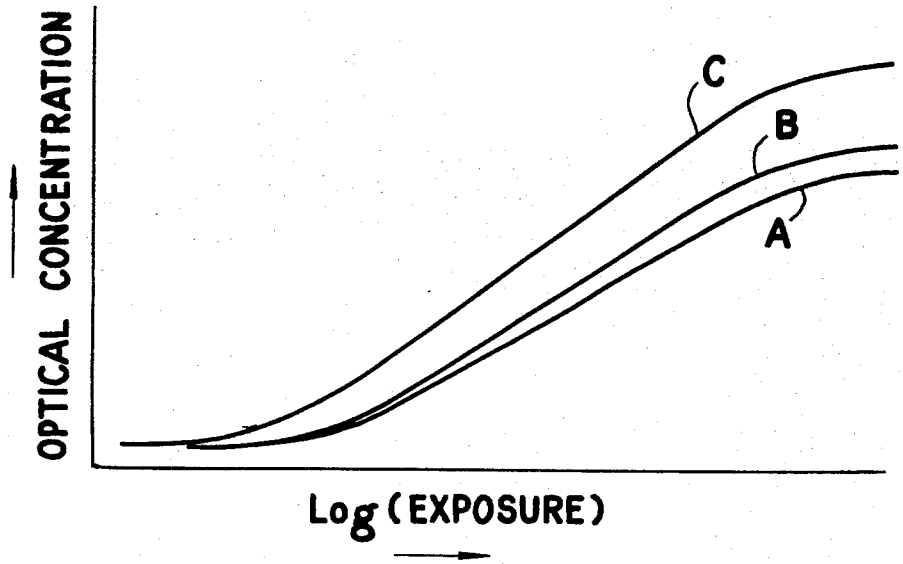
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PHOTOGRAPHIC SENSITIVE MATERIALS CONTAINING MORPHOLINO ALKYLALKENOYLAMIDE POLYMERS

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PHOTOGRAPHIC SENSITIVE MATERIALS CONTAINING MORPHOLINO ALKYLALKENOYLAMIDE POLYMERS

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U.S. Cl. 96—85 10 Claims
Int. Cl. G03c 1/86, 1/04

The present invention relates to a gelatino silver halide photographic sensitive material containing a morpholino alkylalkenoylamide polymer and/or a copolymer containing a morpholino alkylalkenoylamide.

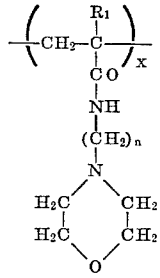
It has hitherto been known that in the production of light-sensitive silver halide photographic emulsions, by adding into the photographic emulsion a natural or synthetic high molecular compound other than gelatin, such as, poly-N-vinyl lactams, dextrin, laminarin, manan, hydroxy ethylated celluloses, and the like, the covering power of said emulsion, that is, a value of the optical density divided by the gram number of developed silver per one square decimeter is increased and hence the contrast and the maximum density can be increased. (Cf.: U.S. Patent 3,058,826; French Patent 1,261,846; Belgian Patent 611,622; Belgian Patent 611,623; and U.S. Patent 3,003,878.)

However, as clear from the curves shown in the accompanying drawing, the sensitivity near the lower end of curve (B) showing the characteristic curve of a photographic emulsion containing the above-mentioned high molecular compound is substantially same as that of curve (A) showing the characteristic curve of a photographic emulsion containing no such a high molecular compound.

Therefore, an object of this invention is to provide a photographic silver halide emulsion having improved sensitivity, maximum density, and contrast.

The inventors have found that by incorporating a polymer of morpholino alkylalkenoylamide and/or a copolymer containing morpholino alkylalkenoylamide in a photographic gelatino silver halide emulsion that has been sensitized into the most suitable sensitivity with a usual chemical sensitizer, such as, unstable sulfur compounds, reducing agents, and gold compounds, the sensitivity of the emulsion is further increased. Moreover, as shown in curve (C) in the accompanying drawing it has been confirmed that in this case, not only the covering power, contrast, and maximum density but also the sensitivity at the lower end portion of the characteristic curve is largely increased, and hence this is a very profitable sensitizing process in practice.

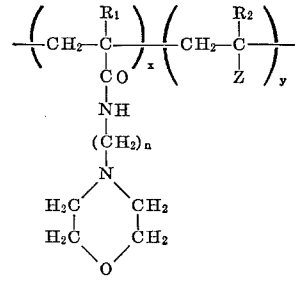
The morpholino alkylalkenoylamide copolymer is shown by the following general formula



(I)

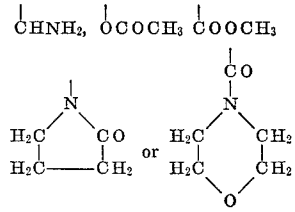
wherein R_1 represents H or CH_3; X represents a positive integer; and n is 1, 2, or 3, and the copolymer containing

morpholino alkylalkenoylamide is shown by the following general formula



(II)

wherein R_1 and R_2 each represents H or CH_3, x and y are positive integres, n is 1, 2, or 3, and Z represents



For producing such polymers or copolymers, for example, poly-N1morpholino methylacrylamide may be produced by polymerizing N-morpholino methylacrylamide obtained by the reaction of acrylamide, Formalin, and morpholine. Further, the copolymer of morpholino methylacrylamide may be obtained by polymerizing a mixture of N-morpholino methylacrylamide and vinyl acetate, methyl acrylate, acrylamide, vinyl pyrrolidone, or acryloylmorpholine. In this case, however, it is desirable that more than 30 mole percent of N-morpholino methylacrylamide is present in the copolymer. Since the compatibility of the polymer or copolymer with gelatin is lowered if the polymerization degree is too high, it is desirable that the intrinsic viscosity of the polymer or the copolymer in N,N-dimethylformamide is $[\eta] \leq 2.0$ (35° C.).

The amount of the polymer or the copolymer to be incorporated in an emulsion in this invention may be selected desirably but the most suitable amount of it for increasing the sensitivity, gamma, and maximum density is influenced by the type of photographic silver halide emulsion and purposes. In general, it is suitable that the amount of the polymer of morpholino alkylalkenoylamide and/or the copolymer containing morpholino alkylalkenoylamide is 3–40% by weight, in particular, 6–20% by weight of the whole mediums in the photographic gelatino silved halide emulsion. Furthermore, in the present invention, instead of adding directly into the photographic gelatino silver halide emulsion layer, the polymer of morpholino alkylalkenoylamide and/or the copolymer of morpholino alkylalkenoylamide may be incorporated in a layer adjacent the photographic silver halide emulsion layer in an amount of 10–40% by weight.

The polymer or the copolymer may be added in any step in the emulsion but it is suitable to add after the secondary ripening and before applying the emulsion on a support. The polymer or the copolymer may be added as powders but it profitably added as a 10–20% aqueous solution of it. At that, since a hydrolysis is liable to occur if the pH of the aqueous solution is higher than 7, it is preferable to adjust the pH to 4–6.

The present invention can be applied to any types of silver halide emulsions, e.g., to a silver-iodide-bromide emulsion and to a silver-chloride-bromide emulsion. The photographic silver halide emulsion used in this invention may be one that has been subjected to a sulfur sensitiza-

tion and/or a gold sensitization and may contain a light sensitizer, a polyalkyleneoxide sensitizer, various stabilizers, a hardening agent, coating aids, and couplers.

As a support or base for the photographic material of this invention, usual supports for photographic emulsions may be used, such as, a glass plate, a triacetylcellulose film base, a polyethylene terephthalate film base, polycarbonate film base, polystyrene film base, polypropylene film base, a baryta paper, and the like.

The invention will be explained more in detail referring to the following examples for synthesizing the polymer or the copolymer of morpholino alkylalkenoylamide and preferred examples of this invention but it should be understood that the invention is not limited to them.

Synthesis 1

An aqueous solution of 71 g. of acrylamide in 200 ml. of water was added with 1 g. of hydroquinone and then 120 ml. of 30% Formalin. While stirring the solution, 87 g. of morpholine was slowly added dropwise into the solution and after finishing the addition and then increasing the temperature of the system to 70° C., stirring was further continued for 3 hours to finish the reaction. The product was filtered and, after distilling off water from the product under a reduced pressure, distilled in vacuo to give N-morpholino methylacrylamide (B.P. 136–138° C./0.6 mm. Hg). The melting point of the product after recrystallizing from benzene was 92–93° C.

Elementary analysis as $C_8H_{14}O_2N_2$. Calculated: C, 56.45%; H, 8.29%; and N, 16.46%. Found: C, 56.57%; H, 8.04%; and N, 16.62%.

Synthesis 2

Into 400 ml. of a 20% aqueous isopropyl alcohol solution was dissolved 100 g. of the N-morpholino methylacrylamide in Synthesis 1, and the solution was added with 0.5 g. L-ascorbic acid and 0.6 ml. of a 30% aqueous hydrogen peroxide solution and maintained for 5 hours at 40° C. in a nitrogen stream. The product was dialyzed for 1 day using a cellophane diaphragm and dried by freezing to give 80 g. of a water-soluble polymer of N-morpholino methylacrylamide having the intrinsic viscosity of 0.2

Synthesis 3

In 600 ml. of absolute ethyl alcohol were mixed 129 g. of ethyleneimine, 500 g. of morpholine, and 3 g. of concentrated sulfuric acid and the mixture was refluxed for 12 hours. After distilling off ethyl alcohol and excess morpholine under reduced pressure, the system was subjected to a vacuum distillation to give 200 g. of morpholino ethylamine at a boiling point of 69–73° C./5 mm. Hg.

Into 500 ml. of toluene was added 90.5 g. of acryloylchloride and a mixture of 130 g. of the morpholino ethylamine obtained in the above procedure and 101 g. of triethylamine was added dropwise into thus prepared solution while stirring under ice-cooling. After filtering off thus precipitated triethylamine hydrochloride, the product was added with a small amount of hydroquinone to distil off the toluene and then subjected to a vacuum distillation to give the crystal of N-morpholino ethylacrylamide having the melting point of 160° C. at a boiling point of 131–140° C./0.06 mm. Hg.

Elementary analysis as $C_9H_{16}N_2O_2$. Calculated: N, 15.22%. Found: N, 15.25%.

Synthesis 4

Into 76 ml. of dimethyl formamide was dissolved 24 g. of the N-morpholino ethylacrylamide in Synthesis 3, the solution was then added with 0.05 g. of azobisiobutyronitrile and stirred for 4 hours at 70° C. in a nitrogen stream. Dimethylformamide was concentrated and the product was dissolved in water, dialyzed, and dried by freezing to give 11 g. of poly-N-morpholino ethylacrylamide.

Synthesis 5

While stirring under cooling by a cooling medium, a mixture of 91 g. (1 mol) of acryloyl chloride and 300 ml. of toluene was added dropwise a mixture of 144 g. (1 mol) of N-aminopropylmorpholine and 101 g. (1 mol) of triethylamine at temperatures lower than 10° C. After stirring the system for 3 hours at room temperature, thus formed triethylamine hydrochloride was filtered, and the product was dried by granular sodium hydroxide and, after distilling off the toluene, subjected to a vacuum distillation in a nitrogen stream with the addition of a small amount of hydroquinone to give 73 g. of N-morpholino propylacrylamide (B.P. 149–152° C./0.05 mm. Hg) (yield 37%).

Elementary analysis as $C_{10}H_{18}N_2O_2$. Calculated: N, 14.13%. Found N, 14.08%.

Synthesis 6

A solution of 30 g. of morpholino propylacrylamide in 100 ml. of dimethylformamide was added with 0.03 g. of azobisisobutyronitrile and the system was polymerized for 8 hours at 70° C. in a nitrogen stream. After the polymerization, the greater part of dimethylformamide was removed by a reduced-pressure distillation and then the product was dissolved into water and dialized using a cellophane diaphragm. By drying thus obtained product by freezing, 20 g. of polymorpholino propylacrylamide was obtained. The intrinsic viscosity of the product in dimethylformamide at 35° C. was 0.125.

Synthesis 7

A solution of 85 g. of methylacrylamide in 200 ml. of water was added with 1 g. of hydroquinone and 120 ml. of 30% Formalin. Into the solution was added dropwise 87 g. of morpholine with stirring while increasing the temperature of the system to 50–60° C. Thereafter, the system was stirred for another 3 hours at 70° C. to finish the reaction. The product was filtered and, after distilling off water under reduced pressure, was subjected to a vacuum distillation to give N-morpholino methylmethacrylamide (B.P. 134–138° C./0.5 mm. Hg). After recrystallizing from benzene, the melting point of the product was 82–84° C.

Elementary analysis as $C_9H_{16}O_2N_2$. Calculated: C, 58.67%; H, 8.75%; N,15.21%. Found: C, 59.35%; H, 8.72%; N, 15.19%.

Synthesis 8

Into 70 ml. of water was dissolved 30 g. of the N-morpholino methylmethacrylamide obtained in Example 7, and the solution was stirred for 4 hours in a nitrogen stream at 70° C. with the addition of 0.09 g. of potassium peroxide. The product was dialized and dried by freezing to give 11 g. of a water-solution polymer having the intrinsic viscosity of 0.47.

Synthesis 9

Into 300 ml. of 30% isopropyl alcohol were dissolved 71 g. of N-morpholino methylacrylamide and 29 g. of acrylamide and the system was stirred for 4 hours at 40° C. in a nitrogen stream while adding 0.5 g. of L-ascorbic acid and 6 ml. of an aqueous 30% hydrogen peroxide solution. The solution was dialized for 1 day using a cellophane diaphragm and dried by freezing to give 65 g. of water-soluble polymer having the intrinsic viscosity of 0.2.

Synthesis 10

Into 300 ml. of an aqueous 30% isopropyl alcohol solution were dissolved 90 g. of N-morpholino methylacrylamide and 10 g. of acrylamide and the solution was stirred for 4 hours at 40° C. in a nitrogen stream while adding 0.5 g. of L-ascorbic acid and 6 ml. of an aqueous 30% hydrogen peroxide solution. The solution was

dialized for 1 day using a cellophane diaphragm and dried by freezing to give 76 g. of a water-soluble polymer having the intrinsic viscosity of 0.26.

Synthesis 11

Into 300 ml. of an aqueous 30% isopropyl alcohol solution were dissolved 51 g. of N-morpholino methylacrylamide and 49 g. of acrylamide and the solution was stirred for 4 hours at 40° C. in a nitrogen stream while adding 0.5 g. of L-ascorbic acid and 6 ml. of an aqueous 30% hydrogen peroxide solution. The solution was dialized for 1 day using a cellophane diaphragm and dried by freezing to give 57 g. of a water-soluble polymer having the intrinsic viscosity of 0.5.

Synthesis 12

Into 300 ml. of water were dissolved 85 g. of N-morpholino methylacrylamide and 56 g. of vinylpyrrolidone and the solution was stirred for 4 hours at 40° C. in a nitrogen stream while adding 0.75 g. of L-ascorbic acid and 3 ml. of an aqueous 30% hydrogen peroxide solution. The solution was then dialized for 1 day using a cellophane diaphragm and dried by freezing to give 118 g. of a water-soluble polymer having the intrinsic viscosity of 0.65.

Synthesis 13

Into 300 ml. of an aqueous 25% isopropyl alcohol solution were dissolved 54 g. of N-morpholino methylacrylamide and 54 g. of acryloylmorpholine and the solution was stirred for 6 hours at 40° C. in a nitrogen stream while adding 1.5 g. of L-ascorbic acid and 5.3 ml. of an aqueous 30% hydrogen peroxide solution. Thus obtained product was dialized for 1 day using a cellophane diaphragm and dried by freezing to give 60 g. of water-soluble polymer having the intrinsic viscosity of 0.1.

EXAMPLE 1

A photographic gelatino silver halide emulsion for high-sensitive negative photographic materials containing 1.8 mol of silver halides consisting of 5.0 mol of silver iodide and 95.0 mol of silver bromide 250 g. of gelatin, that has been ripened with a sulfur sensitizer and a gold sensitizer into the most suitable sensitivity was divided into three equal parts, and each part of them was added with 10 g. of each of the following materials.

(a) inactive gelatin,
(b) polyvinylpyrrolidone, molecular weight 40,000 and
(c) poly-N-morpholino methylacrylamide $[\eta]=0.25$.

Then each emulsion was added with a sensitizing dye, a stabilizer, a coating aid, and a hardening agent in equal proportion and then coated on a triacetylcellulose film base in a same film thickness, followed by drying. The coated film was exposed at 1/20 of second in a sensitometer of 5400° K. in intensity scale and developed for 150 minutes at 20° C. in a developing solution of the composition:

	Grams
1-phenyl-3-pyrazolidone	0.2
Sodium sulfite (anhydrous)	100
Hydroquinone	7
Borax	10
Boric acid	3
Potassium bromide	1
Water to 1 liter.	

The photographic densities of thus developed photographic films were measured, the results of which are shown in the following table.

TABLE 1

	Relative sensitivity giving density of 0.1 on fog	Relative sensitivity giving density of 0.5 on fog	Gamma	Fog
(a)	100	100	1.17	0.10
(b)	97	105	1.26	0.10
(c)	131	151	1.34	0.10

As shown in the above table, the gamma and the sensitivity of the photographic emulsion were increased by the addition of poly-N-morpholino methylacrylamide. Furthermore, while the addition of polyvinylpyrrolidone does not increase the intensity at the lower end portion of the characteristic curve, the sensitivity of that portion can be increased by the addition of poly-N-morpholino methylacrylamide.

EXAMPLE 2

A photographic gelatino silver halide emulsion for high-sensitive negative photographic materials containing 3.0 mol of silver halides consisting of 5.0 mol percent of silver iodide and 95.0 mol percent of silver bromide and 1050 g. of gelatin and had been ripened into the most suitable sensitivity with a sulfur sensitizer and a gold sensitizer was divided into 10 equal parts. Each part of them was added with 50 ml. of an aqueous 10% solution of each of the following materials:

(d) inactive gelatin,
(e) poly-N-morpholino methylacrylamide $[\eta]=0.12$,
(f) poly-N-morpholino methylmethacrylamide,
(g) copolymer of N-morpholino methylacrylamide (70 mol percent and acrylamide (30 mol percent),
(h) copolymer of N-morpholino methylacrylamide (50 mol percent) and acrylamide (50 mol percent),
(i) copolymer of N-morpholino methylacrylamide (30 mol percent) and acrylamide (70 mol percent),
(j) copolymer of N-morpholino methylacrylamide (50 mol percent) and vinyl acetate (50 mol percent),
(k) copolymer of N-morpholino methylacrylamide (50 mol percent) and methylacrylate (50 mol percent),
(l) copolymer of N-morpholino methylacrylamide (50 mol percent) and vinylpyrrolidone (50 mol percent), and
(m) copolymer of N-morpholino methylacrylamide (50 mol percent) and acryloylmorpholin (50 mol percent).

Each emulsion was endowed with panchromatic property by adding a sensitizing dye and then added with 20 ml. of an aqueous 1% solution of 4-hydroxy-6-methyl-1,3,3*a*,7-tetra-azaindene as a stabilizer, 1.5 ml. of an aqueous 10% solution of chrome alum as a hardening agent, and 1.5 ml. of an aqueous 4% solution of saponin as a coating aid. The emulsion was coated on a triacetylcellulose film base in a same thickness and dried. Thus obtained photographic sensitive film was exposed at 1/20 of second in a sensitometer of 5400° K. in intensity scale and developed for 7 minutes at 20° C. in the solution of the following composition:

	Grams
N-methyl-P-aminophenol sulfate	2
Sodium sulfite (anhydrous)	100
Hydroquinone	5
Borax	2
Water to 1 liter.	

The results of measuring the photographic densities of these developed films are shown in the following table.

TABLE 2

	Relative sensitivity giving density of 0.1 on fog	Relative sensitivity giving density of 0.5 on fog	Gamma	Fog
(d)	100	100	0.81	0.06
(e)	104	120	1.05	0.06
(f)	115	129	1.00	0.07
(g)	120	129	1.06	0.07
(h)	123	148	1.14	0.07
(i)	135	155	1.08	0.07
(j)	120	141	1.12	0.06
(k)	112	123	0.98	0.06
(l)	110	127	1.02	0.07
(m)	112	126	1.01	0.06

EXAMPLE 3

A gelatino silver-iodide-bromide emulsion for high sensitive X-ray films that had been chemically ripened into the most suitable sensitivity was added with each of the following compounds in an amount of 5 g. per 0.6 mol of the silver halide in the emulsion;

(n) inactive gelatin
(o) poly-N-morpholino ethylacrylamide
(p) poly-N-morpholino propylacrylamide.

After adding a stabilizer, hardening agent and coating aid, the emulsion was coated upon a subbed polyethylene terephthalate film base in a same thickness each and then dried.

Thus obtained photographic sensitive film was exposed at 1/20 of second in a sensitometer of intensity scale having a blue filter and developed in a metolhydroquinone developing solution of a high pH. As the results of measuring the photographic densities, it was confirmed that the sensitivity of the photographic sensitive film added with polymer (o) or polymer (p) was higher than that of the sensitive film added with additive (n).

EXAMPLE 4

A solution of 26 g. of potassium chloride, 7 g. of potassium bromide, and 8 g. of gelatin in 230 ml. of water was maintained at 55° C. Into the above solution was added an aqueous solution of 50 g. of silver nitrate in 920 ml. of water with stirring at 55° C. Then, after adding 100 g. of gelatin, the system was further stirred for 15 minutes, solidified by cooling with ice, divided into fine parts, and rinsed with water until the conductivity of the emulsion became 1,500 micro mho/cm.

The emulsion was dissolved again while heating, and, after adding 24 g. of sensitizing gelatin and 80 g. of inactive gelatin, heated to 55° C. for 100 minutes. Into thus obtained emulsion was dissolved 20 g. of poly-N-morpholino methyl acrylamide, and the solution was added with 40 ml. of a 0.05% methyl alcohol solution of 3 - aryl - 3' - ethyl - 5 - (2 - (1 - ethyl - 4 - quinolinidene) ethylidene) - 5', 6' - dimethyl - 4 - oxothiazolinooxycyanine iodide and 300 ml. of a 5% aqueous alkaline solution of N-n-octadecyl-1-hydroxy-4-sulfo-2-naphthamide. The mixture was coated on a subbed triacetylcellulose film base in a thickness of about 5 microns.

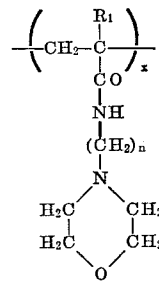
As the results of measuring by means of a sensitometer, the cyan coupling color photographic emulsion layer showed a high coupling density by a same exposure as compared with an emulsion layer prepared by using the same materials and by the same procedures but using an equivalent amount of inactive gelatin instead of the poly-N-morpholino methylacrylamide.

EXAMPLE 5

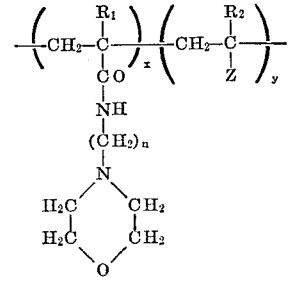
The photographic emulsion in Example 1 was coated in a thickness of about 10 microns upon a triacetylcellulose film base and the film was divided into two parts. One of them was further coated with an aqueous solution (I) of 13 g. of gelatin and 8 g. of poly-N-morpholino methylacrylamide in 1 liter of water in a thickness of about 2 microns and another film was coated with an aqueous solution (II) of 25 g. of gelatin in 1 liter of water in a thickness of about 2 microns, and they were dried. As the results of conducting the exposure and development as in Example 1, the case of coating solution (I) showed the higher maximum density than the case of coating solution (II).

What we claim is:

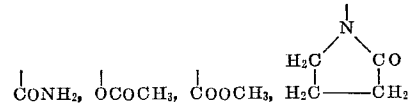
1. A photographic sensitive material comprising a support and a silver halide photographic emulsion layer, said emulsion layer containing at least one additive selected from the group consisting of a polymer shown by the general formula



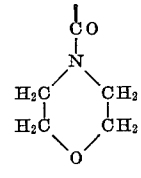
wherein R_1 represents a member selected from the group consisting of H and CH_3; x is a positive integer; and n is 1, 2, or 3 and a copolymer shown by the general formula



wherein R_1 and R_2 each represents a member selected from the group consisting of H and CH_3; x and y are positive integers; n is 1, 2, or 3; and Z represents a member selected from the group consisting of



and



2. The photographic sensitive material according to claim **1** whertin said polymer is selected from poly-N-morpholino methylacrylamide and poly-N-morpholino methylmethacrylamide.

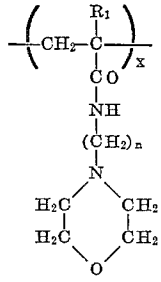
3. The photographic sensitive material according to claim **1** wherein said copolymer is selected from N-morpholino methylacrylamide-acrylamide copolymer, N-morpholino methylacrylamide-vinyl acetate copolymer, N-morpholino methylacrylamide-methylacrylate copolymer, N - morpholino methylacrylamide - vinylpyrrolidone copolymer, and N-morpholino methylacrylamide-acryloyl morpholinecopolymer.

4. The photographic sensitive material according to claim **1** wherein said emulsion layer contains said additive in an amount of 3–40% by weight, based on the whole mediums in said emulsion.

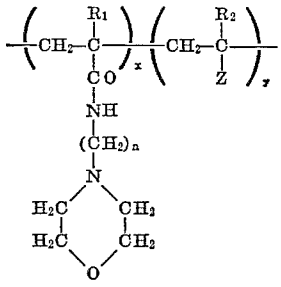
5. The photographic sensitive material according to claim **1** wherein said additive is incorporated in said emulsion layer by adding it after the secondary ripening and before coating on the support.

6. The photographic sensitive material according to claim **5** wherein said additive is added as a 10–20% aqueous solution having a pH of 4 to 6.

7. A photographic sensitive material comprising a support, a silver halide phitographic emulsion layer, and a subsidiary layer adjacent the emulsion layer, at least one of said layers containing at least one additive selected from the group consisting of a polymer shown by the general formula

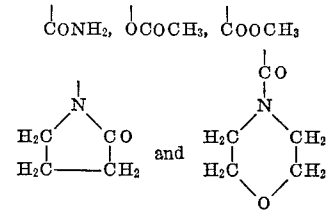


wherein R_1 represents a member selected from the group consisting of H and CH_3; x is a positive integer; and n is 1, 2, or 3 and a copolymer shown by the general formula



wherein R_1 and R_2 each represents a member selected from the group consisting of H and CH_3; x and y are

positive integers; n is 1, 2, or 3; and Z represents a member selected from the group consisting of



8. The photographic sensitive material according to claim 7 wherein said polymer is selected from poly-N-morpholino methylacrylamide and poly-N-morpholino methylmethacrylamide.

9. The photographic sensitive material according to claim 7 wherein said copolymer is selected from N-morpholino methylacrylamide-acrylamide copolymer, N-morpholino methylacrylamide-vinyl acetate copolymer, N-morpholino methylacrylamide - methylacrylate copolymer, N-morpholino methylacrylamide-vinylpyrrolidone copolymer, and N-morpholino methylacrylamide-acryloyl morpholine copolymer.

10. The photographic sensitive material according to claim 4 wherein said emulsion layer contains said additive an an amount of 6–20% by weight based on the whole mediums in said emulsion.

References Cited

UNITED STATES PATENTS

3,178,269	4/1965	Minsk et al.	96—114
3,271,158	9/1966	Allentoff et al.	96—114
3,341,332	9/1967	Nakajima et al.	96—107

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96—87, 114