

- [54] **PROCESS FOR HARDENING GELATIN IN PHOTOGRAPHIC LAYERS WHICH CONTAIN A THICKENER AND HARDENER BY UTILIZING ACRYLIC ACID-ACRYLAMIDE COPOLYMERS**
- [75] Inventors: **Ikutaro Horie; Taksuhi Miyazako; Takeo Shimada**, all of Minami-ashigara, Japan
- [73] Assignee: **Fuji Photo Film Co., Ltd.**, Minami-ashigara, Japan
- [22] Filed: **June 7, 1974**
- [21] Appl. No.: **477,236**
- [30] **Foreign Application Priority Data**
June 7, 1973 Japan..... 48-64041
- [52] **U.S. Cl.**..... **260/8; 96/94 R; 96/111; 96/114; 96/114.8**
- [51] **Int. Cl.²**..... **C08L 89/00**
- [58] **Field of Search**..... **260/8; 96/111, 114, 114.8, 96/94 R**

[56]		References Cited	
		UNITED STATES PATENTS	
2,486,192	10/1949	Minsk et al.	260/89.7
2,504,074	4/1950	Jones	260/8
3,284,207	11/1966	Stonham	96/114
3,628,957	12/1971	Franco et al.	96/87 R
3,746,547	7/1973	Tsuji et al.	96/84
<i>Primary Examiner</i> —Melvyn I. Marquis			
<i>Assistant Examiner</i> —Edward Woodberry			
<i>Attorney, Agent, or Firm</i> —Sughrue, Rothwell, Mion, Zinn & Macpeak			

[57] **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 and 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.

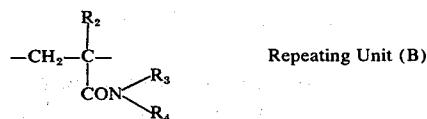
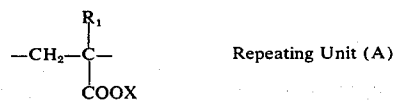
These objects have been attained by the incorporation of an acrylic acid-acrylamide copolymer into the system containing gelatin, thickener and hardener. According to this invention, hardened gelatin layers having sufficiently high melting temperature and high

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):



in which 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 1 to 6 carbon atoms which can contain oxo, hydroxy or alkoxy 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 alkoxy groups for R₃ and R₄ are groups such as methyl, ethyl, butyl, tert-butyl, hexyl, cyclohexyl, benzyl, 1,1-dimethyl-3-oxobutyl, 1,1-dimethyl-3-hydroxybutyl, hydroxyethyl, methoxyethyl, hydroxyethoxyethyl, morpholinoethyl, etc., groups. Suitable examples of rings formed by the combination of R₃ and R₄ are rings such as morpholino, N-methylpiperazino, piperidino, pyrrolidino, hexamethyleneimino, etc., rings. Suitable examples of ammonium groups are those of triethanolamine, diethanolamine, ethanolamine, 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 0.3 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° to 90°C using a polymerization catalyst such as potassium persulfate, ammonium persulfate or po-

tassium perphosphate. 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-diethylacrylamide, N-methylolacrylamide, N-hydroxyethylacrylamide, N-tert-butylacrylamide, N,N-dibutylacrylamide, N-cyclohexylacrylamide, diacetone acrylamide, N-(1,1-dimethyl-3-hydroxybutyl)acrylamide, N-(β -morpholino)ethylacrylamide, N-benzylacrylamide, N-acryloylmorpholine, N-methacryloylmorpholine, N-methyl-N'-acryloylpiperazine, 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°–90°C. The reaction product was cooled to room temperature (about 20°–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 (0.3 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°–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°–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, (0.6 mol) of methacrylamide, 16 g of sodium hydroxide dissolved in 500 ml of water, and 350mg of potassium persulfate as a polymerization catalyst. After purging with nitrogen, stirring was effected for 2 hours while keeping the temperature at 70°–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°–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°–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°–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°–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.

Yield 80.4 g (85 %), $n = 0.69$.

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, vinyloxazolidone, vinylmethylimidazole or vinylpyridine in an amount of up to about 5 mol %.

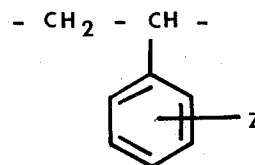
The photographic layers according to this invention include gelatin, a thickener, a hardener and the polymer of this invention. Modified gelatin as well as conventional unmodified gelatin can be used. All of gelatins and derivatives thereof generally used for photography can be preferably employed in 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 carboxy 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 anhydrides as described in U.S. Pat. No. 3,118,766; phenyl glycidyl ethers as described in Japanese Pat. Publication No. 26845/67; vinylsulfone compounds as described in U.S. Pat. No. 3,132,945; N-allylvinylsulfonamides as described in British Pat. No. 861,414; maleimides as described in U.S. Pat. No. 3,186,846; acrylonitriles 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 Pat. Publication No. 26845/67; acid esters as described in U.S. Pat. No. 2,763,639; alkanesultones 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); Photographic 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 "thickener" 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 methylvinyl ether and maleic acid anhydride, a copolymer containing semiamide of maleic acid as disclosed

in British Pat. No. 630,016, a copolymer containing semister 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 Pat. Publication No. 3582/60, etc. Particularly, polymers comprising the following repeating unit are useful:



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 30 to 70 centipoises, is obtained at 40°C with a gelatin coating composition.

As hardeners, compounds generally used for hardening photographic layers can be advantageously employed. Suitable hardeners 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 mucochloric acid, mucobromic acid, mucophenoxychloric acid, mucophenoxybromic acid, formaldehyde, dimethylolurea, trimethylolmelamine, 1,3-bis(diallylamino)methylurea, 1,3-bis(piperidinomethyl)urea, glyoxal, monomethylglyoxal, 2,3-dihydroxy-1,4-dioxane, 2,3-dihydroxy-5-methyl-1,4-dioxane, succinaldehyde, 2,5-dimethoxytetrahydrofuran or glutaraldehyde; active vinyl compounds such as divinyl sulfone, methylenebismaleimide, 5-acetyl-1,3-diacryloyl-hexahydro-s-triazine, 1,3,5-triacryloyl-hexahydro-s-triazine or 1,3,5-trivinylsulfonyl-hexahydro-s-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-sulfoanilino)-s-triazine-sodium salt, 2,4-dichloro-6-(2-sulfoethylamino)-s-triazine, bischloromethyl sebacate or N,N'-bis(2-chloroethylcarbonyl)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-diglycidyl-5-(γ-acetoxy-β-oxypropyl)isocyanurate; ethyleneimine compounds such as 2,4,6-triethyleneimino-s-triazine, 1,6-hexamethylene-N,N'-bise-thyleneurea or bis-β-ethyleneiminoethylthioether; methanesulfonic acid ester compounds such as 1,2-di(methanesulfonyl)ethane, 1,4-di(methanesulfonyl)-butane or 1,5-di(methanesulfonyl)pentane; carbodiimide compounds such as dicyclohexylcarbodiimide, 1-cyclohexyl-3-(3-trimethylaminopropyl)car-

bodiimide-p-toluenesulfonate or 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide-hydrochloride; isoxazole compounds such as -dimethylisoxazole persulfate, -dimethylisoxazole.persulfate, 2-ethyl-5-phenylisoxazole-3'-sulfonate or 5,5'-(p-phenylene)-bis-isoxazole; inorganic compounds such as chrome alum or chromium acetate.

The amount of a hardener significantly varies depending upon its hardening ability. Generally, a suitable 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 depends 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, preferably 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 polymethyl methacrylate latex; lubricants such as liquid paraffin, polyfluorohydrocarbons or polyalkyl (or aryl) polysiloxane; 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-methoxybenzotriazole, 4-methoxy- α -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 oxonole 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 presence of at least one photographic layer of this invention.

All supports generally used for photographic materials can be employed. Cellulose ester films such as cellulose nitrate or cellulose acetate, polyester films such as polyethylene terephthalate, polyvinyl acetal films, polyvinyl 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 hydrophilic high molecular weight binder. Suitable silver halides are silver bromide, silver bromiodide, silver bromiodchloride, silver bromochloride, silver chloride, silver iodide, etc., and suitable hydrophilic high molecular weight binders are gelatin or gelatin derivatives as described above with up to about 20 % by weight of the gelatin or gelatin derivative being replaced by hydrophilic high molecular weight substances which are generally used as binders for photographic layers. Such hydrophilic high molecular weight

substances are natural high molecular weight substances and derivatives thereof such as albumin or agar, cellulose derivatives such as carboxy cellulose alkyl ester, hydroxyethyl cellulose or carboxymethylhydroxyethyl cellulose, synthetic high molecular weight substances such as polyvinyl alcohol, polyacrylamide, polyvinyl pyrrolidone, polyacrylic acid, polyacrylic acid ester or a copolymer of maleic acid anhydride with another vinyl compound. The silver halide emulsions can contain silver halide particles of the so-called modified 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. 2,448,060; 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 cyanine 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 compounds and azaindenes. Furthermore, the emulsions can contain plasticizers such as glycerine or coating adjuvants as described above, as well as antistatic agents, ultraviolet absorbing agents, fluorescent brighteners, 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 benzoylacetoanilide or pivaloylacetoanilide compounds, magenta forming couplers such as the pyrazolone or indazolone compounds and cyan forming couplers such as the phenol or naphthol compounds are preferably used. Suitable examples of color forming couplers which can be employed are disclosed in U.S. Pat. Nos. 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; 3,253,294; 3,034,892; 3,476,563; etc.

The silver halide emulsions include various photographic silver halide emulsions, for example, orthochromatic emulsions, panchromatic emulsions, infrared-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 auxiliary 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 bromiodide 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 bromiodide emulsion containing 3.3 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

	1A	Light-Sensitive Material 1B	1C	1D
Thickener (mg)	25	25	25	25
Hardener (mg)	1.2	0.8	0.8	0.6
Polymer (1) (mg) (this invention)	—	—	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)		Swelling Rate (%)	
	1 Day	11 Days	1 Day	11 Days
1A	57	64	400	270
1B	46	56	490	370

TABLE 2-continued

Light-Sensitive Material	Melting Temperature (°C)		Swelling Rate (%)	
	1 Day	11 Days	1 Day	11 Days
1C	63	64	790	620
1D	51	61	960	750

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 bromiodide 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, mucochloric acid as a hardener and Polymer (2) of this invention in the amounts shown in Table 3 per kg of each emulsion.

TABLE 3

	2A	Light-Sensitive Material 2B	2C	2D
Thickener (g)	20	20	20	20
Hardener (g)	3.0	2.0	2.0	1.0
Polymer (2) (g) (this invention)	—	—	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)	Swelling Rate (%)
2A	55	320
2B	42	440
2C	60	500
2D	40	650

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 (I) 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 bromiodochloride 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-amylphenoxy)butylamido-4-methoxybenzoylacetoanilide as a yellow forming coupler, 1-hydroxy-4-chloro-N-dodecyl-2-naphthoamide as a cyan forming coupler and 1-(2,4,6-trichlorophenyl)-3-{3-(2,4-di-tert-amylphenoxy)acetoamidobenzamido-} 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''-trisacryloyl-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 27°C. The results obtained are shown in Table 5.

TABLE 5

Light-Sensitive Material	Polymer (this invention) (mg)	Melting Temperature (°C)	Swelling Rate (%)
3A	—	60	290
3B	(3), 40	62	510
3C	(6), 40	62	480
3D	(7), 40	62	480
3E	(8), 40	60	360

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 con-

tained 0.4 g of 2,4,6-triethylenimine-1,3,5-triazine as a hardener, 15 g of poly-p-vinylbenzenesulfonic 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

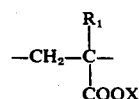
Light-Sensitive Material	Polymer (this invention) (g)	Melting Temperature (°C)	Swelling Rate (%)
4A	—	50	310
4B	(5), 0.2	53	380
4C	(5), 0.5	55	420
4D	(5), 1.0	60	550
4E	(5), 2.0	60	560
4F	(5), 3.0	60	560

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.

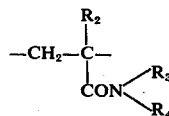
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

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):



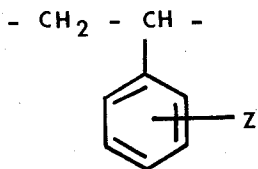
and about 5 to 95 mol % of the following repeating unit (B):



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 R₃ and R₄ 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, or 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-

13

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



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

14

(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 ethyleneimine 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.

* * * * *

30

35

40

45

50

55

60

65