United States Patent [19]

Priem et al.

[11] **3,867,152**

[45] **Feb. 18, 1975**

[54] **PHOTOGRAPHIC SILVER HALIDE MATERIAL**

[75] Inventors: **Jan Jozef Priem**, Mortsel; **Walter Frans De Winter**, Berchem; **Jan Bernard Lambrechts**, Antwerpen, all of Belgium

[73] Assignee: **Agfa-Gevaert N.V.**, Mortsel, Belgium

[22] Filed: **May 29, 1973**

[21] Appl. No.: **364,327**

[30] **Foreign Application Priority Data**

June 22, 1972 Great Britain 29386/72

[52] **U.S. Cl.** ..... **96/63,** 96/50 R, 96/66 R, 96/66 T, 96/67, 96/87 R, 96/114

[51] **Int. Cl.** **G03c 1/04,** G03c 5/26

[58] **Field of Search** ..... 96/114, 67, 87 R, 50, 63, 96/66 T

[56] **References Cited**

UNITED STATES PATENTS

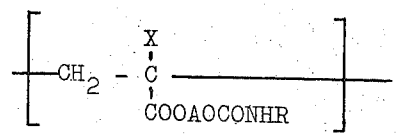
3,316,097	4/1967	Minsk et al.	96/114
3,488,708	1/1970	Smith	96/114
3,607,290	9/1971	Butler	96/114
3,775,129	11/1973	Dodwell	96/114

Primary Examiner—Ronald H. Smith

Attorney, Agent, or Firm—A. W. Breiner

[57] **ABSTRACT**

Polymeric compounds having recurring units of the formula:



wherein: X is hydrogen or methyl, A is C_1–C_5 alkylene and R is alkyl or aryl,

are described for use in photographic silver halide material. The compounds reduce the formation of sludge and pressure marks upon processing, especially processing at elevated temperature, of the exposed elements.

13 Claims, No Drawings

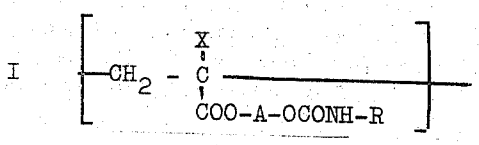
PHOTOGRAPHIC SILVER HALIDE MATERIAL

The present invention relates to photographic radiation sensitive silver halide elements and more particularly to radiation-sensitive silver halide elements with reduced tendency to formation of sludge and pressure marks on rapid processing, after exposure, at elevated temperature.

It is known to use techniques for automatic processing of exposed photographic materials. In order to reduce the time that the materials pass through the automatic processing machines, where they are conducted from one processing station to another by means of roller pairs, processing is carried out at elevated temperatures, say above 30°C. Under these severe processing conditions the physical and photographic properties of the materials are impaired the more because in these materials for rapid processing the gelatin content of the silver halide emulsions is reduced considerably as compared with the gelatin content used in emulsions for normal processing. For instance, owing to the very low gelatin content, the machine-processed materials show repeated pressure marks from the roller pairs by which they are guided in the processing machine. Moreover, some sort of gelatin sludge is deposited on the first transport rollers and/or formed at the surface of the fixing bath.

It is possible to reduce these pressure marks and sludge formation by appropriate hardening of the material, more particularly of the protective gelatin top layer, but with these short processing times this unfortunately results in an unacceptable lowering of the gradation, and also of the emulsion speed.

It has now been found possible to reduce or eliminate the pressure marks and sludge formation without affecting the gradation and emulsion speed to a noteworthy extent by incorporating in the radiation sensitive silver halide emulsion layer or a hydrophilic colloid layer in water-permeable relationship with the said emulsion layer, preferably in the gelatin protective antistress layer, a novel polymeric compound containing recurring units of the following formula I:



wherein

A is a straight-chain or branched-chain C_1–C_5 alkylene group,

X is hydrogen or methyl,

R is alkyl including substituted alkyl, or aryl e.g., phenyl including substituted aryl e.g., phenyl substituted by alkyl.

The present invention thus provides a photographic material comprising at least one silver halide emulsion layer and at least one polymeric compound as defined above.

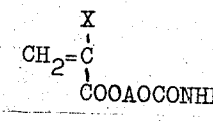
The present invention also provides a method of producing photographic images by exposure and processing of a photographic silver halide material comprising at least one silver halide emulsion layer wherein the said emulsion layer or a hydrophilic colloid layer in water-permeable relationship therewith comprises a polymeric compound as defined above.

The polymeric compounds for use according to the present invention are homopolymers or copolymers. The polymeric materials may comprise in addition to the recurring units of the above formula recurring units of other copolymerized monomers for example recurring units of acrylic acid and methacrylic acid, acrylamide and methacrylamide as well as the N-alkylated derivatives thereof, alkyl acrylates and alkylmethacrylates e.g., methyl- and butylacrylate, acrylonitrile, ethylene, vinyl esters e.g., vinyl acetate and the vinyl ester of versatic acid, vinyl ethers especially those the aliphatic ether group of which comprises at most 4 C-atoms vinyl chloride, vinylidene chloride, styrene, butadiene, etc.

The effectiveness of the polymeric compounds for use according to the present invention is due to the recurring units of the above general formula, and therefore the polymeric compounds preferably comprise at least 15 mole percent, preferably at least 50 mole percent of these recurring units. The copolymerized monomers should be such that they have no deleterious effect on the photographic properties of the silver halide emulsion layers.

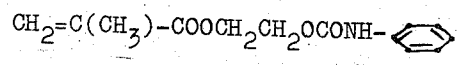
Though the molecular weight of the polymeric compounds used is of minor importance and the best range can be easily determined by means of some simple tests the compounds generally have a molecular weight comprised between 10^3 and 10^7.

The monomeric compounds of the following formula II:



II:

wherein X, A, and R have the same significance as above, which are used in the preparation of the polymeric compounds having recurring units of the above general formula I, can be prepared by reaction of the appropriate isocyanate with a hydroxyalkyl(meth)acrylate as is illustrated by the following preparations. Preparation I : N-phenyl-methacryloyloxy ethylcarbamate of the formula:



was prepared as follows:

In a 5 litre reaction vessel fitted with thermometer, stirrer, reflux condenser and dropping funnel were placed in 2.250 liter of dry diisopropyl ether, 9 moles of phenyl isocyanate and some copper curlings as polymerisation inhibitor. The mixture was heated to the reflux temperature (82°C) and 9 moles of hydroxyethyl methacrylate were added dropwise in 1 hour. Refluxing was continued for another hour whereupon the solution was poured with stirring in 16 litres of hexane. The droplets of liquid monomer become solid after a few minutes. The monomer was separated by suction. Yield: 89.5 percent. Melting point : 58°C.

		Calculated	found
Analysis:	C	62.65	62.65–62.70
	N	5.62	5.65–64.00
	H	6.03	6.05–6.10

Preparation II : N-n-butyl-methacryloyloxy ethylcarbamate of the formula:

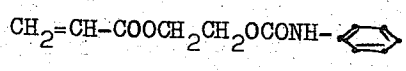
$CH_2=C(CH_3)-COOCH_2CH_2OCONHC_4H_9$

was prepared as follows:

In a 1 litre reaction vessel fitted with stirrer, thermometer, reflux condenser, and dropping funnel were placed : 250 ml of diisopropyl ether, 1 mole of butyl isocyanate and some crystals of m-dinitrobenzene as polymerisation inhibitor. The mixture was heated to 80°C and 1 mole of hydroxyethylmehtacrylate was dropwise added. After the addition, the mixture was refluxed for 4 hours. The solvent was then removed by evaporation and the residue subjected to fractional destillation. The monomer fraction distills at 120°C/0.1 mm. Yield : 72 percent.

The monomer is a clear, colourless liquid which solidifies at −3°C. NMR-analysis showed that the monomer comprised 5 percent of unreacted hydroxyethyl methacrylate.

Preparation III : N-phenyl-acryloyloxy ethylcarbamate of the formula:



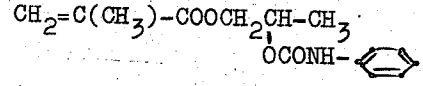
was prepared as follows:

In a 500 ml reaction vessel fitted with stirrer, reflux condenser, thermometer and dropping funnel were placed : 250 ml of diisopropyl ether, 1 mole of phenylisocyanate and some crystals of n-dinitrobenzene as polymerization inhibitor. The mixture was heated to 82°C whereupon 1.1 mole of hydroxyethyl acrylate was added dropwise in 15 min. After the addition, the mixture was refluxed for 1 hour, and then poured into an excess of hexane. The monomer that crystallized was filtered off and dried. Yield : 83 percent.

100 g of monomer was dissolved in 200 ml of diisopropyl ether, filtered while hot and poured into an excess of hexane. The crystallized monomer had a melting point of 50°–53°C.

NMR-analysis reveals the presence of a little unreacted hydroxyethyl acrylate and diphenyl urea (formed by traces of water with the phenylisocyanate).

Preparation IV : N-phenyl-methacryloyloxypropylcarbamate of the formula:

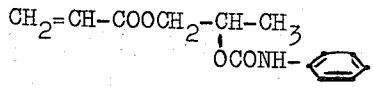


was prepared as follows:

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and dropping funnel were placed: 1 mole of phenyl isocyanate and some crystals of m-dinitrobenzene. The mixture was heated to 80°C whereupon 1 mole of β-hydroxypropyl methacrylate was added dropwise in 10 minutes with stirring. The temperature rose to 100°C whereupon the mixture was heated for 1 h 30 min. at 100°C. A clear light-yellow liquid was obtained. After having left standing overnight in a refrigerator the product crystallized. Melting point : 62°–64°C.

		Calculated	Found
Analysis	N :	5.32	5.36–5.35
	C :	64.00	64.35–63.90
	H :	6.46	6.95–6.85

Preparation V : N-phenyl-acryloyloxy propyl carbamate of the formula:



was prepared as follows:

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and dropping funnel were placed: 1 mole of phenyl isocyanate and some crystals of m-dinitrobenzene. The mixture was heated to 60°C whereupon 1 mole of freshly distilled β-hydroxypropyl acrylate was added so that the temperature did not rise above 70°C. The mixture was then stirred for 30 minutes at 70°C.

The viscous monomer obtained was used as such without any further treatment, for emulsion polymerization as described in preparation F hereinafter.

The polymeric compounds can be prepared by known polymerisation techniques, preferably by emulsion polymerisation as is illustrated by the following preparations.

Preparation A : Poly(N-phenyl-methacryloyloxyethyl carbamate)

In a reaction vessel fitted with stirrer, thermometer, reflux condenser, and dropping funnel 3.4 litres of demineralized water and 50 g of the sodium salt of oleyl methyl tauride were placed. The solution was heated to 65°C whereupon 1000 g of N-phenyl methacryloyl oxyethyl carbamate were added. At 65°C 200 ml of a 5 percent aqueous solution of the sodium salt of 4,4'-azo-bis (4-cyanovaleric acid) were added dropwise with stirring in 20 min. The latex formed was stirred for 4 hours at 60°C and then 30 min. at 90°C. After cooling and filtering, 4250 ml of a latex with pH 6 was obtained. Solids content : 23.4 g/100 ml. The latex has a surface tension of 39.25 dyne/cm and the average particle size determined by turbidimetry was 80 nm.

The intrinsic viscosity of the isolated polymer measured in methylene chloride at 25°C was 0.90 dl/g.

Preparation B : Co(butyl acrylate/N-phenyl-methacryloyloxyethyl carbamate) (50:50)

In a reaction vessel fitted with stirrer, thermometer, reflux condenser, and dropping funnel 400 ml of demineralized water and 5 g of the sodium salt of oleyl methyl tauride were placed. The solution was heated to 60°C whereupon 50 g of butyl acrylate and 50 g of N-phenyl-methacryloyloxyethyl carbamate were added. The emulsion was heated to 80°C and 20 ml of a 5 percent aqueous solution of 4,4'-azo-bis(4-)cyanovaleric acid) were added in 15 min. The mixture was further heated for 1 hour at 90°C whereupon the latex formed was cooled and filtered. 500 ml of latex with a solids content of 19.6 g/100 ml were obtained.

pH:	7
Surface tension:	42.5 dyne/cm
Average particle size:	52 nm
Intrinsic viscosity (25°C/tetrahydrofuran):	0.90 dl/g

Preparation C : Poly(N-butyl-methacryloyloxyethyl carbamate)

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and dropping funnel, 380 ml of demineralized water and 10 g of the sodium salt of oleyl methyl tauride were placed. The solution was heated to 80°C whereupon the monomer was added at once. Then 40 ml of a 2.5 percent aqueous solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) were added with stirring in about 15 min. The temperature rose to about 90°C whereupon, after an additional heating at this temperature for 1 hour the latex formed was cooled to room-temperature and filtered. 490 ml of latex with a solids content of 20.92 g/100 ml were obtained:

pH:	6.85
Surface tension:	34.3 dyne/cm
Average particle size:	54 nm
Instrinsic viscosity (25°C/methylene chloride):	0.52 dl/g

Preparation D : poly(N-phenyl-acryloyloxyethyl carbamate)

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and dropping funnel, 350 ml of demineralized water, 10 g of the sodium salt of oleyl methyl tauride and 100 g of monomer were placed. The mixture was heated to 70°C whereupon 40 ml of a 2.5 percent aqueous solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) were added dropwise with stirring in 20 min. The temperature rose to 80°C and the mixture was stirred at this temperature for 1 hour. After cooling and filtering, 430 ml of latex with a solids content of 21.7 g/100 ml were obtained.
pH : 5.5
Surface tension : 34.5 dyne/cm
Average particle size : 80 nm

Preparation E : poly(N-phenyl-methacryloyloxypropyl carbamate)

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and dropping funnel, 500 ml of demineralized water, 15 g of the sodium salt of oleyl methyl tauride and 150 g of monomer were placed. The mixture was heated to 80°C whereupon 70 ml of a 2.5 percent aqueous solution of the sodium salt of 4,4'-azo-bis (4-cyanovaleric acid) were added dropwise in 15 min. The mixture was then stirred for 1 hour at 90°C whereupon the emulsion was cooled and filtered. 520 ml of latex with a solids content of 22.2 g/100 ml.
pH : 5.1
Surface tension : 34 dyne/cm
Average particle size : 55 nm
Intrinsic viscosity (25°C/methylene chloride) : 0.238 dl/g

Preparation F : poly(N-phenyl-acryloyloxypropyl carbamate)

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and dropping funnel 300 ml of demineralized water, 9 g of the sodium salt of oleyl methyl tauride and 90 g of monomer were placed. The mixture was heated to 80°C whereupon 36 ml of a 2.5 percent solution of the sodium salt of 4,4'-azo-bis(4-cyanovaleric acid) were added dropwise in 15 min. The temperature rose from 80° to 95°C. Stirring was then continued for 30 min. at 80°C. After cooling and filtering 340 ml of latex having a solids content of 223 g/100 ml were obtained
pH : 4.8
Surface tension : 35 dyne/cm
Average particle size : 67 nm
Intrinsic viscosity (25°C/methylene chloride): 0.356 dl/g.

The polymeric compounds for use according to the present invention may be incorporated into the silver halide emulsion or another layer of the photographic material which is in water-permeable relationship with the said emulsion layer. They are preferably used in a gelatin protective antistress layer coated on top of the emulsion layer.

The polymeric compounds of use according to the present invention may be used in any type of light-sensitive material. Various silver salts may be used as light-sensitive salt e.g., silver bromide, silver iodide, silver chloride, or mixed silver halides, e.g., silver chlorobromide or silver bromoiodide. The invention is of particular importance for mechanical processing at elevated temperature i.e., above 30°C of silver bromoiodide emulsions.

The silver halide emulsions for being processed after exposure at elevated temperature in an automatic processing machine generally are silver halide emulsions having a very low content of hydrophilic colloid e.g., gelatin. The ratio of hydrophilic colloid, more particularly gelatin, to silver halide expressed as silver nitrate is preferably comprised between 0.2 and 0.6.

The emulsion may be a negative emulsion or a direct-positive emulsion which comprises fogged silver halide. In direct-positive emulsions fogging may be effected by known means e.g., by light and preferably, by chemical sensitization to fog e.g., by means of reducing agents such as hydroxylamine, hydrazine, formaldehyde, tin-(II)chloride, thiourea dioxide, etc., and/or by means of noble metal compounds such as gold compounds. In addition thereto fogging may also occur by increasing the pH of the emulsion by means of alkaline substances such as sodium or potassium hydroxide.

The silver halides are dispersed in the common hydrophilic colloids such as gelatin, casein, zein, polyvinyl alcohol, carboxymethylcellulose, alginic acid, etc., gelatin being however favoured.

The amount of polymeric compound employed in the light-sensitive halide emulsion layer or in the colloid layer in water-permeable relationship therewith depends on the particular compound, the particular type of emulsion and the desired effect and can vary within very wide limits. The optimum amount of each individual polymeric compound to be added is best determined for each particular type of emulsion by trial. Generally, the most suitable concentration in the particular colloid layer involved is comprised between 5 and 50 percent by weight relative to the weight of the hydrophilic colloid. The polymeric compounds can be added in the form of loose powder but they are preferably added from an aqueous solution or dispersion (i.e., a latex) e.g., prepared as described above by emulsion polymerisation. In the form of a latex the polymeric compounds are easily incorporated in the hydrophilic

colloid coating compositions and fully compatible with the hydrophilic colloid, more particularly gelatin.

The silver halide emulsions of the radiation-sensitive elements comprising the polymeric compounds in accordance with the present invention may be chemically as well as spectrally sensitized. They may be chemically sensitized by any of the accepted procedures. The emulsions may be digested with naturally active gelatin or sulphur compounds may be added such as allyl thiocyanate, allyl thiourea, sodium thiosulphate, etc. The emulsions may also be sensitized by means of reductors for instance tin compounds as described in our United Kingdom Pat. Specification No. 789,823 and by means of small amounts of noble metal compounds e.g., of gold, platinum, palladium, iridium, ruthenium and rhodium as described by R. Koslowsky, Z.wiss.Phot. 46, 67–72 (1951). Representative noble metal compounds are ammonium chloro palladate, potassium chloroplatinate, potassium chloroaurate and potassium aurithiocyanate. These chemical sensitizers can be added separately or together during no matter what step of emulsion preparation e.g., before, during or after the chemical ripening.

The emulsions may further comprise compounds that sensitize the emulsion by development acceleration for example alkylene oxide polymers. These alkylene oxide polymers may be of various type e.g., polyethylene glycol having a molecular weight of 1500 or more, alkylene oxide condensation products or polymers as described among others in U.S. Pat. Nos. 1,970,578, 2,240,472, 2,423,549, 2,441,389, 2,531,832 and 2,533,990, in United Kingdom Pat. Specification Nos. 920,637, 940,051, 945,340 and 991,608 and in Belgian Pat. Specification No. 648,710. Other compounds that sensitize the emulsion by development acceleration and that are suitable for use in combination with the polymeric compounds of use according to the invention are the quaternary ammonium and phosphonium compounds and ternary sulphonium compounds as well as onium derivatives of amino-N-oxides as described in United Kingdom Pat. Specification No. 1,121,696.

The emulsions may be spectrally sensitized e.g. by means of the common methine dyes such as neutrocyanines, basic or acid carboxyanines, rhodacyanines, hemicyanines, styryl dyes, oxonol dyes and the like. Such like spectrally sensitizing dyes have been described by F. M. Hamer in "The cyanine dyes and related compounds" (1964). Direct-positive emulsions may comprise desensitizing dyes e.g., as described in United Kingdom Pat. Specification No. 1,155,404.

The emulsions may comprise the common emulsion stabilizers e.g., homopolar or salt-like compounds of mercury with aromatic and heterocyclic rings (e.g., mercaptotriazoles) simple mercury compounds, mercury sulphonium double salts and other mercury compounds of the kind described in Belgian Pat. Specification Nos. 524,121, 677,337, 707,386 and 709,195. Other suitable emulsion stabilizers are the azaindenes, particularly the tetra- or pentaazaindenes and especially those substituted by hydroxy- or amino groups. Suchlike compounds have been described by Birr in Z.wiss.Phot. 47, 2–58 (1952). The emulsions may further comprise as stabilizers heterocyclic nitrogen-containing mercapto compounds such as benzothiazoline-2-thione and 1-phenyl-5-mercapto-tetrazole, sulphinic acids such as benzene sulphinic acid and toluene sulphinic acid, thiosulphonic acids such as benzene thiosulphonic acid, toluene thiosulphonic acid, p-chlorobenzene thiosulphonic acid sodium salt, propyl thiosulphonic acid potassium salt, butyl thiosulphonic acid potassium salt, etc. They may further comprise or be developed in the presence of compounds that are particularly effective as antifoggants for materials that are processed at elevated temperatures e.g., heterocyclic compounds with nitro-substituents e.g., nitroindazole and nitrobenztriazole as described in French Pat. Specification No. 2,008,245, nitrobenzylidene pyridinium and nitrobenzylidene quinolinium compounds as well as the onium compounds described in published German Pat. Application No. 2040876; further the nitrobenzene compounds described in co-pending Application 43,517/71 and the nitrile compounds described in copending Application 43,518/71.

The photographic silver halide materials may further comprise surface active compounds, e.g., the fluorinated surfactants of United Kingdom Pat. No. 1,293,189, plasticizers, matting agents, e.g., polymethyl methacrylate and silica particles, colour couplers, hardening agents e.g., formaldehyde, dialdehydes, halogen substituted aldehyde acids such as mucochloric and mucobromic acid, etc.

As is known, in the automatic processing at elevated temperatures of radiation-sensitive silver halide elements it is preferred to use a hardening developer. In these developers the hardening agent is generally an aldehyde hardener particularly aliphatic dialdehydes e.g. maleic aldehyde and glutaraldehyde which may be used as such or in the form of their bisulphite addition products.

The following example illustrates the present invention.

EXAMPLE

A silver bromoiodide X-ray emulsion (2 mole percent iodide) comprising per kg an amount of silver halide equivalent to 190 g of silver nitrate, 74 g of gelatin, 545 mg of 5-methyl-7-hydroxy-s-triazole[1,5-a]pyrimidine, 6.5 mg of 1-phenyl-5-mercaptotetrazole and 0.45 mg of mercury cyanide was divided into three aliquot portions A, B and C.

The three emulsion portions were coated under identical circumstances on both sides of a polyethylene terephthalate support and then overcoated with a gelatin antistress layer comprising formaldehyde as hardening agent. To the coating solutions of the gelatin protective layers for emulsions B and C, the latices of preparations A and B respectively were added in an amount of 25 percent by weight of dry polymer relative to the amount of dry gelatin.

The materials were exposed through a continuous wedge with constant 0.15 and then automatically processed in a 90 seconds processing machine. Development occurred for 23 seconds at 35°C in Agfa-Gevaert's hardening developer for automatic processing G 138 which comprises hydroquinone and 1-phenyl-3-pyrazolidinone as developing agents and glutaraldehyde as hardener.

The sensitometric results obtained are listed in the table below.

The values given for the speed are relative values with respect to reference material A, the speed of which has been given a value of 100.

The table also includes values for the abrasion resistance (A.R.). These values are the pressures (in gram)

necessary to be applied to a steel ball having a diameter of ¼ inch to make it penetrate completely through the wet hydrophilic colloid layers (on both sides of the support) on which the ball is placed, when the ball is drawn over the material.

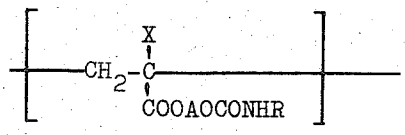
The value given for the sludge is the amount of sludge formed per sq.m of developed double-coated film material.

Material	Fog	Gradation	Relative Speed	A.R. side 1	A.R. side 2	g sludge sq. M
A	0.05	2.99	100	450	450	0.22
B	0.05	2.96	101	700	800	0.12
C	0.05	2.85	100	800	900	0.19

Whereas the automatically processed material A was of unsatisfactory quality due to the pressure marks, materials B and C showed practically no pressure marks.

We claim:

1. Photographic silver halide material to be further processed comprising a support and at least one silver halide emulsion layer wherein the said emulsion layer or a hydrophilic colloid layer in water-permeable relationship with the said emulsion layer comprises a polymeric compound comprising recurring units of the formula:



wherein:
X is hydrogen or methyl,
A is a straight-chain or branched-chain C_1–C_5 alkylene group, and
R is an alkyl or aryl group.

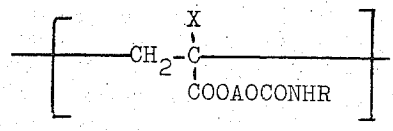
2. Photographic silver halide material according to claim **1** wherein the ratio of hydrophilic colloid binder to silver halide in the said emulsion layer is comprised between 0.2 and 0.6.

3. Photographic silver halide material according to claim **1**, wherein the polymer is present in a protective gelatin antistress layer.

4. Photographic material according to claim **1**, wherein the said polymeric compound is present in the said layer in an amount of 5 to 50 percent by weight relative to the weight of the hydrophilic colloid.

5. Photographic material according to claim **1** wherein the emulsion is a silver bromoiodide emulsion.

6. Method of producing photographic images by processing of an exposed photographic silver halide material comprising at least one silver halide emulsion layer wherein the said emulsion layer or a hydrophilic colloid layer in water-permeable relationship therewith comprises a polymeric compound having recurring units of the formula:



wherein:
X is hydrogen or methyl,
A is a straight-chain or branched-chain C_1–C_5 alkylene group, and
R is an alkyl or aryl group.

7. Method according to claim **6**, wherein processing occurs at a temperature above 30°C.

8. Method according to claim **6**, wherein the said polymeric compound is present in the said layer in an amount of 5 to 50 percent by weight relative to the weight of dry hydrophilic colloid.

9. Method according to claim **6**, wherein in the said emulsion layer the ratio of hydrophilic colloid to silver halide is comprised between 0.2 and 0.6.

10. Method according to claim **6**, wherein the emulsion is a silver bromoiodide emulsion.

11. Method according to claim **6**, wherein the polymer is present in a protective gelatin antistress layer.

12. Method according to claim **6**, wherein processing occurs by means of a hardening developer.

13. Method according to claim **12**, wherein the developer comprises glutaraldehyde.

* * * * *