PROCESS FOR HARDENING GELATIN IN PHOTOGRAPHIC LAYERS WHICH CONTAIN A THICKENER AND HARDENER BY UTILIZING ACRYLIC ACID-ACRYLAMIDE COPOLYMERS

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ABSTRACT
A process for hardening gelatin which comprises incorporating an acrylic acid-acrylamide copolymer into a system containing gelatin, a thickener and a hardener. Hardened gelatin layers having sufficiently high melting temperatures and high swelling can be obtained, which are useful as photographic layers.

8 Claims, No Drawings
PROCESS FOR HARDENING GELATIN IN PHOTOGRAPHIC LAYERS WHICH CONTAIN A THICKENER AND HARDENER BY UTILIZING ACRYLIC ACID-ACRYLAMIDE COPOLYMERS

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to a process for hardening gelatin.

2. Description of the Prior Art
Gelatin is used in the production of photographic light-sensitive materials as a binder for photographic layers such as a silver halide emulsion layer, a protective layer, a filter layer, an intermediate layer, an undercoating layer and an antihalation layer or a backing layer. A light-sensitive material having some of these layers containing gelatin is processed, after exposure, under various conditions with processing solutions having different compositions. In the course of such processing, if the layers containing gelatin in the photographic material are not treated with a hardener, the layers swell excessively and tend to be injured because of their poor water resistance. The gelatin sometimes even dissolves when processed at higher temperatures. The performance of the light-sensitive material is thus deteriorated. Various hardeners for gelatin have been used for eliminating these defects of gelatin.

Recently, processes for applying multiple photographic layers simultaneously (for example, as disclosed in U.S. Pat. No. 2,761,791) have been put into practice as the production of photographic light-sensitive materials increases. In practicing such processes, a coating composition must have a relatively high viscosity. Therefore, a thickener is usually used to increase the viscosity of the coating composition. However, the application of a hardener to the system containing gelatin due to a thickener is disadvantageous in that the gelatin layer is leached out in the photographic processing, or the swelling of the photographic layers is reduced to extend the processing time when a hardener is used in such an amount as to provide satisfactory resistance against injury and to control thoroughly the occurrence of reticulation, which is a significant problem particularly in rapid processing at high temperature. Particularly when compounds having anionic sites such as carboxy or sulfo groups in the molecule are used as thickeners, such anionic sites have mutual electrostatic action with cationic sites such as amino groups in the gelatin molecule to hinder the hardening effect of the hardener thus requiring use of the hardener in a large amount. Such a large amount of hardener is not only wasteful but also tends to adversely affect the photographic properties.

SUMMARY OF THE INVENTION

An object of this invention is to eliminate the disadvantages which occur in hardening the system containing gelatin together with a thickener.

Specifically, an object of this invention is to provide photographic layers having both a high melting temperature and high swelling using a relatively a smaller amount of a hardener as compared with the prior art.

These objects have been attained by the incorporation of an acrylic acid-acrylamide copolymer into the system containing gelatin, thickener and hardener. According to this invention, hardened gelatin layers having sufficiently high melting temperature and high swelling can be obtained by adding an acrylic acid-acrylamide copolymer together with a hardener to the system containing gelatin and a thickener. Gelatin layers thus obtained are useful as photographic layers.

DETAILED DESCRIPTION OF THE INVENTION

The acrylic acid-acrylamide copolymers used in this invention are those containing repeating units selected from acrylic acid and derivatives thereof and repeated units selected from acrylamide and derivatives thereof.

Useful copolymers are those containing about 5 to 95 mol % of the following repeating unit (A) and about 5 to 95 mol % of the following repeating unit (B):

\[-\text{CH}_2-\text{C}(-\text{COO})_\text{R}_\text{s}\text{R}_\text{t}\]

Repeating Unit (A)

\[-\text{CH}_2-\text{C}(-\text{CON})_\text{R}_\text{s}\text{R}_\text{t}\]

Repeating Unit (B)

in which \(\text{R}_\text{s}\) and \(\text{R}_\text{t}\) are each a hydrogen atom or a methyl group, \(\text{R}_\text{s}\) and \(\text{R}_\text{t}\) are each a hydrogen atom or an alkyl group having 1 to 6 carbon atoms which can contain oxo, hydroxy or alkoxo groups or can combine to form a non-metal atom (e.g., carbon, oxygen and/or nitrogen) containing 5 to 7 membered ring, and \(X\) is a hydrogen atom, a sodium atom, a potassium atom, a lithium atom or an ammonium group.

Suitable examples of alkyl groups having 1 to 6 carbon atoms which may include oxo, hydroxy or alkoxo groups for \(\text{R}_\text{s}\) and \(\text{R}_\text{t}\) are groups such as methyl, ethyl, butyl, tert-butyl, hexyl, cyclohexyl, benzyl, 1,1-dimethyl-3-oxobutyl, 1,1-dimethyl-3-hydroxybutyl, hydroxyethyl, methoxymethyl, hydroxyethoxyethyl, morpholinoethyl, etc., groups. Suitable examples of groups formed by the combination of \(\text{R}_\text{s}\) and \(\text{R}_\text{t}\) are rings such as morpholino, N-methylpiperazino, piperidino, pyrrolidino, hexamethylenimino, etc., rings. Suitable examples of ammonium groups are those of triethanolamine, diethanolamine, ethanamine, ammonia, etc.

If the copolymers used in this invention have too low a molecular weight, they improve the swelling of photographic layers during processing to a lesser extent, while too great a molecular weight is also disadvantageous in that the compatibility with gelatin is deteriorated and they are difficult to handle due to the resulting high viscosity. Therefore, copolymers having a limiting viscosity in the range of about 0.5 to about 6.0 measured at 30°C using a 1% by weight aqueous solution of sodium chloride are usually desired.

Copolymers containing 30 to 80 mol % of the aforesaid repeating unit (A) and 20 to 70 mol % of the aforesaid repeating unit (B) are particularly useful.

The copolymers used in this invention can be easily synthesized by reacting one or more compounds selected from acrylic acid and derivatives thereof with one or more compounds selected from acrylamide and derivatives thereof in a desired ratio in a solvent such as water, water-methanol or water-ethanol with heating to about 70°C to 90°C using a polymerization catalyst such as potassium persulfate, ammonium persulfate or po-
to adjust the molecular weight, isopropanol can be used as a chain transfer agent. Examples of acrylic acid and derivatives thereof are acrylic acid or methacrylic acid, and examples of acrylamide or derivatives thereof are acrylamide, methacrylamide, N,N-dimethylacrylamide, N,N-diethyacrylamide, N-methylolacrylamide, N-hydroxyethylacrylamide, N-tert-butylacrylamide, N,N-dibutylacrylamide, N-cyclohexylacrylamide, N-diisopropylacrylamide, N-(1,1-dimethyl-3-hydroxybutyl)acrylamide, N-(β-morpholino)ethylacrylamide, N-benzylacrylamide, N-acryloylphosphine, N-methacryloylphosphine, N-methyl-N′-acryloylpyperazine, N-acryloylpiperidine, N-acryloylpyrrolidine, N-acryloylhexamethyleneimine, etc.

The preparation of the copolymers which can be used in this invention is shown below. The limiting viscosity in the following preparation examples is represented as a value measured at 30°C using a 1% aqueous solution of sodium chloride.

PREPARATION EXAMPLE 1
Preparation of Polymer (1)
Into a one-liter flask provided with a stirrer were placed 43.2 g (0.6 mol) of acrylic acid, 28.4 g (0.4 mol) of acrylamide, 600 ml of water, 2 ml of isopropanol and 350 mg of potassium persulfate as a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°C – 90°C. The reaction product was cooled to room temperature (about 20°C – 30°C), neutralized with an aqueous solution of potassium hydroxide and then put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.

Yield 92.0 g (97.4 %), n = 4.98.

PREPARATION EXAMPLE 2
Preparation of Polymer (2)
Into a one-liter flask provided with a stirrer were placed 50.4 g (0.7 mol) of acrylic acid, 25.5 g (0.34 mol) of methacrylamide, 500 ml of water, 1 ml of isopropanol and 350 mg of potassium persulfate as a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°C – 90°C. The reaction product was cooled to room temperature, neutralized with an aqueous solution of potassium hydroxide and then put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.

Yield 94.1 g (92 %), n = 2.41.

PREPARATION EXAMPLE 3
Preparation of Polymer (3)
Into a one-liter flask provided with a stirrer were placed 43 g (0.5 mol) of methacrylic acid, 35.5 g (0.5 mol) of acrylamide, 500 ml of water, 2 ml of isopropanol and 350 mg of potassium persulfate as a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°C – 90°C. The reaction product was cooled to room temperature, neutralized with an aqueous solution of sodium hydroxide and then put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.

Yield 86.1 g (96 %), n = 3.94.

PREPARATION EXAMPLE 4
Preparation of Polymer (4)
Into a one-liter flask provided with a stirrer were placed 34.4 g (0.4 mol) of methacrylic acid, 16 g of sodium hydroxide dissolved in 500 ml of water, and 350 mg of potassium persulfate as a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°C – 90°C. The reaction product was put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.

Yield 81.8 g (87.0 %), n = 2.83.

PREPARATION EXAMPLE 5
Preparation of Polymer (5)
Into a one-liter flask provided with a stirrer were placed 21.6 g (0.3 mol) of acrylic acid, 49.7 g (0.7 mol) of acrylamide, 3 ml of isopropanol, 500 ml of water and 350 mg of potassium persulfate as a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°C – 90°C. The reaction product was cooled to room temperature, neutralized with an aqueous solution of sodium hydroxide and then put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.

Yield 77.5 g (99.5 %), n = 5.11.

PREPARATION EXAMPLE 6
Preparation of Polymer (6)
Into a one-liter flask provided with a stirrer were placed 50.4 g (0.7 mol) of acrylic acid, 38.1 g (0.3 mol) of N,N-diethylacrylamide, 500 ml of water, 2 ml of isopropanol and 350 mg of a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°C – 90°C. The reaction product was cooled to room temperature, neutralized with an aqueous solution of potassium hydroxide and then put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.

Yield 107 g (93 %), n = 2.45.

PREPARATION EXAMPLE 7
Preparation of Polymer (7)
Into a one-liter flask provided with a stirrer were placed 57.6 g (0.8 mol) of acrylic acid, 33.8 g (0.2 mol) of diacetone acrylamide, 45 g of potassium hydroxide dissolved in 500 ml of water and 350 mg of potassium persulfate as a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°C – 90°C. The reaction product was put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.

Yield 114.3 g (94 %), n = 2.79.

PREPARATION EXAMPLE 8
Preparation of Polymer (8)
Into a one-liter flask provided with a stirrer were placed 43.2 g (0.6 mol) of acrylic acid, 28.4 g (0.4 mol) of acrylamide, 400 ml of water, 70 ml of isopropanol and 400 mg of potassium persulfate as a polymerization initiator. After purging with nitrogen, stirring was effected for 3 hours at 70°C – 80°C. The reaction product was cooled to room temperature, neutralized with an aqueous solution of potassium hydroxide and then put into a cellophane membrane, which was then dialyzed in running water overnight and then freeze-dried.
The copolymers used in this invention can be prepared by copolymerizing acrylic acid or derivatives thereof, acrylamide or derivatives thereof and, if desired, one or more other monomers capable of forming addition polymers therewith such as alkyl esters of acrylic acid or methacrylic acid, styrene and derivatives thereof, vinyl esters, vinyl ethers, acrylonitriles, maleic acid anhydride, vinylpyrrolidone, vinylolxazolidone, vinylmethyImimidazole or vinylpyrrolidine in an amount of up to about 5 mol %.

The photographic layers according to this invention include gelatin, a thickener, a hardener and the polymer of this invention. Modified gelatin as well as conventional unmodified gelatin can be used. All of gelatins and derivatives thereof generally used for photography can be preferably employed in this invention.

For example, gelatin and gelatin derivatives which include gelatin which is treated with a reagent having one group capable of reacting with the amino groups, imino groups, hydroxy groups or carboxyl groups, which are contained in the gelatin molecule as a functional group, and a gelatin graft polymer wherein the molecular chain of another high molecular weight substance is grafted onto the gelatin molecule, can be employed.

As reagents for preparing the gelatin derivative, there are illustrated, e.g., isocyanates as described in U.S. Pat. No. 2,614,928; acid chlorides; acid anhydrides; acid esters as described in U.S. Pat. No. 3,118,766; phenyl glycidyl ethers as described in Japan Patent Publication No. 26845/67; vinylsulfone compounds as described in U.S. Pat. No. 3,132,945; N-allylvinylsulfonamicides as described in British Patent No. 861,414; maleimides as described in U.S. Pat. No. 3,186,844; and acrylates as described in U.S. Pat. No. 2,594,293; polyalkylene oxides as described in U.S. Pat. No. 3,312,553; epoxy compounds as described in Japanese Patent Publication No. 26845/67; acid esters as described in U.S. Pat. No. 2,763,639; alkane sulfonates as described in British Pat. No. 1,033,189; and the like. Also, as the branch high molecular weight materials to be grafted to the gelatin molecule, many compounds are described in U.S. Pat. Nos. 2,763,625; 2,831,767; 2,956,884; or in Polymer Letters, 5, 595 (1967); Polymeric Science Engineering, 9, 148 (1965); Journal of the Polymer Science, A-1, 9, 3199 (1971); and the like. Polymers or copolymers of monomers generally called vinyl monomers such as acrylic acid, methacrylic acid or the ester, amide or nitrile derivatives thereof can widely be used. Hydrophilic vinyl polymers having some compatibility with gelatin, such as the polymers or copolymers of acrylic acid, acrylamide, methacrylamide, hydroxyalkyl acrylate, hydroxyalkyl methacrylate or the like are particularly preferred.

Thickeners are high molecular weight compounds which increase the viscosity of a coating composition of gelatin and are quite compatible with gelatin. The term “thicker” as used herein designates those high molecular weight compounds which function to increase the viscosity of a gelatin containing coating composition and any such material which has the function of increasing the viscosity of such a coating solution to a viscosity of about 30 to about 100 centipoises at 40°C can be employed. Suitable thickeners are hydroxyethyl cellulose, hydroxypropyl cellulose, a copolymer of vinylvinyl ether and maleic acid anhydride, a copolymer containing semiamide of maleic acid as disclosed in British Pat. No. 630,016, a copolymer containing semimicelle of maleic acid as disclosed in British Pat. No. 632,174, an ammonia-treated copolymer of styrene and maleic acid anhydride as disclosed in British Pat. No. 676,459, a vinyl polymer having a sulfonic acid group as disclosed in Japanese Patent Publication No. 3582/60, etc. Particularly, polymers comprising the following repeating unit are useful:

- CH₂ - CH -

in which Z is a sulfonic acid group or the salts thereof with, for example, the sodium, potassium, ammonium and like salts.

Generally, the amount of the thickener is suitably in the range of about 0.001 to about 0.5 parts by weight per part by weight of gelatin. The thickener is usually added so that a viscosity of about 30 to about 100 centipoises, preferably about 30 to 70 centipoises, is obtained at 40°C with a gelatin coating composition.

As thickeners, compounds generally used for hardening photographic layers can be advantageously employed. Suitable thickeners are, for example, those as described in C.E.K. Mees & T.H. James, The Theory of the Photographic Process, 3rd Ed., pp. 55 – 60; Macmillan, New York (1966), U.S. Pat. Nos. 3,316,095; 3,232,764; 3,288,775; 2,732,303; 3,635,718; 3,232,763; 2,732,316; 2,586,168; 3,103,437; 3,017,280; 2,983,611; 2,725,294; 2,725,295; 3,100,704; 3,091,537; 3,321,313 and 3,543,292; British Pat. Nos. 974,723; 994,869 and 1,167,027; etc. Typical examples are aldehyde compounds such as mucocholic acid, mucobromic acid, mucophenoxychloric acid, mucophenoxybromic acid, formaldehyde, dimethylurea, trimethylolmelamine, 1,3-bis(diallylaminomethyl)urea, 1,3-bis(piperidinomethyl)urea, glyoxal, monomethylglyoxal, 2,3-dihydroxy-1,4-dioxane, 2,3-dihydroxy-5-methyl-1,4-dioxane, succinaledehyde, 2,5-dimethoxytetrahydrofuran or glutaraldehyde; active vinyl compounds such as divinyl sulfone, methylenebismaleimide, 5-acyctyl-1,3-diacyrcyloxy-hexahydros-triazine, 1,3,5-triazacycloxy-hexahydros-triazine or 1,3,5-trivinylsulfonylhexahydros-triazine; active halogen compounds such as 2,4-dichloro-6-hydroxy-s-triazine sodium salt, 2,4-dichloro-6-methoxy-s-triazine, 2,4-dichloro-6-(4-sulfobenzyl)-s-triazine sodium salt, 2,4-dichloro-6-(2-sulfoethylamino)-s-triazine, bischloromethyl sebacate or N,N'-bis-(2-chloroethylcarbamyl) piperazine; epoxy compounds such as bis(2,3-epoxypropyl)-methylpropylammonium p-toluenesulfonate, 1,4-bis(2′,3′-epoxypropyloxy)butane, 1,3,5-triglycidylisocyanurate or 1,3,5-triglycidyl-5-(γ-acetoxy-β-oxpropyl)isocyanurate; ethyleneimine compounds such as 2,4,6-triethylhexeneimino-s-triazine, 1,6-hexamethylene-N,N'-bis-hexyleneurea or bis-β-ethyleneiminothioether; methanesulfonic acid ester compounds such as 1,2-dichloro-3(3-trimethylaminopropyl)carbodi-
bodiimide p-toluenesulfonate or 1-ethyl-3-(3-dime-
thylaminopropyl)carbodiimide hydrochloride; isox-
azole compounds such as dimethylisoxazole persulfate,
dimethylisoxazole persulfate, 2-ethyl-5-phenylisox-
azole-3-sulfonate or 5,5’-(p-phenylene)-bis-isoxazole;
inorganic compounds such as chrome alum or chro-
mium acetate.

The amount of a hardener significantly varies de-
pending upon its hardening ability. Generally, a suit-
able amount is on the order of about 0.0001 to about
0.1 parts, preferably 0.001 to 0.05 parts by weight per
part by weight of gelatin.

The amount of a polymer used in this invention de-
pends upon the types and amounts of thickener and
hardener used therewith. Generally, a suitable amount
is on the order of about 0.001 to about 0.1 parts, pref-
erably 0.01 to 0.05 parts by weight per part by weight
of gelatin.

The photographic layers according to this invention
can contain the aforesaid gelatin, thickener, hardener,
the polymer of this invention and, if desired, substances
which are conventionally added to photographic layers.
For example, matting agents such as silica, strontium
barium sulfate or a polyethyl methacrylate latex;
lubricants such as liquid paraffin, polyfluorohydrocar-
bons or polyalkyl (or aryl) polisoxolane; surface active
agents such as saponin, polyethyleneglycol monolauryl
ether, etc., for example, as described in U.S. Pat. Nos.
2,271,623; 2,831,766; 2,992,108; 3,068,101;
3,133,816; 3,408,193; 3,666,478, etc.; antistatic
agents, for example, such as those described in U.S.
Pat. Nos. 2,739,888; 3,428,456; 3,551,152; 3,655,386;
3,686,368, etc.; ultraviolet absorbing agents such as
2-(2-hydroxy-3,5-di-sec-butylphenyl)-5-methoxyben-
zotriazole, 4-methoxy-cyanocinnamic acid n-dodecyl
ester, etc., as described in U.S. Pat. Nos. 2,685,512;
3,253,921; 3,415,649; 3,514,293; 3,533,794, etc.; dyes
such as mononole dyes, styryl dyes, etc., for example,
those described in U.S. Pat. Nos. 3,445,231;
3,540,887; 3,560,214; 3,647,460; 3,746,539, etc., can
be used.

The photographic layers of this invention can be
light-sensitive silver halide emulsion layers containing
light-sensitive silver halide particles.

The photographic light-sensitive materials according
to this invention have at least one silver halide emulsion
layer on a support and are characterized by the pres-
ence of at least one photographic layer of this invention.

All supports generally used for photographic materi-
als can be employed. Cellulose ester films such as cel-
lose nitrate or cellulose acetate, polyester films such as
polyethylene terephthalate, polyvinyl acetel films, poly-
vinyl chloride films, polystyrene films, polycarbonate
films, baryta papers, polyethylene-coated papers, etc.,
are preferred.

Silver halide emulsions which are preferably used are
those having silver halide particles dispersed in a hy-
drophilic high molecular weight binder. Suitable silver
halides are silver bromide, silver bromiodochloride, silver
bromochloride, silver chloride, silver iodide, etc., and suitable hydrophilic high molecular weight binders are gelatin or gelatin deriva-
tives as described above with up to about 20 % by
weight of the gelatin or gelatin derivative being re-
placed by hydrophilic high molecular weight substances
which are generally used as binders for photo-
graphic layers. Such hydrophilic high molecular weight
substances are natural high molecular weight sub-
stances and derivatives thereof such as albumin or agar,
cellulose derivatives such as carboxy cellulose alkyl
ester, hydroxyethyl cellulose or cellulose hydroxyl-
yethyl cellulose, synthetic high molecular weight sub-
stances such as polyvinyl alcohol, polyacrylamide, pol-
viny1 pyrrolidone, polyacrylic acid, polyacrylic acid
ester or a copolymer of maleic acid anhydride with
another vinyl compound. The silver halide emulsions
contain silver halide particles of the so-called modi-
ified halide type was described in U.S. Pat. No.
3,622,318, British Pat. No. 635,841, etc.

The silver halide emulsions can be sensitized with
active gelatin or sulfur compounds as described in U.S.
Pat. Nos. 1,574,944; 1,623,499; and 2,410,689. Also,
they can be sensitized with noble metal salts such as
palladium or gold as described in U.S. Pat. Nos.
2,448,960; 2,399,083 and 2,642,361, reducing agents
such as stannous salts as described in U.S. Pat. No.
2,487,850, as well as polyalkylene oxide derivatives.
Moreover, they can be spectrally sensitized with cyan-
ine or merocyanine dyes as described in U.S. Pat.
Nos. 2,519,001; 2,666,761; 2,734,900; 2,739,964 and
3,481,742.

The silver halide emulsions can contain antifogging
agents or stabilizing agents such as mercury com-
ounds and azaindene. Furthermore, the emulsions
can contain plasticizers such as glycine or coating
adjuvants as described above, as well as antistatic
agents, ultraviolet absorbing agents, fluorescent brighten-
ers, antioxidants, dyes, etc.

Moreover, two-equivalent or four-equivalent color
forming couplers can be present in the emulsion. For
example, yellow forming couplers of the open chain
type ketomethylene type such as the benzoylacetoani-
di or pivaloylacetanilide compounds, magenta form-
ing couplers such as the pyrazoline or indazole com-
ounds and cyan forming couplers such as the phenol
or naphthol compounds are preferably used. Suitable
examples of color forming couplers which can be em-
ployed are disclosed in U.S. Pat. 2,278,658;
3,227,550; 3,265,506; 3,227,554; 3,408,194;
3,415,652; 2,600,788; 3,062,653; 3,419,391;
3,516,831; 3,615,506; 3,617,291; 2,327,293;
2,423,730; 2,908,573; 3,311,476; 2,523,294;
3,034,892; 3,476,563; etc.

The silver halide emulsions include various photo-
graphic silver halide emulsions, for example, ortho-
chromatic emulsions, panchromatic emulsions, infra-
red-sensitive emulsions, emulsions for use in recording
X-rays and other invisible rays, color photographic
emulsions such as emulsions containing color forming
couplers, emulsions containing a dye developing agent,
emulsions containing a dye which can be bleached, etc.

The photographic light-sensitive material according
to this invention can contain non-light-sensitive auxi-
liary layers such as filter layers, intermediate layers,
antihalation layers, undercoating layers or backing
layers. These auxiliary layers can contain hydrophilic
high molecular weight binder and, if desired, various
additives such as colorants or antioxidants.

The hydrophilic high molecular weight substances
used in the silver halide emulsion layers and auxiliary
layers in a photographic light-sensitive material are
hardened with the aforesaid hardeners.

The photographic light-sensitive material according
to this invention can be processed by conventional
methods. Temperatures in the range of 20°C or lower
to 60°C or higher are applicable for processing. The photographic layers in the photographic light-sensitive material of this invention are particularly suitable for rapid processing at high temperature which is effected at temperatures above 30°C, since they possess both a high melting temperature and a high swelling rate.

Processing solutions are used without particular limitation in this invention, and all of the conventional processing solutions can be employed.

According to this invention, gelatin layers containing a thickener which have a high melting temperature and high swelling are obtained. These layers are very useful as photographic layers, and a photographic material having such photographic layers can be used to rapidly provide a photographic image with high sensitivity.

This invention will be further described in greater detail by reference to the following examples. Unless otherwise indicated, all parts, percentages, ratios and the like are by weight.

EXAMPLE 1

A preparation was made for photographic light-sensitive materials used for a reversal color film to be processed in coupler-containing developer which were provided with a red-sensitive silver halide emulsion layer with a 3 μ thickness, a green-sensitive silver halide emulsion layer with a 2.5 μ thickness, a yellow filter layer with a 1 μ thickness and a blue-sensitive silver halide emulsion layer with a 3 μ thickness on an undercoated polyethylene terephthalate film (thickness: 84 μ). A silver halide emulsion used in the red-sensitive layer was a silver bromoiodide emulsion containing 2.0 mol % of iodide, which contained 4.5 % of silver halide and 5.4 % of gelatin. The silver halide emulsion used in the green-sensitive layer and the blue-sensitive layer was a silver bromoiodide emulsion containing 3.5 mol % of iodide, which contained 4.5 % of silver halide and 5.4 % of gelatin. The yellow filter layer comprised gelatin containing a yellow dye. Each of the red-sensitive layer, the green-sensitive layer, the yellow filter layer and the blue-sensitive layer in each light-sensitive material contained poly-p-vinylbenzenesulfonic acid-potassium salt as a thickener and 2,4-dichloro-6-hydroxy-s-triazine-sodium salt as a hardener and Polymer (1) of this invention in the amounts shown in Table 1 per g of gelatin contained in each layer.

| TABLE 1 |
|---|---|---|---|
| Light-Sensitive Material (g) | 1A | 1B | 1C | 1D |
| Thickener (mg) | 25 | 25 | 25 | 25 |
| Hardener (mg) | 1.2 | 0.8 | 0.8 | 0.6 |
| Polymer (1) (mg) | — | — | 50 | 50 |

After preparing, light-sensitive materials 1A to 1D were kept under the conditions of a temperature of 25°C and a relative humidity of 60 % for 1 or 11 days. Then, the photographic layers were measured as to melting temperature in a 0.2 N aqueous solution of sodium hydroxide and the swelling rate in water at 27°C. The results obtained are shown in Table 2.

| TABLE 2 |
|---|---|---|---|
| Light-Sensitive Material | Melting Temperature (°C) | 1 Day | 11 Days | Swelling Rate (%) | 1 Day | 11 Days |
| 1A | 57 | 64 | 400 | 270 |
| 1B | 46 | 56 | 490 | 370 |

The results in Table 2 show that the light-sensitive materials containing the polymer of this invention have a higher melting point and a higher swelling rate as compared with those containing no polymer of this invention. That is, the use of the polymer according to this invention can provide photographic layers having a high melting temperature and also a high swelling rate.

EXAMPLE 2

The photographic light-sensitive materials were prepared by applying a silver halide emulsion layer having a thickness of 12 μ and sensitized in a panchromatic manner on an undercoated cellulose triacetate film (thickness: 130 μ). A silver halide emulsion used for the emulsion layer in each photographic light-sensitive material was a silver bromoiodide emulsion containing 5 mol % of iodide, which contained 10 % of silver halide and 11 % of gelatin. Each silver halide emulsion contained poly-p-vinylbenzenesulfonic acid potassium salt as a thickener, mucocloric acid as a hardener and Polymer (2) of this invention in the amounts shown in Table 3 per g of each emulsion.

| TABLE 3 |
|---|---|---|---|---|---|
| Light-Sensitive Material | 2A | 2B | 2C | 2D |
| Thickener (g) | 20 | 20 | 20 | 20 |
| Hardener (g) | 3.0 | 2.0 | 2.0 | 1.0 |
| Polymer (2) (g) | — | — | 1.5 | 1.5 |

After preparation, Light-Sensitive Materials 2A to 2D were kept under the conditions of a temperature of 25°C and a relative humidity of 60 % for 7 days. Then, the photographic layers were measured as to the melting temperature in a 0.2 N aqueous solution of sodium hydroxide and the swelling rate in water at 27°C. The results obtained are shown in Table 4.

| TABLE 4 |
|---|---|---|---|---|---|
| Light-Sensitive Material | Melting Temperature (°C) | 2A | 2B | 2C | 2D |
| Thickener (g) | 55 | 55 | 55 | 55 |
| Hardener (g) | 3.0 | 3.0 | 3.0 | 3.0 |
| Polymer (2) (g) | 1.5 | 1.5 | 1.5 | 1.5 |

As is apparent from the results of Table 4, the photographic layers containing the polymer of this invention exhibited a higher melting temperature and a higher swelling rate as compared with those containing no polymer of this invention.

EXAMPLE 3

A preparation was made for color photographic light-sensitive materials provided with a blue-sensitive silver halide emulsion layer with a 3.6 μ thickness, a gelatin intermediate layer (1) with a 0.9 μ thickness, a red-sensitive silver halide emulsion layer with a 3 μ thickness, a gelatin intermediate layer (II) with a 1.1 μ thickness,
a green-sensitive silver halide emulsion layer with a 4 μ thickness and a gelatin protective layer with a 0.7 μ thickness on an undercoated cellulose triacetate film (thickness: 130 μ). The silver halide emulsion used for the blue-sensitive layer was a silver bromoiodochloride emulsion containing 6.8 mol % of chloride and 1.2 mol % of iodide, which contained 9 % of silver halide and 10 % of gelatin. The silver halide emulsion used for the red-sensitive layer and the green-sensitive layer was a silver bromochloride emulsion containing 30 mol % of bromide, which contained 10 % of silver halide and 12 % of gelatin. The blue-sensitive layer, the red-sensitive layer and the green-sensitive layer contained 2′-chloro-5′-2-(2,4 -di-tert-amylophenylo) butylamido-4-methoxybenzoylacetoaminid as a yellow forming coupler, 1-hydroxy-4-chloro-N-dodecyl-2-naphtoamid as a cyan forming coupler and 1-(2,4,6-trichlorophenyl)-3-(3-(2,4-dinit-tert-amylophenylo)acetoamidobenzamid as 5-pyrazolone as a magenta forming coupler, respectively. Each of the intermediate layer (I), the red-sensitive layer, the intermediate layer (II), the green-sensitive layer and the protective layer in each light-sensitive material contained 1.2 mg of 2,4-dichloro-6-hydroxy-s-triazine sodium salt as a hardener and 25 mg of poly-p-vinylbenzenesulfonic acid-potassium salt as a thickener per g of gelatin contained in each layer, but contained no polymers of this invention. The blue-sensitive layer in each light-sensitive material contained 1 mg of 2,4-dichloro-6-hydroxy-s-triazine sodium salt as a hardener (1), 1 mg of N,N,N′,N′′-trisacyrlyl-1,3,5 hexahydrotriazine as a hardener (2), 20 mg of poly-p-vinylbenzenesulfonic acid-potassium salt as a thickener and the polymer of this invention shown in Table 5 per g of gelatin contained in the layer.

After preparation, the light-sensitive materials were kept under the conditions of a temperature of 25°C and a relative humidity of 60 % for 7 days. Thereafter, the photographic layers were measured as to the melting temperature in a 0.2 N aqueous solution of sodium hydroxide and the swelling rate in water at 25°C. The results obtained are shown in Table 5.

### TABLE 5

<table>
<thead>
<tr>
<th>Light-Sensitive Material</th>
<th>Polymer (this invention) (mg)</th>
<th>Melting Temperature (°C)</th>
<th>Swelling Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>-</td>
<td>60</td>
<td>290</td>
</tr>
<tr>
<td>3B</td>
<td>(3), 40</td>
<td>62</td>
<td>510</td>
</tr>
<tr>
<td>3C</td>
<td>(6), 40</td>
<td>62</td>
<td>490</td>
</tr>
<tr>
<td>3D</td>
<td>(7), 40</td>
<td>62</td>
<td>480</td>
</tr>
<tr>
<td>3E</td>
<td>(8), 40</td>
<td>60</td>
<td>360</td>
</tr>
</tbody>
</table>

It is apparent from the results in Table 5 that the photographic light-sensitive materials containing the polymer of this invention show a higher swelling rate without reducing the melting temperature as compared with the photographic material containing no polymer of this invention.

### EXAMPLE 4

Light-sensitive materials used for indirect X-ray photography were prepared by applying a light-sensitive emulsion layer with a 4 μ thickness on an undercoated cellulose triacetate film (thickness: 175 μ). The silver halide emulsion used in the emulsion layer in each light-sensitive material was a silver iodide emulsion containing 2 mol % of iodide, which contained 25 % of silver halide and 9 % of gelatin. Each emulsion contained 0.4 g of 2,4,6-triethyleneimino-1,3,5-triazine as a hardener, 15 g of poly-p-vinylbenzensulfonic acid potassium salt as a thickener and the polymer of this invention shown in Table 6 per kg of each emulsion.

After preparation, the light-sensitive materials were kept under the conditions of a temperature of 25°C and a relative humidity of 60 % for 7 days. Thereafter, the photographic layers were measured as to the melting temperature in a 0.2 N aqueous solution of sodium hydroxide and the swelling rate in water at 27°C. The results obtained are shown in Table 6.

### TABLE 6

<table>
<thead>
<tr>
<th>Light-Sensitive Material</th>
<th>Polymer (this invention) (g)</th>
<th>Melting Temperature (°C)</th>
<th>Swelling Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A</td>
<td>-</td>
<td>50</td>
<td>310</td>
</tr>
<tr>
<td>4B</td>
<td>(5), 0.2</td>
<td>53</td>
<td>380</td>
</tr>
<tr>
<td>4C</td>
<td>(3), 0.5</td>
<td>55</td>
<td>420</td>
</tr>
<tr>
<td>4D</td>
<td>(5), 1.0</td>
<td>60</td>
<td>550</td>
</tr>
<tr>
<td>4E</td>
<td>(3), 2.0</td>
<td>60</td>
<td>560</td>
</tr>
<tr>
<td>4F</td>
<td>(3), 3.0</td>
<td>60</td>
<td>560</td>
</tr>
</tbody>
</table>

As is apparent from the results in Table 6, the use of the polymer of this invention can increase the swelling rate of photographic layers. Moreover, the results obtained in this example confirm that the melting temperature of photographic layers is raised by the use of such a polymer.

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.

What is claimed is:

1. A process for hardening gelatin which comprises incorporating an acrylic acid-acrylamide copolymer into the system containing gelatin, a thickener and a hardener; said acrylic acid-acrylamide copolymer being a copolymer containing about 5 to 95 mol % of the following repeating unit (A):

```
CH=CH
```

and about 5 to 95 mol % of the following repeating unit (B):

```
CH=CH
```

wherein R₁ and R₂ are each a hydrogen atom or a methyl group, R₃ and R₄ are each a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms, or wherein R₅ and R₆ can combine to form a non-metal atom containing 5-, 6- or 7-membered ring, and X is a hydrogen atom, a sodium atom, a potassium atom, a lithium atom, an ammonium group, said acrylic acid-acrylamide copolymer being present in said system at about 0.001 to about 0.1 parts by weight per part by weight of gelatin, and having a limiting viscosity ranging from about 0.3 to about 6.0 measured at 30°C using a 1 % by weight aqueous solution of sodium chlo-
3,926,869

3,926,869

ride; and said thickener being a high molecular weight polymer comprising the following repeating unit:

- CH₂ - CH -

wherein Z is a sulfonic acid group or a sulfonic acid salt group, said thickener being capable of increasing the viscosity of a gelatin solution to about 30 to about 100 centipoises at about 40°C.

2. The process for hardening gelatin of claim 1, wherein said alkyl group of said acrylic acid-acrylamide copolymer is a substituted alkyl group containing oxo, hydroxy or alkoxy groups as substituents.

3. The process for hardening gelatin of claim 2, wherein said copolymer contains said repeating unit (A) at 30 to 80 mol% and said repeating unit (B) at 20 to 70 mol%.

4. The process for hardening gelatin of claim 1, wherein said copolymer includes in addition up to 5 mol% of repeating units of a monomer copolymerizable with said repeating units (A) and (B).

5. The process for hardening gelatin of claim 1, wherein said hardener is an aldehyde compound, an active vinyl compound, an active halogen containing compound, an epoxy compound, an ethylenimine compound, a methane sulfonic acid ester compound, a carbodiimide compound, an isoxazole compound, or an inorganic hardener.

6. The process for hardening gelatin of claim 1, wherein said thickener is the sodium or potassium salt of poly-p-vinylbenzenesulfonic acid.

7. The process for hardening gelatin of claim 1, wherein said thickener is present in said system at about 0.001 to about 0.5 parts by weight per part by weight of gelatin.

8. The process for hardening gelatin of claim 7, wherein said hardener is present in said system at about 0.0001 to about 0.1 parts by weight per part by weight of gelatin.

* * * * *