENTION

Accordingly, the first purpose of this invention is to provide a process for preparing a light-sensitive material aptitude for reduction treatment of which is improved without increasing the coating silver amount, rapidly and without causing the increasing of viscosity of coating solution with the lapse of time.

The second purpose of this invention is to provide a process for preparing a light-sensitive material for photomechanical process having a coating layer with excellent transparency.

The purposes of this invention can be achieved by coating at least one light-sensitive silver halide emulsion layer on a support and a light-insensitive upper layer consisting of a hydrophilic colloid on an upper portion of the emulsion layer and, simultaneously or after this coating, coating a composite solution in which a nondiffusion polymeric hardener is contained in a gelatin solution in an amount enough to make the melting time of the layer made by this composite solution larger than the melting time of the emulsion layer on the above-mentioned light-insensitive upper layer so that the gelatin coating amount is in the range of from 0.05 g/m^2 to 0.5 g/m^2.

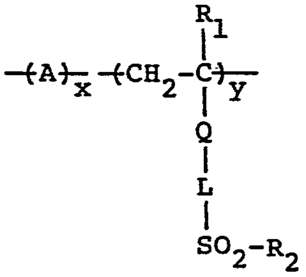
DETAILED DESCRIPTION OF THE INVENTION

An important aspect of the present invention involves making a gelatin thin layer by coating a gelatin solution containing a nondiffusion polymeric hardener on a light-insensitive upper layer so that the gelatin coating amount is in the range of from 0.05 g/m^2 to 0.5 g/m^2. The presence of this layer can prevent the viscosity from increasing with the lapse of time which takes place conventionally when a polymeric hardener is added to a coating solution for the light-insensitive upper layer containing a large amount of gelatin. Also, since such a gelatin thin layer is not coated directly on an emulsion layer but coated through a light-insensitive upper layer, the aptitude for reduction treatment and film strength can be sufficiently maintained. Moreover, when a matting agent is contained in the light-insensitive upper layer, an advantage in which the transparency of all the coating films increases by coating the above-mentioned gelatin thin layer on the upper part of light-insensitive upper layer can be obtained.

The gelatin of the gelatin thin layer of this invention is not particularly restricted, but, preferably, a so-called inert gelatin which shows little activity with respect to photographic property is used. The gelatin coating amount is set in 0.05 to 0.5 g/m^2, particularly 0.05 to 0.2 g/m^2. The gelatin concentration of this gelatin solution is desired to be thin, particularly it is desired to be 0.1 to 2 weight %, more particularly 0.5 to 1.5 weight %. As a coating solvent, water or organic solvents (especially, those having a compatibility with water) can be used, but, in general, water is most preferable. To this gelatin solution, various surface active agents can be added as coating aid. As the surface active agent, natural surface active agents such as saponin, nonionic surface active agents such as alkyleneoxide type, glycidol type and the like, anionic surface active agents containing an acidic group such as carboxylic acid, sulfonic acid (e.g., those described in U.S. Patent 3,415,649), phosphoric acid, sulfates, phosphates and the like, and amphoteric surface active agents such as amino acids, aminosulfonic acids, sulfates or phosphates of amine alcohol and the like are preferably used.

The nondiffusion polymeric hardener used in this invention is a polymeric compound having a reactive group which can react with gelatin and possesses the nondiffusibility because of being a large molecules. The specific examples include the polymeric hardeners which are well known by patents such as Japanese Patent Application (OPI) No. 66841/81, British Patent 1,322,971, U.S. Patent 3,671, 256 and the like and books such as D.M. Burness and J. Pouradier, The Theory of the Photographic Process, 4th ed. (T.H. James ed.), Macmillan, New York, 1977, p. 84, G.A. Campbell, L.R. Hamilton and I.S. Ponticello, Polymeric Amine and Ammonium Salts (E.J. Goethals ed.), Pergamon Press, New York, 1979, pp. 321-322 and the like.

Of the polymeric hardeners, those represented by the general formulae (I), (II) and (III) described below are preferred. Particularly, those represented by the general formula (I) are preferred.



$$-(A)_x-(CH_2-\underset{\underset{\underset{\underset{SO_2-R_2}{|}}{L}}{\underset{|}{Q}}}{\overset{\overset{R_1}{|}}{C}})_y-$$

(I)

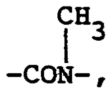
wherein A represents an ethylenically unsaturated monomer unit copolymerizable with a monomer unit set forth on the right side; R_1 represents a hydrogen atom or a lower alkyl group having from 1 to 6 carbon atoms; Q represents $-CO_2-$, $-CO\overset{\overset{R_1}{|}}{N}-$ (wherein R_1 has the same meaning as defined above) or an arylene group having from 6 to 10 carbon atoms; L represents a divalent group having from 3 to 15 carbon atoms and containing at least one linking group selected from the members consisting of $-CO_2-$ and $-CO\overset{R_1}{\underset{|}{N}}-$ (wherein R_1 has the same meaning as defined above) or a divalent group having from 1 to 12 carbon atoms and containing at least one linking group selected from the members consisting of $-O-$, $-\overset{R_1}{\underset{|}{N}}-$, $-CO-$, $-SO-$, $-SO_2-$, $-SO_3-$, $-SO_2\overset{R_1}{\underset{|}{N}}-$, $-\overset{R_1}{\underset{|}{N}}CO\overset{R_1}{\underset{|}{N}}-$ and $-\overset{R_1}{\underset{|}{N}}CO_2-$ (wherein R_1 has the same meaning as defined above); R_2 represents a vinyl group or a functional precursor group thereof selected from the members consisting of $-CH{=}CH_2$ and $-CH_2CH_2X$ (wherein X represents a group capable of being substituted with a nucleophilic group or a group capable of being released in the form of HX upon a base; and x and y each represents molar percent, x being from 0 to 99% and y being from 1 to 100%.

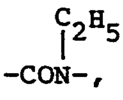
Examples of ethylenically unsaturated monomers represented by A of the general formula (I) include ethylene, propylene, 1-butene, isobutene, styrene, chloromethylstyrene, hydroxymethylstyrene, sodium vinylbenzenesulfonate, sodium vinylbenzylsulfonate, N,N,N-trimethyl-N-vinylbenzylammonium chloride, N,N-dimethyl-N-benzyl-N-vinylbenzylammonium chloride, α-methylstyrene, vinyltoluene, 4-vinylpyridine, 2-vinylpyridine, benzyl vinylpyridinium chloride, Nvinylacetamide, N-vinylpyrrolidone, 1-vinyl-2-methylimidazole, a monoethylenically unsaturated ester of an aliphatic acid (e.g., vinyl acetate and acryl acetate, etc.), an ethylenically unsaturated monocarboxylic or dicarboxylic acid and a salt thereof (e.g., acrylic acid, methacrylic acid, itaconic acid, maleic acid, sodium acrylate, potassium acrylate and sodium methacrylate, etc.), maleic anhydride, an ester of an ethylenically unsaturated monocarboxylic or dicarboxylic acid (e.g., n-butyl acrylate, n-hexyl acrylate, hydroxyethyl acrylate, cyanoethyl acrylate, N,N-diethylaminoethyl acrylate, methyl methacrylate, n-butyl methacrylate, benzyl methacrylate, hydroxyethyl methacrylate, chloroethyl methacrylate, methoxyethyl methacrylate, N,N-diethylaminoethyl methacrylate, N,N,N-triethyl-N-methacryloyloxyethylammonium-p-toluene sulfonate, N,N-diethyl-N-methyl-N-methacryloyloxyethylammonium-p-toluene sulfonate, dimethyl itaconate and monobenzyl maleate, etc.), an amide of an ethylenically unsaturated monocarboxylic or dicarboxylic acid (e.g., acrylamide, N,N-dimethylacrylamide, N-methylolacrylamide, N-(N,N-dimethylaminopropyl)acrylamide, N,N,N-trimethyl-N-(N-acryloylpropyl)ammonium-p-toluene sulfonate, sodium 2-acrylamido-2-methylpropane sulfonate, acryloyl morpholine, methacrylamide, N,N-dimethyl-N'-acryloyl propane diamine propionate betaine, and N,N-dimethyl-N'-methacryloyl propane diamine acetate betaine, etc.). Preferred examples of ethylenically unsaturated monomers represented by A of the general formula (I) include water soluble monomers, for example sodium vinylbenzenesulfonate, sodium vinylbenzylsulfonate, N,N,N-trimethyl-N-vinylbenzylammonium chloride, N,N-dimethyl-N-benzyl-N-vinylbenzylammonium chloride, sodium acrylate, N,N,N-triethyl-N-methacryloyloxyethylammonium-p-toluene sulfonate, N,N-diethyl-N-methyl-N-methacryloyloxyethylammonium-p-toluene sulfonate, acrylamide, N,N,N-trimethyl-N-(N-acryloylpropyl)ammonium-p-toluene sulfonate, sodium 2-acrylamido-2-methylpropane sulfonate, N,N-dimethyl-N'-acryloyl propane diamine propionate betaine, N,N-dimethyl-N'-methacryloyl propane diamine acetate betaine, etc. Particularly preferred examples of ethylenically unsaturated monomers represented by A of the general formula (I) include water soluble anionic monomers are water soluble amphoteric monomers, for example sodium vinylbenzenesulfonate, sodium vinylbenzylsulfonate, sodium acrylate, sodium 2-acrylamido-2-methylpropane sulfonate, N,N-dimethyl-N'-acryloyl propane diamine propionate betaine, N,N-dimethyl-N'-methacryloyl propane diamine acetate betaine, etc. and acrylamide.

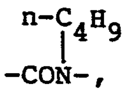
Further, when the polymer according to the present invention is used as a cross-linked latex, "A" includes not only the ethylenically unsaturated monomers described above but also monomers having at least two copolymerizable ethylenically unsaturated groups (e.g., divinylbenzene, methylenebisacrylamide, ethylene glycol diacrylate, trimethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylene glycol dimethacrylate and neopentyl glycol dimethacrylate, etc.).

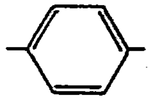
Examples of R_1 of the general formula (I) include a methyl group, an ethyl group, a butyl group and an n-hexyl group.

Examples of Q of the general formula (I) include the following groups: $-CO_2-$, $-CONH-$,


$-CO\underset{}{N}(CH_3)-$,


$-CON(C_2H_5)-$,


$-CON(n\text{-}C_4H_9)-$,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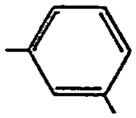
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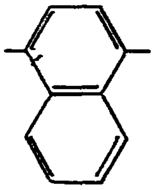
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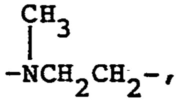
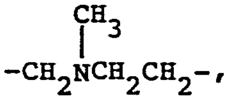
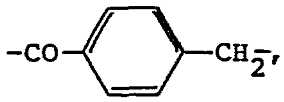
Examples of L of the general formula (I) include the following groups: $-CH_2CO_2CH_2-$, $-CH_2CO_2CH_2CH_2-$, $-CH_2CH_2CO_2CH_2CH_2-$, $-(CH_2)_5CO_2CH_2CH_2-$, $-(CH_2)_{10}CO_2CH_2CH_2-$, $-CH_2NHCOCH_2-$, $-CH_2NHCOCH_2CH_2-$, $-(CH_2)_3NHCOCH_2CH_2-$, $-(CH_2)_5NHCOCH_2CH_2-$, $-(CH_2)_{10}NHCOCH_2-CH_2-$, $-CH_2OCH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$,

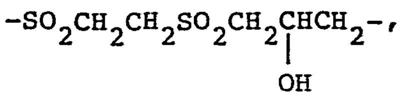

$-N(CH_3)CH_2CH_2-$,


$-CH_2N(CH_3)CH_2CH_2-$,

$-COCH_2CH_2-$, $-CH_2COCH_2CH_2-$,


,

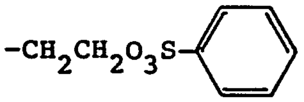
$-SOCH_2CH_2-$, $-CH_2SOCH_2CH_2-$, $-SO_2CH_2CH_2-$, $-SO_2CH_2CH_2SO_2CH_2CH_2-$,


$-SO_2CH_2CH_2SO_2CH_2CH(OH)CH_2-$,

$-SO_3CH_2CH_2CH_2-$, $-SO_3CH_2CO_2CH_2CH_2-$, $-SO_3CH_2CH_2CO_2CH_2CH_2-$, $-SO_2NHCH_2CO_2CH_2CH_2-$, $-SO_2NHCH_2CH_2CO_2CH_2CH_2-$, $-NHCONHCH_2CH_2-$, $-CH_2NHCONHCH_2CH_2-$, $-NHCO_2CH_2CH_2-$ and $-CH_2NHCO_2CH_2CH_2-$.

Examples of R_2 of the general formula (I) include the following groups: $-CH=CH_2$, $-CH_2CH_2Cl$, $-CH_2CH_2Br$,

$-CH_2CH_2O_3SCH_3$,



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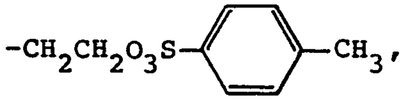
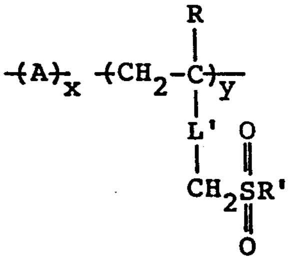


$-CH_2CH_2OH$, $-CH_2CH_2O_2CCH_3$, $-CH_2CH_2O_2CCF_3$ and $-CH_2CH_2O_2CCHCl_2$.

Other preferred examples of the polymeric hardeners are described in U.S. Patent 4,161,407, which have a repeating unit represented by the following general formula (II):

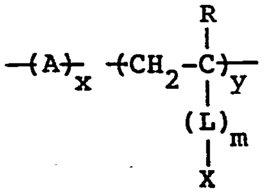


$$-(A)_x-(CH_2-\underset{\underset{CH_2SO_2R'}{|}}{\underset{L'}{\underset{|}{\overset{\overset{R}{|}}{C}}}})_y- \qquad \text{(II)}$$

wherein A represents an ethylenically unsaturated monomer unit copolymerizable with a monomer unit set forth on the right side and A may contain one or more kind(s) of ethylenically unsaturated monomer unit; x and y each represents molar percent, x being from 10 to 95% and y being from 5 to 90%; R represents a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms; R' represents $-CH=CH_2$ or $-CH_2CH_2X$ (wherein X represents a group capable of being substituted with a nucleophilic group or a group capable of being released in the form of HX upon a base); and L' represents an alkylene group (more preferably a linking group selected from an alkylene group having from 1 to 6 carbon atoms, such as a methylene group, an ethylene group, an isobutylene group, etc.), an arylene group having from 6 to 12 carbon atoms (for example, a linking group selected from a phenylene group, a tolylene group, a naphthalene group, etc.), -COZ- or $-COZR_3-$ (wherein R_3 represents an alkylene group having from 1 to 6 carbon atoms or an arylene group having from 6 to 12 carbon atoms and Z represents an oxygen atom or NH).

Examples of A of the general formula (II) include the same examples of A of the general formula (I), examples of R of the general formula (II) include the same examples of R_1 of the general formula (I) and examples of R' of the general formula (II) include the same examples of R_2 of the general formula (I), all of which are described above.

Still other preferred examples of the polymeric hardeners are described in British Patent 1,534,455, which have a repeating unit represented by the following general formula (III):



$$-(A)_x-(CH_2-\overset{\displaystyle R}{\underset{\substack{|\\(L)_m\\|\\X}}{C}})_y- \qquad \text{(III)}$$

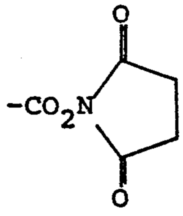
wherein A represents an ethylenically unsaturated monomer unit copolymerizable with a monomer unit set forth on the right side; R represents a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms; L represents a divalent linking group having from 1 to 20 carbon atoms (more preferably a divalent group having from 1 to 12 carbon atoms and containing at least one linking group selected from the members consisting of -CONH- and -CO-); X represents an active ester group; x and y each represents molar percent, x being from 0 to 95% and y being from 5 to 100; and m represents 0 or 1.

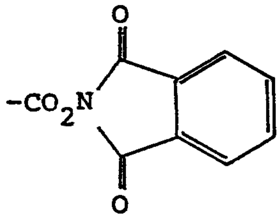
Examples of A of the general formula (III) include the same examples of A of the general formula (I) and examples of R of the general formula (III) include the same examples of R_1 of the general formula (I), both of which are described above.

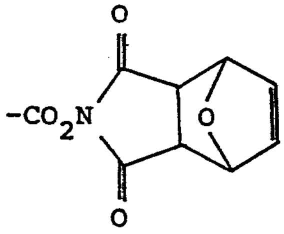
Examples of L of the general formula (III) include the following groups: $-CONHCH_2-$, $-CONHCH_2CH_2-$, $-CONHCH_2CH_2CH_2-$, $-CONHCH_2CH_2CH_2CH_2CH_2-$, $-COCH_2CH_2OCOCH_2CH_2-$, $-CONHCH_2CONHCH_2-$, $-CONHCH_2CONHCH_2CONHCH_2-$, $-COCH_2-$,

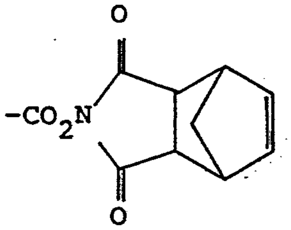
$-CONHCH_2NHCOCH_2CH_2SCH_2CH_2-$ and $-CONHCH_2OCOCH_2CH_2-$.

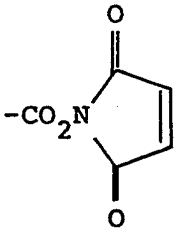
Examples of X of the general formula (III) include the following groups:

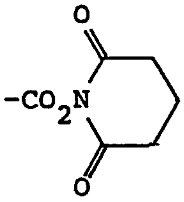


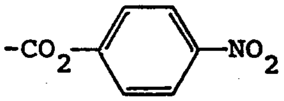


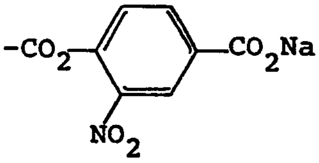


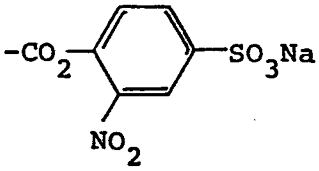


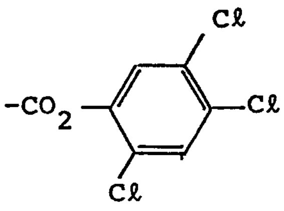

O
-CO2N
O

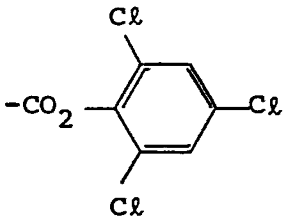

O
-CO2N
O

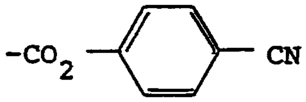

-CO2
NO2


-CO2
CO2Na
NO2


-CO2
SO3Na
NO2


Cℓ
-CO2
Cℓ
Cℓ



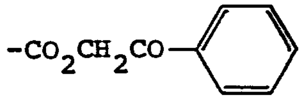


$-CO_2CH_2CN$

$-CO_2CH_2CO_2C_2H_5$

$-CO_2CH_2CONH_2$

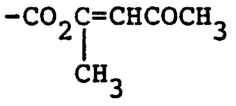
$-CO_2CH_2COCH_3$



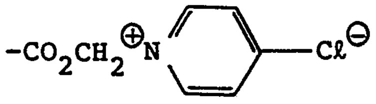
$-CO_2CH_2CO_2CH=CH_2$

$-CO_2N=CHCH_3$

$-CO_2N=C(CH_3)_2$

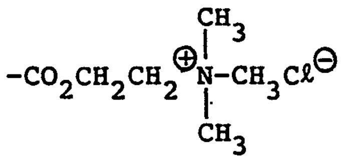


$-CO_2\underset{CH_3}{\underset{|}{C}}=CHCOCH_3$



$-CO_2CH_2CH_2Br$

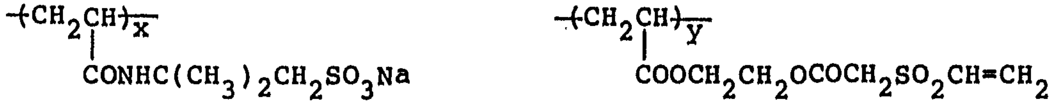
$-CO_2CH_2CH_2CN$



$-CO_2CH_2CH_2\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}-CH_3Cl^{\ominus}$

Specific examples of the compounds which can be used in the present invention are set forth below, but the present invention is not to be construed as being limited thereto.

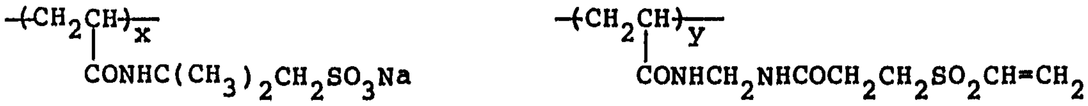
P-1



$-(CH_2CH)_x-$ with CONHC$(CH_3)_2CH_2SO_3Na$; $-(CH_2CH)_y-$ with $COOCH_2CH_2OCOCH_2SO_2CH=CH_2$

x/y=3/1

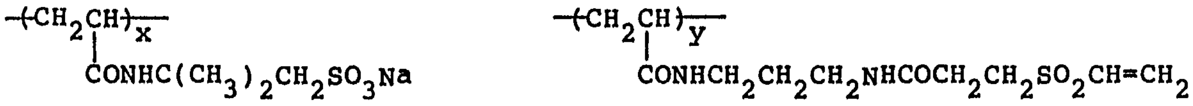
P-2



$-(CH_2CH)_x-$ with $CONHC(CH_3)_2CH_2SO_3Na$; $-(CH_2CH)_y-$ with $CONHCH_2NHCOCH_2CH_2SO_2CH=CH_2$

x/y=3/1

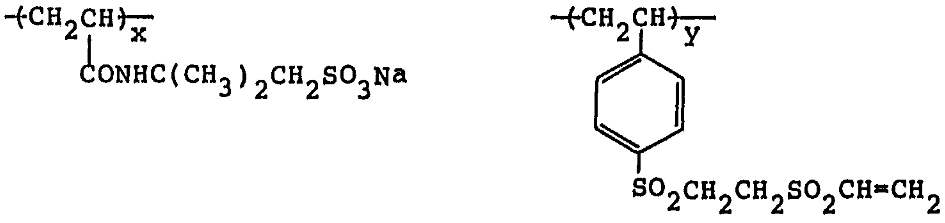
P-3



$-(CH_2CH)_x-$ with $CONHC(CH_3)_2CH_2SO_3Na$; $-(CH_2CH)_y-$ with $CONHCH_2CH_2CH_2NHCOCH_2CH_2SO_2CH=CH_2$

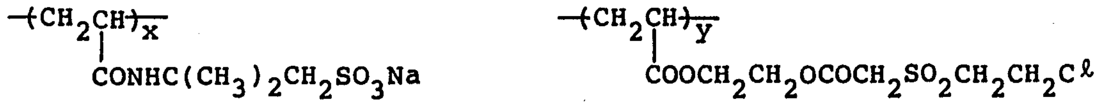
x/y=3/1

P-4



x/y=3/1

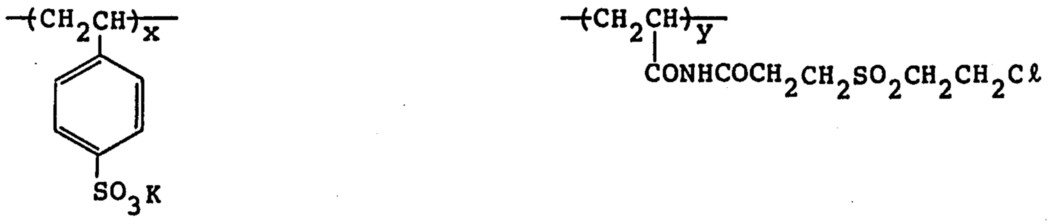
P-6



$$-(CH_2CH)_x- \;\; -(CH_2CH)_y- \quad \text{with } CONHC(CH_3)_2CH_2SO_3Na \text{ and } COOCH_2CH_2OCOCH_2SO_2CH_2CH_2C\ell$$

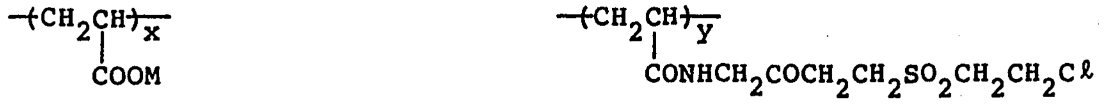
x/y=3/1

P-7



x/y=3/1

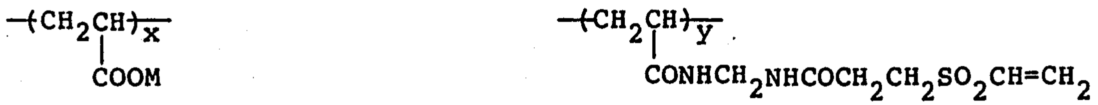
P-8



$$-(CH_2CH)_x- \;\; -(CH_2CH)_y- \quad \text{with } COOM \text{ and } CONHCH_2COCH_2CH_2SO_2CH_2CH_2C\ell$$

x/y=10/1

P-9



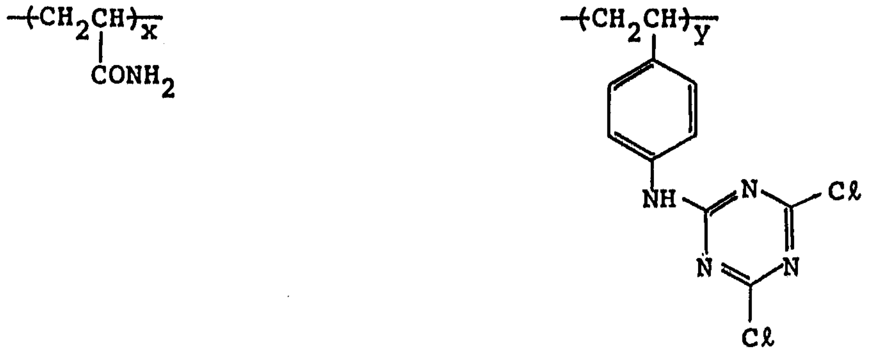
$$-(CH_2CH)_x- \;\; -(CH_2CH)_y- \quad \text{with } COOM \text{ and } CONHCH_2NHCOCH_2CH_2SO_2CH=CH_2$$

x/y=10/1

P-10

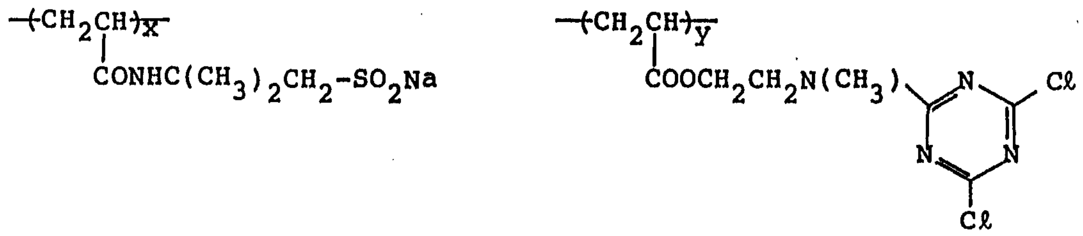
x/y=3/1

P-11



x/y=20/1

P-12

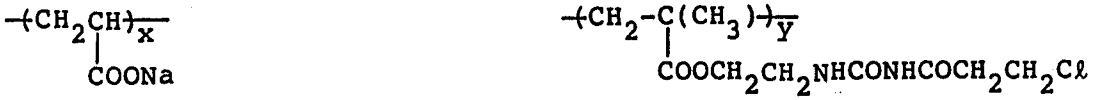


x/y=5/1

P-13

x/y=10/1

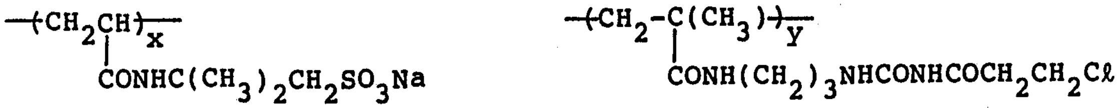
P-14



$$-\!\!(CH_2\underset{\displaystyle COONa}{CH})_x\!\!-\quad -\!\!(CH_2-\underset{\displaystyle COOCH_2CH_2NHCONHCOCH_2CH_2Cl}{C}(CH_3))_y\!\!-$$

x/y=5/1

P-15



$$-\!\!(CH_2\underset{\displaystyle CONHC(CH_3)_2CH_2SO_3Na}{CH})_x\!\!-\quad -\!\!(CH_2-\underset{\displaystyle CONH(CH_2)_3NHCONHCOCH_2CH_2Cl}{C}(CH_3))_y\!\!-$$

x/y=10/1

M represents a hydrogen atom, sodium atom or potassium atom, x and y each represents the mole percentage of the starting amount in each unit, and is not limited by the above, and x can take a value of 0 to 99 and y a value of 1 to 100.

Preferred examples of the compounds which can be used in the present invention include compounds having a vinyl sulfone group and the precursor thereof as a functional group capable of reacting with gelatin, for example, P-1, P-2, P-3, P-4, P-6, P-7, P-8 and P-9. Particularly preferred example of the compound includes P-2.

The molecular weight of compounds which can be used in the present invention is at least about 10,000, and it is preferably 10,000 to several hundred thousands with respect to a non-cross-linked compounds.

The addition amount is an amount sufficient to make the melting time of the thin layer made by the low molecular gelatin solution longer than the melting time of the light-sensitive silver halide emulsion layer. The amount of compounds which can be used in the present invention is preferably $5x10^{-4}$ equivalent to 0.1 equivalent, particularly preferably $2x10^{-3}$ equivalent to $4x10^{-2}$ equivalent per 100 g of gelatin used in the gelatin thin layer coated on the light-insensitive upper layer expressed in terms of the amount of functional group capable of reacting with gelatin.

However, the amount of compounds varies corresponding to a melting time of the gelatin thin layer.

The synthesis of polymeric hardener used in this invention is described in detail in the specification of the aforesaid Japanese Patent Application (OPI) No. 42039/83 (corresponding to British Patent 2,108,695A) and can be referred.

The polymeric hardener is added to a gelatin solution directly or more preferably by dissolving it in water or an organic solvent.

In this invention, that the melting time of the thin layer made by the gelatin solution having a low concentration is longer than the melting time of the emulsion layer means that the layer made by the gelatin solution having a low concentration is hardened more strongly than the emulsion layer.

As a means for evaluating the degree of hardening in the hardened layers, it is well known in this field to use degree of swelling when swelling the hardened layer with a certain solution or scratch strength represented by a weight which causes a scratch when the hardened layer is scratched with a weighted needle-like stylus. However, in order to evaluate the present invention, it is most effective to use the time required for a hardened film to melt when it is dipped in a solution kept at a certain specified temperature (melting time: MT). It is most preferred that the measurement of melting time is carried out in a 0.2 N NaOH solution kept at 75°C (but the measurement is not always limited thereto).

In this invention, it is preferred that the melting time of the thin layer made by the gelatin solution is larger than that of the emulsion layer by 50 seconds or more, particularly 100 seconds or more, according to the above mentioned measuring method.

The gelatin solution thus prepared (particularly, a dilute solution) is coated on the light-insensitive upper layer established on the light-sensitive silver halide emulsion layer by the coating processes public known in the field of photographic light-sensitive materials such as extrusion coating, curtain coating, air-knife coating processes and the like. As the occasion demands, all of these layers can be coated by multilayer simultaneous coating, for example, by the methods described in U.S. Patent 2,761,791 and British Patent 837,095.

The coating film thickness of the gelatin solution of this invention is preferably a thin layer having a dry film thickness of less than 0.3 μ, particularly 0.2 μ or less.

For the light-sensitive silver halide emulsion layer of this invention and the coating solution for this, those generally used for light-sensitive materials for photomechanical process can be used.

There is no restriction with respect to the type of silver halide used in the light-sensitive silver halide emulsion layer of the present invention. Silver chlorobromide, silver chloroiodobromide, silver iodobromide, silver bromide and etc. can be used. However, it is particularly preferred to use silver chlorobromide or silver chloroiodobromide containing at least 60% by mol (preferably 75% by mol or more) of silver chloride and 0 to 5% by mol of silver iodide. Form, crystal habit and distribution of size of the silver halide particles are not especially limited, but it is preferred to have a particle size of 0.7 μ or less. The sensitivity of the silver halide emulsion can be increased without increasing the particle size of silver halide by using a gold compound such as chloroaurate or gold trichloride, a salt of noble metal such as rhodium or iridium, a sulfur compound capable of forming silver sulfide by reacting with a silver salt, or a reducing substance such as a stannous salt or an amine. Further, it is possible to add a salt of noble metal such as rhodium or iridium, or an iron compound such as ferricyanide at the time of physical ripening or nucleus forming of silver halide particles.

The photographic emulsion used in the present invention may be subjected to spectral sensitization using a methine dye, etc. These sensitizing dyes may be used individually or as a combination thereof. A combination of sensitizing dyes is often employed particularly for the purpose of supersensitization. The sensitizing dyes may be present in the emulsion together with dyes which themselves have no spectrally sensitizing effects but exhibit a supersensitizing effect or materials which do not substantially absorb visible light but exhibit a supersensitizing effect.

Examples of the useful sensitizing dyes, the combinations of dyes exhibiting the supersensitizing effect and the materials exhibiting the supersensitizing effect are described in <u>Research Disclosure</u>, Vol. 176, No. 17643, page 23, IV-J (December, 1978).

In the photographic emulsion, it is possible to use any known anti-fogging agents as described, for example, in Japanese Patent application (OPI) Nos. 81024/74, 6306/75 and 19429/75, U.S. Patent 3,850,639 such as numbers of heterocyclic compounds including 4-hydroxy-6-methyl-1,3,3a,7-tetra-azaindene, 3-methylbenzothiazole or 1-phenyl-5-mercapto-tetrazole, etc., mercury containing compounds, mercapto compounds, etc.

A surface active agent may be added to the light-sensitive silver halide emulsion layer of the present invention as a coating aid or for the purpose of improving photographic properties.

Examples of useful surface active agents include a natural surface active agent such as saponin, a nonionic surface active agent such as alkylene oxide type, glycidol type, etc.; an anionic surface active agent containing an acid group such as a carboxylic acid, a sulfonic acid (for example, surface active agents as described in U.S. Patent 3,415,649), a phosphoric acid, a sulfuric acid ester, a phosphoric acid ester group, etc.; and an ampholytic surface active agent such as an amino acid, an aminosulfonic acid, or a sulfuric acid or phosphoric acid ester of aminoalcohol, etc.

Polyalkylene oxide compounds which can be used in the present invention include alkylene oxide having from 2 to 4 carbon atoms, for example, ethylene oxide, propylene-1,2-oxide, butylene-1,2-oxide, etc.; preferably condensation products of polyalkylene oxide composed of at least 10 ethylene oxide units and a compound having at least one active hydrogen atom such as water, an aliphatic alcohol, an aromatic alcohol, a fatty acid, an organic amine or a hexitol derivative; and block copolymers of two or more polyalkylene oxides. Namely, examples of the polyalkylene oxide compounds used include polyalkylene glycols, polyalkylene glycol alkyl ethers, polyalkylene glycol aryl ethers, polyalkylene glycol alkylaryl esters, polyalkylene glycol esters, polyalkylene glycol fatty acid amides, polyalkylene glycol amines, polyalkylene glycol block copolymers and polyalkylene glycol graft polymers, etc.

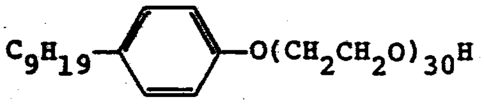
Specific examples of the polyalkylene oxide compounds preferably used in the present invention include the following compounds.

1. $HO(CH_2CH_2O)_9H$

2. $C_{12}H_{25}O(CH_2CH_2O)_{15}H$

3. $C_8H_{17}CH{=}CHC_8H_{16}O(CH_2CH_2O)_{15}H$

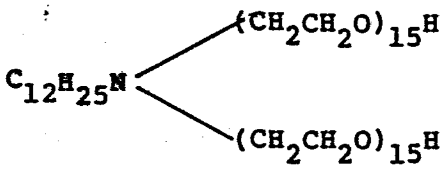
4.



5. $C_{11}H_{23}COO(CH_2CH_2O)_{80}H$

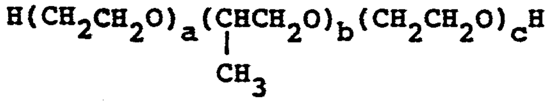
6. $C_{11}H_{23}CONH(CH_2CH_2O)_{15}H$

7.



8. $C_{14}H_{29}N(CH_3)(CH_2CH_2O)_{24}H$

9.



$H(CH_2CH_2O)_a(\underset{CH_3}{CH}CH_2O)_b(CH_2CH_2O)_cH$

a+b+c=50 b:a+c=10:9

It is possible to add a polymer latex composed of a homo- or copolymer of alkyl acrylate, alkyl methacrylate, acrylic acid or cresidyl acrylate, etc., as described in U.S. Patents 3,411,911, 3,411,912, 3,142,568, 3,325,286 and 3,547,650 and Japanese Patent Publication No. 5331/70, etc., to the light-sensitive silver halide emulsion layer in order to improve dimensional stability of the photographic material or improve film properties thereof.

As a hydrophilic colloid binder used in the light-sensitive silver halide emulsion layer of the present invention, it is advantageous to use gelatin, but other hydrophilic colloids can be used.

For example, it is possible to use a protein such as a gelatin derivative, a graft polymer of gelatin and another polymer, albumin or casein, etc.; a saccharide such as a cellulose derivative such as hydroxyethyl cellulose, carboxymethyl cellulose or cellulose sulfate, etc., sodium alginate, etc.; and a hydrophilic synthetic polymeric substance such as a homo- or copolymer including polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinyl pyrazole, etc. Examples of gelatin include not only lime-processed gelatin but also acid-processed gelatin and enzyme-processed gelatin as described in Bull. Soc. Sci. Phot. Japan, No. 16, page 30 (1966) may be used. Further, a hydrolyzed product and an enzymatic decomposition product of gelatin can be used.

It is preferred that the ratio by weight of the hydrophilic colloid binder to silver halide in the light-sensitive silver halide emulsion layer in the present invention is 1/2 or less.

In the present invention, the light-sensitive silver halide emulsion layer is not always composed of one layer but it may be composed of two or more layers. For example, when the light-sensitive silver halide emulsion layer is composed of two layers, it is preferred that the ratio of the total amount of silver halide in the two layers to the hydrophilic colloid binder is 2 or more and that the upper light-sensitive emulsion layer contains a larger amount of hydrophilic colloid binder than the lower light-sensitive emulsion layer.

Further, the amount of silver halide to be coated is from 1.0 to 6.0 g and, preferably, from 1.3 to 4.0 g calculated as silver per square meter. Particularly excellent effects can be obtained when a small amount of silver is coated.

The light-insensitive upper layer of this invention essentially consists of a hydrophilic colloid and the layers having the composition which is generally known as protective layers and inter-layers can be used. The use of gelatin is preferable as the hydrophilic colloid, but instead of gelatin or together with gelatin, the hydrophilic colloids other than the gelatin as described above may be used.

As the gelatin, besides the lime-processed gelatin, the acid-processed gelatin and the enzyme-processed gelatin described in Bull. Soc. Sci. Phot. Japan, No. 16, p. 30 (1966) may be used and the hydrolysis products or enzyme decomposed products of gelatin can also be used.

In this invention, slipping and adhesion resistance can be improved by adding a matting agent in the light-insensitive upper layer. The matting agent described in Research Disclosure, Vol. 176, pp. 22-28 (December, 1978) can be used, and the grains of 0.1 to 10 μ (especially 1 to 5 μ) of silicon dioxide or particularly polymethyl methacrylate are preferred. The amount of the matting agent used is not particularly limited, but, in general, the range in 0.05 g/m^2 to 0.2 g/m^2 is preferable. The process of this invention can also improve the haze which conventionally occurred when the matting agent was used.

A polymer latex may be contained in the light-insensitive upper layer for the purpose of preventing the reticulation which is easy to occur when a layer having a different hardness is established. The usable polymer latex includes a hydrate of a vinyl polymer containing a monomer unit such as an acrylic acid ester, a methacrylic acid ester, styrene, etc., as described in U.S. Patents 2,772,166, 3,325,286, 3,411,911, 3,311,912 and 3,525,620, Research Disclosure, Vol. 195, No. 19551 (July, 1980), etc. A homopolymer of alkyl acrylate or alkyl methacrylate such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, etc., and a copolymer of alkyl acrylate or alkyl methacrylate and vinyl monomer such as acrylic acid, N-methylolacrylamide, etc., are particularly preferred.

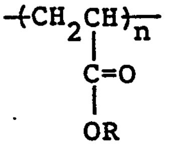
A preferred average particle size of the polymer latex used in the present invention is a range from 0.005 μ to 1 μ and particularly a range from 0.02 μ to 0.1 μ.

By the utilization of polymer latex, the occurrence of reticulation can be extremely effectively prevented. Of the above-described polymer latexes, those having a high glass transition temperature (Tg) are preferred since they also have an ability to improve any antiadhesive property. Particularly, polymer latexes having a glass transition temperature of room temperature or higher are preferred. For example, a hydrate of a homopolymer of vinyl monomer such as methyl methacrylate, ethyl methacrylate, styrene, etc., and a copolymer of such vinyl monomer and other vinyl monomer such as acrylic acid, N-methylolacrylamide, etc., are particularly preferred. The amount of the polymer latex used is preferably from 5% to 200% and more preferably from 10% to 100%, based on the weight of hydrophilic colloid contained in the layer to be added.

The polymer latex can be added to the emulsion layer.

In the following, specific examples of the polymer latexes which can be used in the present invention are set forth, but the present invention is not to be construed as being limited thereto.

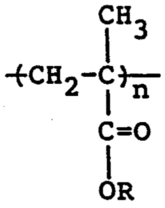
L-1



$$-\!\left(CH_2\underset{\substack{|\\C=O\\|\\OR}}{CH}\right)_n\!-$$

R: $-CH_3$, $-C_2H_5$, $-C_4H_9$

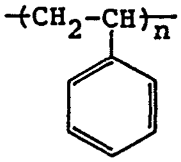
L-2



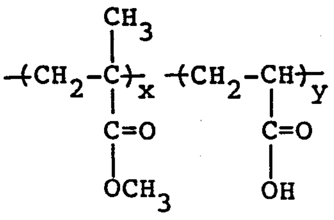
$$-\!\left(CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\C=O\\|\\OR}}{C}}\right)_n\!-$$

R: $-CH_3$, $-C_2H_5$, $-C_4H_9$

L-3



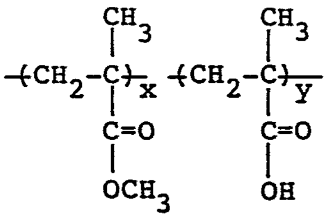
L-4



$$-\!\left(CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\C=O\\|\\OCH_3}}{C}}\right)_x\!-\!\left(CH_2-\underset{\substack{|\\C=O\\|\\OH}}{CH}\right)_y$$

(x/y = 93/7)

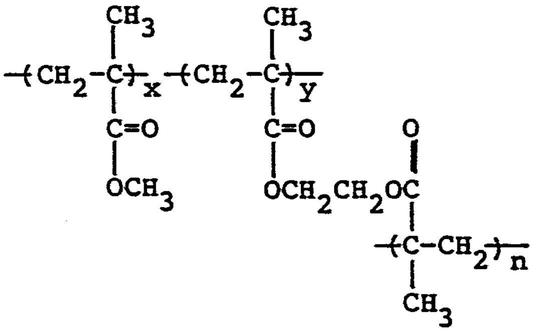
L-5



$$-(CH_2-C(CH_3)(COOCH_3))_x-(CH_2-C(CH_3)(COOH))_y-$$

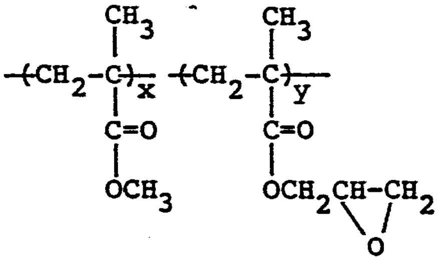
(x/y = 93/7)

L-6



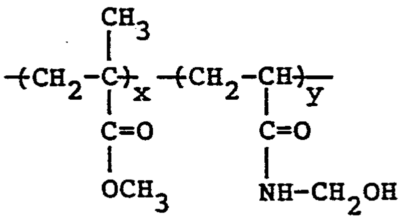
(x/y = 93/7)

L-7



(x/y = 93/7)

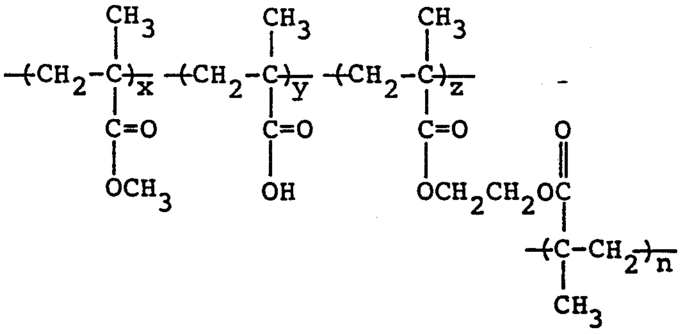
L-8



$$-(CH_2-C(CH_3)(COOCH_3))_x-(CH_2-CH(CONH-CH_2OH))_y-$$

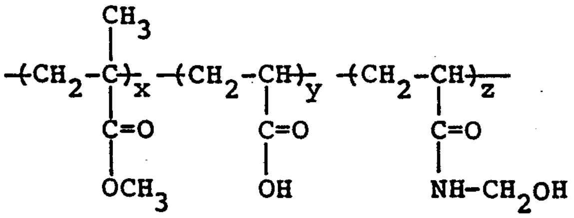
(x/y = 93/7)

L-9



(x/y/z = 93/3/4)

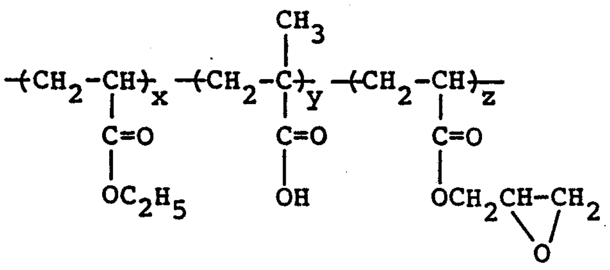
L-10



$$-\!\left(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\displaystyle OCH_3}{C=O}}{C}}\right)_x\!-\!\left(CH_2-\underset{\displaystyle \underset{\displaystyle OH}{C=O}}{CH}\right)_y\!-\!\left(CH_2-\underset{\displaystyle \underset{\displaystyle NH-CH_2OH}{C=O}}{CH}\right)_z\!-$$

(x/y/z = 93/3/4)

L-11



(x/y/z = 93/3/4)

Among the polymer latexes which can be used in the present invention, the molecular weights of L-1 to L-5 are 10,000 to several hundred thousands, and those of L-6 to L-

11 are infinite because those polymer latexes are subjected to gelation by cross-linked.

Synthesis Example of Polymer Latex of Methyl Methacrylate

In a 1000 ml 3-neck flask equipped with a gas inlet conduit, a reflux condenser and a stirrer, 150.0 g of methyl methacrylate was emulsified dispersed in a solution containing 4.28 g of sodium laurylsulfate dissolved in 800 ml of distilled water and to the resulting dispersion was added 9.6 mg of ferrous chloride. To 20 ml of distilled water, 0.41 g of potassium persulfate and then 0.16 g of sodium hydrogen sulfite were dissolved and was added 2.0 ml of 2 N aqueous ammonia to prepare a polymerization initiator. The polymerization initiator was added to the above-described mixture while maintaining the temperature in the flask at 60°C. After 2 hours, the same polymerization initiator as described above was added to the reaction mixture and subjected to post polymerization for 2 hours. After cooling, the reaction mixture was filtered using a thin filter paper to obtain a polymer latex of methyl methacrylate of protein color which has 15.9% by weight of concentration, 0.04 μ of particle size and 6.13 of pH.

Other polymer latexes described above can also be synthesized generally with reference to the synthesis example above.

The light-insensitive upper layer in the present invention may contain a surface active agent, an antistatic agent, a lubricant, colloidal silica, a plasticizer for gelatin, etc., in addition to the above-described hydrophilic colloid binder (for example, gelatin), matting agent and polymer latex.

It is preferred that the light-insensitive upper layer is coated at a total dry thickness of from 0.3 μ to 5 μ and particularly from 0.5 μ to 3 μ.

For hardening of the photosensitive silver halide emulsion layer and the light-insensitive upper layer of this invention, a diffusion low molecular hardener is preferably used. In this case, there is a case in which the low molecular hardener diffuses also to a thin layer made by the aforesaid gelatin solution, hardening the thin layer too, but as the thin layer is hardened by both the low molecular hardener and a non-diffusion polymeric hardener, it can achieve the selective hardening. As these diffusion low molecular hardeners, various organic or inorganic hardeners (independently or in their combination) are used, and typical examples include gelatin harders well known in this field such as aldehyde type compounds such as mucochloric acid, formaldehyde, trimethylolmelamine, glyoxal, 2,3-dihydroxy-1,4-dioxane, 2,3-dihydroxy-5-methyl-1,4-dioxane, succinaldehyde and glutalaldehyde; active vinyl type compounds such as divinyl sulfone, methylene bismaleimide, 1,3,5-triacryloyl-hexahydro-s-triazine, 1,3,5-trivinylsulfonyl-hexahydro-s-triazine, bis(vinylsulfonylmethyl) ether, 1,3-bis-(vinylsulfonyl)propanol-2, bis(α-vinylsulfonylacetamido)-ethane, 1,2-bis(vinylsulfonyl)ethane and 1,1'-bis(vinylsulfonyl)methane; active halogen compounds such as 2,4-dichloro-6-hydroxy-s-triazine; ethyleneimine type compounds such as 2,4,6-triethyleneimino-s-triazine; and the like.

When the diffusion hardener is used, it may be added to either the light-insensitive upper layer or the emulsion layer.

Examples of the preferable layer structures of the light-sensitive material for photo-mechanical process produced by the process for preparation of this invention include the order of an emulsion layer, a light-sensitive upper layer and a gelatin thin layer containing a non-diffusion polymeric hardener from the support; the order of an emulsion layer, a light-insensitive first upper layer, a light-insensitive second upper layer and a gelatin thin layer containing a polymeric hardener from the support; the order of an emulsion layer, a light-insensitive first upper layer, a gelatin thin layer containing a polymeric hardener and a light-insensitive second upper layer from the support and the like. In any layer structure, as a matter of course, a subbing layer may be established between the emulsion layer and the support.

As the supports of the light-sensitive materials for photo-mechanical process of this invention, polyester films such as polyethylene terephthalate films and cellulose ester films such as cellulose triacetate films are preferably used.

The development process of the light-sensitive material for photo-mechanical process produced by the process for preparation of this invention is not especially limited, and any processes generally used for processing of light-sensitive materials for photo-mechanical process can be used. the processing temperature is usually selected from the range of 18°C to 50°C, but the temperature lower than 18°C or higher than 50°C may be used.

The developing solution can contain a known developing agent. As the developing agent, dihydroxy benzenes (e.g., hydroquinone), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone), aminophenols (e.g., N-methyl-p-aminophenol), 1-phenyl-3-pyrazolines, ascorbic acid and heterocyclic compounds such as the compound in which 1,2,3,4-tetrahydroquinoline ring and indolene ring are condensed as described in U.S. Patent 4,067,872 can be used independently or in combination thereof. The developing solution generally contains, besides the above, a public known preservative, an alkali agent, a pH buffer, an antifogging agent and the like, and may contain a dissolving aid, a tone agent, a development accelerator, a surface active agent, an defoaming agent, a water softener, a hardener, a viscosity-imparting agent and the like, as the occasion demands.

A so-called developer for lithographic materials, which is preferably used for this invention, is basically composed of ortho- or paradihydroxybenzene, an alkali agent, a small amount of free sulfites and a sulfurous acid ion buffer and the like.

The ortho- or para-dihydroxybenzene developing agent can be suitably selected from those well known in the field of photograph. The specific examples include hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dimethylhydroquinone and the like.

Among them, the hydroquinone is especially practicable. These developing agents are used independently or by mixing. The addition amount of the developing agent is 1 to 100 g, preferably 5 to 80 g, based on 1 ℓ of the developer. The sulfurous acid ion buffer is used in an amount effective to keep the sulfite concentration in the developer nearly constant, and the examples include aldehyde hydrogensulfite alkali adducts such as formalin sodium hydrogensulfite adduct, keton-hydrogenesulfite alkali adducts such as acetone sodium hydrogenesulfite adduct, carbonyl bisulfurous acid-amine condensation product such as sodium-bis(2-hydroxyethyl)aminomethanesulfonate and the like. The used amount of th sulfurous acid ion buffer is 13 to 130 g based on 1 ℓ of the developer.

The developer used in this invention can control the free sulfurous acid ion concentration by adding a sulfurous acid alkali salt such as sodium sulfite and the like. The addition amount of the sulfite is generally 5 g or less based on 1 ℓ of the developer, particularly, preferable to be 3 g or less, but it may be, of course, larger than 5 g.

In most cases, an alkali halide (especially, bromides such as sodium bromide and potassium bromide) is preferably used as a development modifier. The alkali halide is preferably added in an amount of 0.01 to 10 g, more preferably, 0.1 to 5 g, based on 1 ℓ of the developer.

An alkali agent is added so that the pH in the developer is 9 or more (especially, pH 9.7 to 11.5). For general developers, various amounts of sodium carbonate or potassium carbonate are used as an alkali agent.

As a fixing solution, those having the composition generally used can be used.

As the fixing agent, as well as thiosulfates and thiocyanates, organic sulfur compounds whose effect as fixing agent is known can be used.

The fixing solution may contain a water-soluble aluminium salt as hardener. When the dye image is formed, general processes can be applied.

The development process may be carried out by hand or an automatic developing machine. In the case of processing by an automatic developing machine, the method of carrier (e.g., roller carrier and belt carrier) is not particularly limited, and the carrier type automatic developing machine used in the field can be used. Moreover, for the composition of processing solution and the development methods, the descriptions of U.S. Patents 3,025,779, 3,078,024, 3,122,086, 3,149,551, 3,156,173, 3,224,356, 3,573,914 and the like can be referred.

For the silver halide emulsion layer, other layers, supports, processing methods and the like of the light-sensitive material for photo-mechanical process of this invention, the descriptions of Research Disclosure, Vol. 176, pp. 22-28 (December, 1978) can also be referred.

The reducer used for this invention is not particularly limited and, for example, those described in Mees, The Theory of the Photographic Process mentioned above is effectively used.

Namely, the reduction component such as a permanganate, a persulfate, a ferric salt, a cupric salt, a cerium (IV) salt, a ferricyanide, a bichromate and the like are used independently or together with, and, if necessary, a reducer in which an inorganic acid such as sulfuric acid and alcohols are contained or a reducer in which a reducing component such as hexacyanoferrate (III), ethylenediamine tetraacetic acid ferric salt and the like and a silver halide solvent such as thiosulfate, rhodan salt, thiourea or its derivative and the like and additionally an inorganic acid such as sulfuric acid, if necessary, are contained is used.

To the reducer used in this invention, a compound having a mercapto group as described in Japanese Patent Application (OPI) No. 68419/77 can be further contained as the occasion demands.

The composition of the reducer and treatment conditions (temperature, time, etc.) used for the reduction treatment of this invention are not particularly limited, and can be suitably decided by those skilled in the art.

For the reducer and the reducing method, the descriptions of Japanese Patent Application (OPI) Nos. 140733/76, 68419/77, 14901/78, 119236/79, 119237/79, 2245/80, 2244/77, 17123/80, 79444/80, 81344/80 can be referred to.

Also, for the practical reducing treatment, Keiichi Sakamoto, <u>Retouch Technique Notebook</u>, published by Japan Printing Technique Association (1980) can be referred to.

This invention is further illustrated by the following Examples. However, this invention is not limited to these Examples.

EXAMPLE 1

On a polyethylene telephthalate film support having a subbing layer, the coating solutions of the following prescriptions are coated by multilayer simultaneous coating method according to the instructions of Table 1 to produce Samples 1 to 5.

Coating solution for light-sensitive silver halide emulsion layer

A silver halide emulsion consisting of 80 mol% of silver chloride, 19.5 mol% of silver bromide and 0.5 mol% of silver iodide was prepared by gold sensitization and sulfur sensitization according to the general method. The gelatin contained in this emulsion was 45 wt% based on the silver halide. To this emulsion were successively added 3-carboxymethyl-5-[2-(3-ethyl-thiazolinydene)ethylydene]rhodanine (spectral sensitizer), 4-hydroxy-1,3,3a,7-tetraazaindene (stabilizer), polyoxyethylenenonylphenyl ether containing 50 ethyleneoxide groups and the polymer latex described in Preparation Example, Prescription 3 of Japanese Patent Publication No. 5331/70, and then bis(sulfonylacetamido)ethane (low molecular hardener) was added so as to be 2.6 wt% based on the total dry gelatin of each sample to prepare a coating solution for a silver halide emulsion layer.

Coating solution for light-insensitive upper layer 1

Gelatin	5 g/100 cc H_2O
Polymer latex (L-10)	0.4 g/g gelatin

Sodium dodecylbenzenesulfonate	4 mg/g gelatin
Matting agent (polymethyl methacrylate average grain size of lates: 3.0 to 4.0 μ)	0.05 g/g gelatin

Coating solution for light-insensitive upper layer 2

Gelatin	6 g/100 cc H_2O
Polymer latex (L-10)	not added to Sample 1. added to each of Samples 2 and 3. in an amount of 0.4 g/g gelatin.
Sodium dodecylbenzenesulfonate	4 mg/g gelatin
Matting agent (the same as above)	0.05 g/g gelatin
Polymeric hardener (P-2)	not added to Sample 1. added to Sample 2 in an amount of 80 mg/m^2. added to Sample 3 in an amount of 200 mg/m^2.

Gelatin solution for thin layer

Gelatin	1 g/100 cc H_2O
Sodium dodecylbenzenesulfonate	4 mg/g gelatin
Polymeric hardener (P-2)	added to Sample 4 in an amount of 80 mg/m^2. added to Sample 3 in an amount of 200 mg/m^2.

Next, a dot image was formed on the above samples according to the following method.

Commercial negative gray contact screen (150 line/inch) was contacted to the sample, which was exposed by a white tungsten light for 10 seconds through a step wedge having a step difference of 0.1. The sample was subjected to a high temperature rapid development at 38°C for 20 seconds using the following developer, and then fixed, washed and dried by the general method.

Developer

Sodium carbonate (H_2O)	11 g
Potassium bromide	3 g
Hydroquinone	23 g
1-Phenyl-3-pyrazolidone	0.4 g
Sodium sulfite	67 g
Potassium hydroxide	11 g
Water to make	1 ℓ

The obtained dot strips were immersed in the following cerium type reducer (20°C) and washed.

Reducer

Ceric sulfate	25 g
Conc. sulfuric acid	30 g
Water to make	1 ℓ

The change of dot area of the dot strips thus obtained and the change of density per dot area were measured by microdensitometer, the dot area when the dot having the dot area of 50% has the individual dot density of 2.5 after reduction treatment was calculated, and the reduction width value was obtained by calculating the difference of the both. Next, the reduction time which was required until the density became 2.5 was calculated. The obtained results are shown in Table 2. Furthermore, the melting times of the light-insensitive upper layer and the light-sensitive silver halide layer were measured by the aforesaid method. The obtained results are shown in Table 2. The haze degree of each sample after treatment was measured and the results are also indicated in Table 2.

The haze in this invention means a characteristic value regulated in JIS standard (JIS K 6714) and is shown by the ratio (%) of scattered light/transmission light based on the total light percent transmission, indicating that the lower the value, the higher the transparency of the coating film.

The coating solution in which a polymeric hardener is added was kept at 40°C and preserved with stirring homogeneously and the change of viscosity with the lapse of time was measured using B-type viscosimeter (produced by Tokyo Keiki Co., Ltd.) to obtain the time until the viscosity became 2 times the initial viscosity.

In the successive production, this value is preferred to be as large as possible. When the value becomes small, an insoluble lump based on the reaction of the hardener with gelatin tends to form at the time of coating and the degree of improvement in the property of viscosity increase of coating solution with the lapse of time can be judged by the dimensions of this value.

The obtained results are shown in Table 2.

Table 1

Sample No.		Silver coating amount in emulsion layer	Dry film thickness of light-insensitive upper layer and gelatin coating amount	Dry film thickness of gelatin thin layer and gelatin coating amount	Adding layer of polymeric hardener
1 (Comparison)	Light-insensitive upper layer 2 Emulsion layer Support	3.0 g/m^2	1.0 μ 0.9 g/m^2		not added
2 (Comparison)	Light-insensitive upper layer 2 Emulsion layer Support	"	1.0 μ 0.9 g/m^2		light-insensitive upper layer 2 (80 mg/m^2)
3 (Comparison)	Light-insensitive upper layer 2 Emulsion layer Support	"	1.0 μ 0.9 g/m^2		light-insensitive upper layer 2 (200 mg/m^2)
4 (this invention)	Gelatin thin layer Light-insensitive upper layer 1 Emulsion layer Support	"	1.0 μ 0.9 g/m^2	0.1 μ 0.11 g/m^2	gelatin thin layer (80 mg/m^2)
5 (this invention)	Gelatin thin layer Light-insensitive upper layer 1 Emulsion layer Support	"	1.0 μ 0.9 g/m^2	0.1 μ 0.11 g/m^2	gelatin thin layer (200 mg/m^2)

Table 2

Sample No.	Melting time (sec.)		Reductivity		Property of viscosity increase of coating solution with the lapse of time	Haze
	Light-insensitive layer	Silver halide emulsion layer	reduction width (%)	reduction time (sec.)	Time until viscosity becomes 2 times the initial	
1 (Comparison)	760	760	7	40	-	11.0%
2 (Comparison)	1160	810	14	59	1 hr.	8.5%
3 (Comparison)	1370	830	16	95	0.3 hr.	8.7%
4 (this invention)	1180	800	14	61	45 hr.	8.4%
5 (this invention)	1380	820	16	98	33 hr.	8.0%

Table 2 shows that Sample Nos. 2 to 5, as compared with Sample No. 1, are hardened so that the melting time of the light-insensitive upper layer becomes larger than that of the silver halide emulsion layer. Furthermore, in the comparison between Sample Nos. 2 and 4 and between Sample Nos. 3 and 5, the reduction ability is excellent in every case and the sample on which the polymeric hardener is coated in the larger amount shows the larger reduction width and reduction time, indicating that the samples have almost equal reduction ability. However, for the property of viscosity increase of coating solution with the lapse of time, as apparent from the comparison between Sample Nos. 2 and 4 and between 3 and 5, the property of viscosity increase of coating solution with the lapse of time of Sample Nos. 2 and 3 is remarkably poor and the successive coating under such conditions causes the formation of a lump on the coating surface, resulting in coating problems. Contrary to this, Sample Nos. 4 and 5 of this invention show quite excellent abilities with respect to production, as they have no problems as described above and can be improved with respect to their reduction ability and the property of viscosity increase of coating solution with the lapse of time is also satisfactory.

The samples of Sample Nos. 1 to 5 were subjected to the same development as described above, and the degree of the formation of reticulation after processing was observed for each sample using a microscope, but in every sample, reticulation was not formed.

For the degree of haze, Sample 4 is lower than Sample 2 and Sample 5 lower than Sample 3, and it is apparent that the samples of this invention have excellent transmittance as coating films.

The samples after coating were preserved in an atmosphere of 25°C and 65% RH and the film quality (swelling, MT) sensitometry after 3 days was examined continuously with the lapse of time, and as a result, no significant difference between Samples 2 and 3 and Samples 4 and 5 of this invention was found.

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 process for preparing a silver halide photographic light-sensitive material for photo-mechanical process, comprising the steps of:

coating a light-sensitive silver halide emulsion layer on a support;

coating a light-insensitive upper layer comprised of a hydrophilic colloid on an upper portion of the emulsion layer; and

coating a composite solution on the light-insensitive upper layer, the composite solution containing a non-diffusion polymeric hardener in a gelatin solution in an amount enough to make the melting time of the layer made by the composite solution larger than the melting time of the emulsion layer, the composite solution being coated such that the gelatin coating amount is in the range of 0.05 g/m^2 to 0.5 g/m^2.

2. A process for preparing a silver halide photographic light-sensitive material for photo-mechanical process as claimed in Claim 1, wherein a diffusion low molecular compound is present in the coating solution of the light-sensitive silver halide emulsion layer.

3. A process for preparing a silver halide photographic light-sensitive material for photo-mechanical process as claimed in Claim 1, wherein a diffusion low molecular

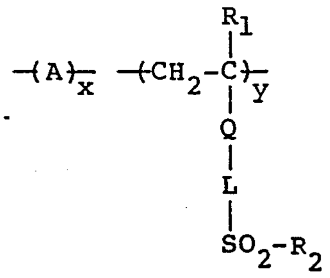
hardener is present in the coating solution of the light-insensitive upper layer.

4. A process for preparing a silver halide light-sensitive material for photo-mechanical process as claimed in Claim 1, wherein a matting agent is present in the coating solution for the light-insensitive upper layer.

5. A process for preparing a silver halide photographic light-sensitive material for photo-mechanical process as claimed in Claim 1, wherein the coating composite solution on the light-insensitive upper layer is coated so that the gelatin coating amount is in the range of 0.05 g to 0.2 g/m^2.

6. A process for preparing a silver halide photographic light-sensitive material for photo-mechanical process as claimed in Claim 1, wherein gelatin is present in the composite solution coated on the light-insensitive upper layer in a concentration in the range of 0.1 to 2 wt%.

7. A process for preparing a silver halide photographic light-sensitive material for photo-mechanical process as claimed in Claim 1, wherein the polymeric hardener is a compound having the general formula (I):



$$-(A)_x-(CH_2-\underset{\substack{|\\ Q\\ |\\ L\\ |\\ SO_2-R_2}}{\overset{\substack{R_1\\ |}}{C}})_y-$$

(I)

wherein A is an ethylene type unsaturated monomer which can be copolymerized with the monomer unit shown to its right; R_1 is a hydrogen atom or a lower alkyl group containing 1 to 6 carbon atoms; Q is any of $-CO_2-$, $-CO-\overset{\substack{R_1\\ |}}{N}-$ (wherein R_1 is the same as the above) or an arylene group having 1 to 6 carbon atoms; L represents a di-valent group containing 3 to 15 carbon atoms and at least one of $-CO_2-$ and $-CO\overset{\substack{R_1\\ |}}{N}-$ is the same as described above or a di-valent group containing 1 to 12 carbon atoms and at least one of $-O-$ $-\overset{\substack{R_1\\ |}}{N}-$, $-CO-$, $-SO-$, $-SO_2-$, $-SO_3-$, $-SO_2N-$, $-\overset{\substack{R_1\\ |}}{N}CO\overset{\substack{R_1\\ |}}{N}-$ and $-\overset{\substack{R_1\\ |}}{N}CO_2-$ (wherein R_1 is the same as above) bonds; R_2 is a vinyl group or a functional group which becomes its precursor, that is either $-CH=CH_2$ or $-CH_2CH_2X$; X is a group which can be substituted by a nucleophilic group or a group which can be eliminated in the form of HX by a base; x and y represent mole percentages, and x is in the range of 0 to 99 and y is in the range of 1 to 100.