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3,713,834

POLYMERIC BINDERS FOR PHOTOGRAPHIC EMULSIONS

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24 Claims

ABSTRACT OF THE DISCLOSURE

A photosensitive silver halide emulsion wherein the emulsion binder comprises an amine-diamide polymer or copolymer.

BACKGROUND OF THE INVENTION

This invention relates to photography and more particularly, to novel photosensitive photographic elements, particularly novel photosensitive emulsions.

As a result of the known disadvantages of gelatin, in particular, its variable photographic properties and its fixed physical properties, for example, its diffusion characteristics; much effort has been expended in the past in order to replace gelatin with a suitable synthetic colloid binder for photographic silver halide emulsions. Many synthetic polymeric materials have heretofore been suggested as peptizers for silver halide emulsions, however, these have generally not functioned satisfactorily and frequently have not fulfilled all of the basic requirements for a photosensitive silver halide emulsion binder listed following:

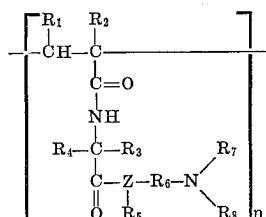
- (1) Absent (or constant) photographic activity;
- (2) Ability to form an adsorption layer on microcrystals of silver halide permitting stable suspensions to be obtained;
- (3) Ability to form adsorption layers as described in (2) above which do not prevent growth of silver halide microcrystals during physical ripening; and
- (4) Solubility in water solution.

In addition, hithertofore, much emphasis has been placed on the ability of the synthetic polymeric material to mix with gelatin, as this property has been critical for employment in partial substitution reactions with gelatin. Consequently, many synthetic polymers of the prior art have been materials which allow for the growth of silver halide crystals only in the presence of gelatin.

A class of synthetic polymers have now been found which is not susceptible to the deficiencies of the prior art and which may replace gelatin entirely in photosensitive silver halide emulsions.

SUMMARY OF THE INVENTION

The present invention is directed to a photosensitive silver halide emulsion wherein the silver halide crystals are disposed in a synthetic polymeric binder comprising a polymer having in its structure repeating units represented by the formula:



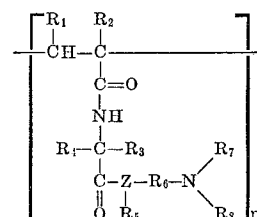
wherein R_1 , R_3 and R_4 each is hydrogen, lower alkyl group, e.g., 1-4 carbon alkyl group, preferably methyl or ethyl, or halogen, e.g., chloro, bromo or iodo; R_2 is hydrogen, lower alkyl, halogen or cyano; Z is oxygen or

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nitrogen; R_5 , when Z is oxygen, is an electron pair, and when Z is nitrogen, is hydrogen or lower alkyl, e.g., 1-4 carbon alkyl group, preferably methyl or ethyl; R_6 is a lower alkyl or cycloalkyl group, e.g., a 1-4 carbon alkyl or cycloalkyl group; R_7 and R_8 each is hydrogen, lower alkyl group or lower cycloalkyl group, e.g., 1-4 carbons and any combination of R_5 , R_6 , R_7 and R_8 may be taken together to form a 3-7 atom ring structure, and n is a positive integer greater than 1. In an alternative embodiment, the above-described polymer comprises only a portion of the binder, the remainder constituting gelatin or a second synthetic polymer.

DETAILED DESCRIPTION OF THE INVENTION

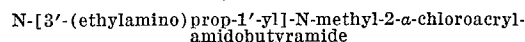
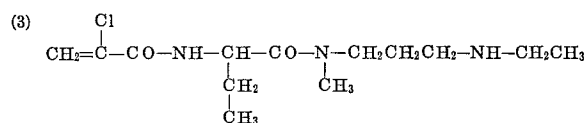
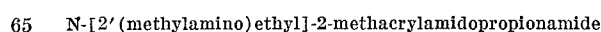
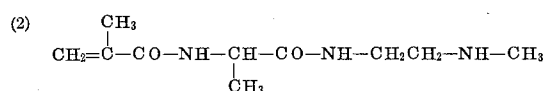
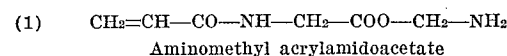
The present invention is directed to photosensitive silver halide emulsions wherein photosensitive silver halide crystals are disposed in a synthetic polymeric binder comprising a polymer having in its structure repeating units represented by the formula:



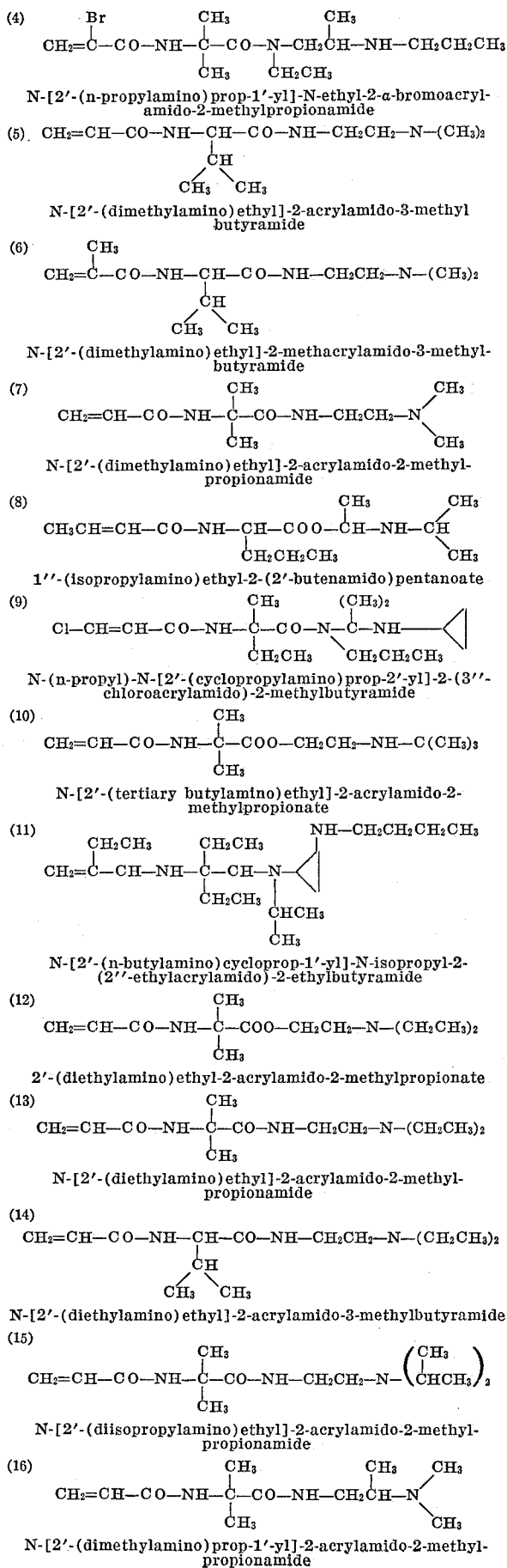
wherein R_1 , R_2 , R_3 and R_4 each is hydrogen, lower alkyl group, e.g., 1-4 carbon alkyl group, preferably methyl or ethyl, or halogen, e.g., chloro, bromo or iodo; and R_2 is additionally cyano; Z is oxygen or nitrogen; R_5 , when Z is oxygen, is an electron pair and when Z is nitrogen, is hydrogen or lower alkyl, e.g., 1-4 carbon alkyl group, preferably methyl or ethyl; R_6 is a lower alkyl or cycloalkyl group, e.g. a 1-4 carbon alkyl or cycloalkyl group; R_7 and R_8 each is hydrogen, lower alkyl group or lower cycloalkyl group, e.g., 1-4 carbons, and any combination of R_5 , R_6 , R_7 and R_8 may be taken together to form a 3-7 atom ring structure, and n is a positive integer greater than 1.

Such polymers have been found to substantially provide all of the basic requirements for a gelatin substitute, as delineated above. The emulsions of the present invention are readily sensitized by conventional sensitizing agents and are characterized by excellent latent image stability and excellent film speed. In addition, the emulsions of the present invention are much more stable against degradation, particularly hydrolysis and the growth of microorganisms than gelatin.

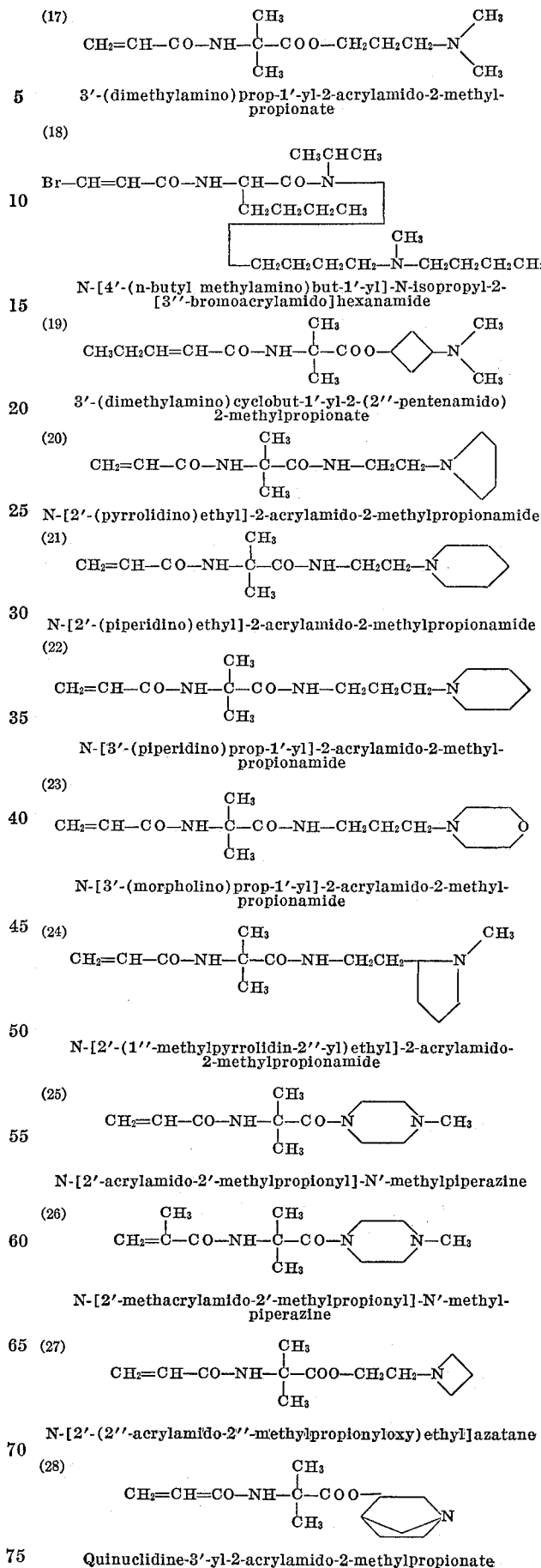
As examples of monomers suitable for providing the amine-diamide polymers, mention may be made of the following:



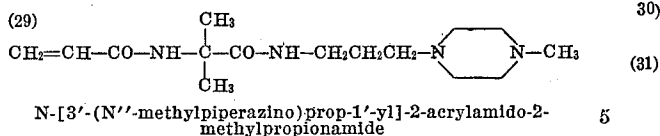
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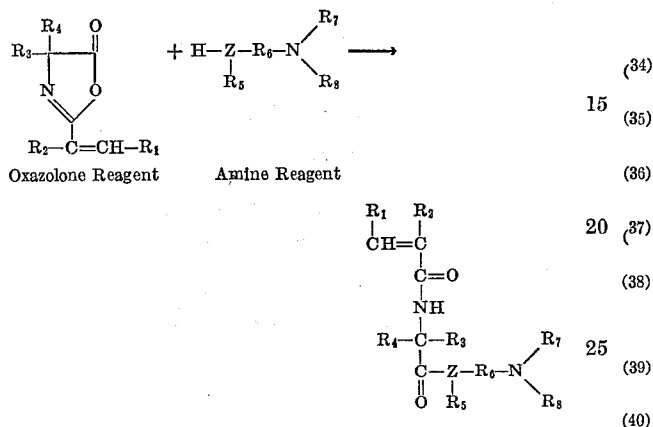
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The monomers employed in forming the polymers suitable for use in the present invention may be prepared by the following general procedure:



The oxazolone reagent may be dissolved in an inert solvent such as hexane or methylene chloride and a stoichiometric amount of amine reagent may be added to the solution. The desired monomer crystallizes out of solution in relatively high yield and purity. The monomer may be collected by filtration, washed with hexane or methylene chloride and vacuum dried.

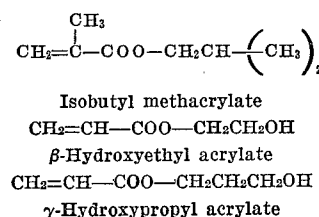
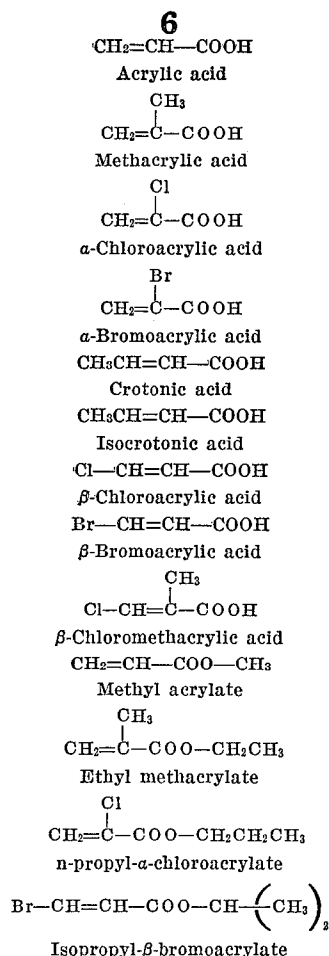
The following table illustrates suitable monomers prepared according to the above-indicated general procedure.

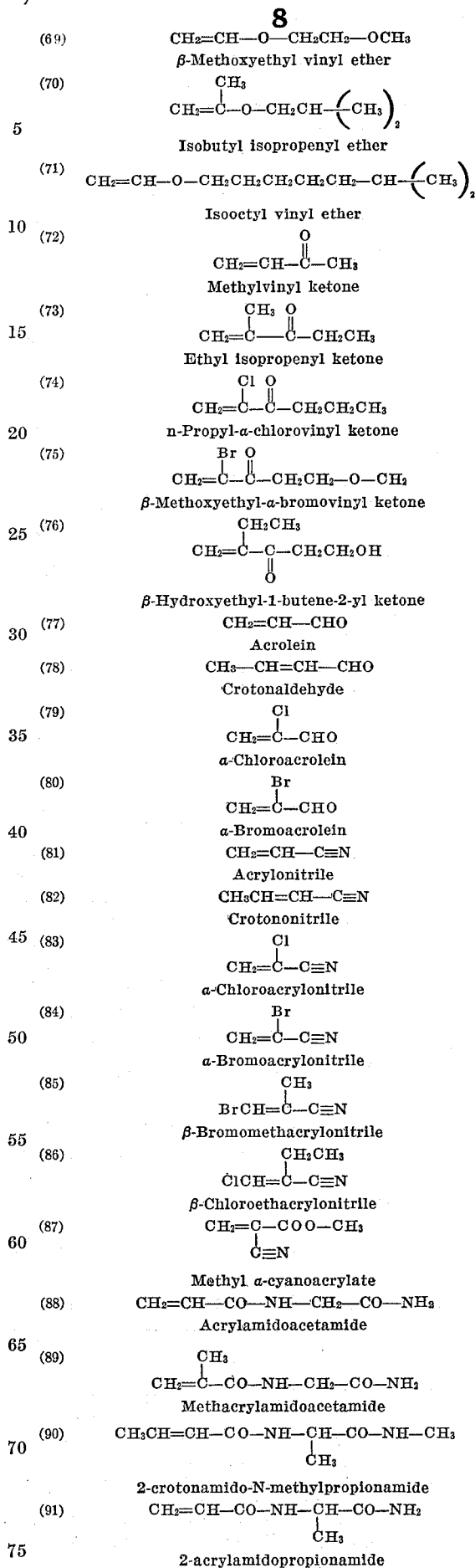
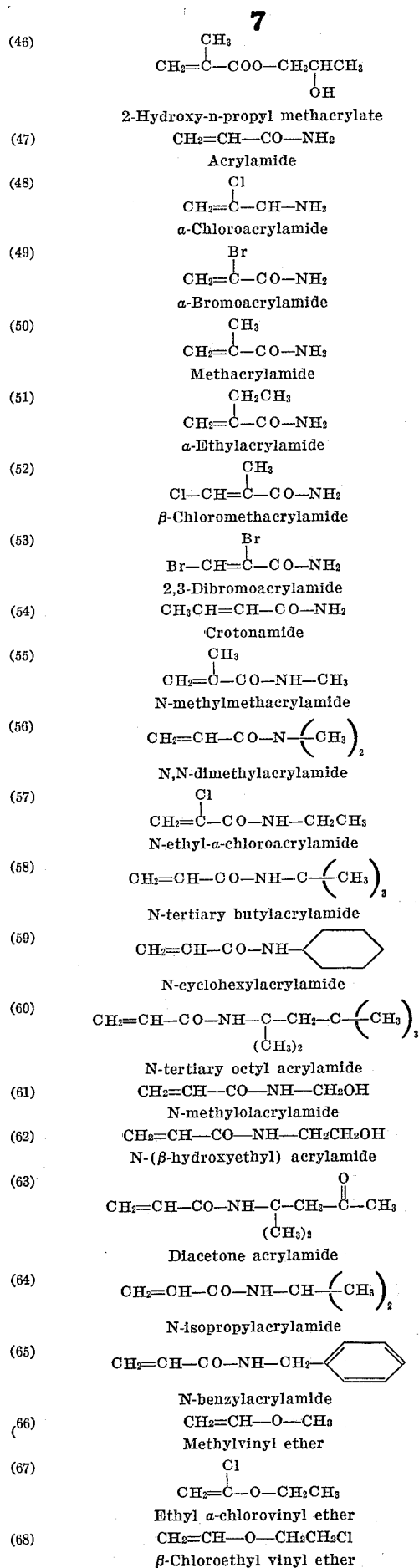
TABLE 1

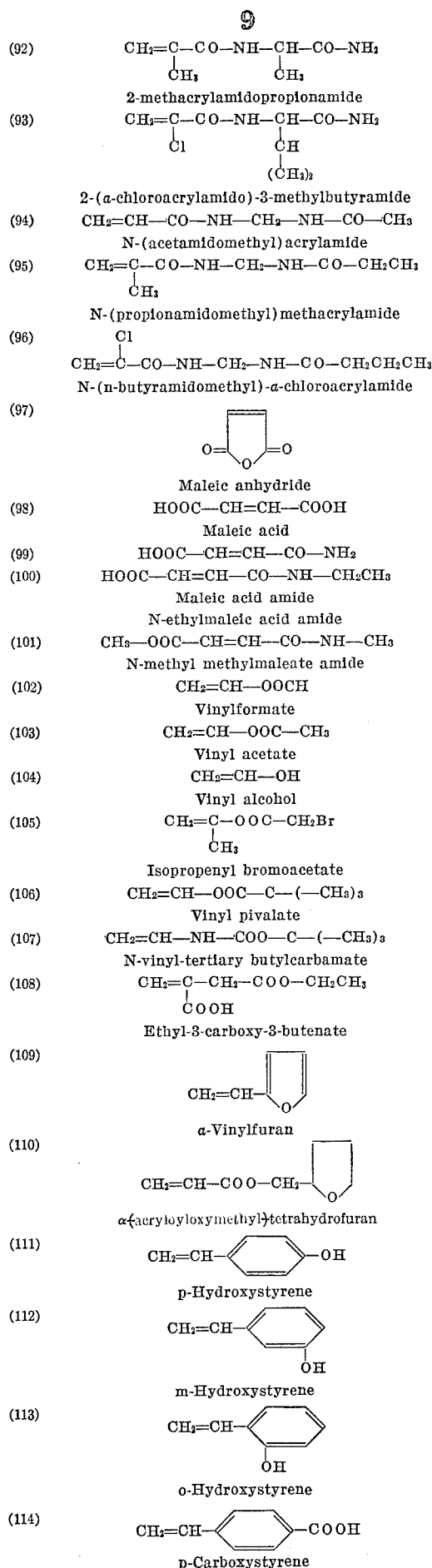
Oxazolone reagent	Amine reagent	Reaction solvent	Appearance	M.P., °C.	Percent yield	Elemental analysis					
						Theoretical			Found		
						C	H	N	C	H	N
2-vinyl-1-isopropyl-5-oxazolone	N,N-dimethyl ethylenediamine	Hexane	White crystals	118-120	-----	-----	-----	-----	-----	-----	-----
2-isopropenyl-4-isopropyl-5-oxazolone	do	Diethyl ether	do	117-119	-----	-----	-----	-----	-----	-----	-----
2-vinyl-4,4-dimethyl-5-oxazolone	do	Hexane	do	76-78	85.0	58.2	9.8	18.5	58.1	9.4	18.4
Do	β -(Tertiary butylamino)ethanol nitrate	Acetone	do	157-159	31.0	48.9	7.8	13.2	49.0	8.1	13.1
Do	β -(Diethylamino) ethanol	Diethyl ether	Colorless oil	(1)	83.0	-----	-----	-----	-----	-----	-----
Do	N,N-diethyl-ethylenediamine	Hexane	White crystals	71-72	60.0	61.1	9.9	16.5	60.8	10.3	16.3
2-vinyl-4-isopropyl-5-oxazolone	do	do	do	83-84	-----	-----	-----	-----	-----	-----	-----
2-vinyl-4,4-dimethyl-5-oxazolone	N,N-diisopropylethylenediamine	do	do	74-75	63.0	63.6	10.3	14.8	63.6	10.5	14.7
Do	2-(dimethylamino)-1-aminopropane	do	do	54-55	43.0	59.7	9.6	17.4	59.6	9.7	17.4
Do	3-(dimethylamino)-1-propanol	Diethyl ether	Colorless oil	(1)	59.5	9.1	11.6	58.3	9.7	9.2	-----
Do	2-pyrrolidinoethylamine	Hexane	White crystals	124-125	92.5	61.6	9.2	16.6	62.0	9.3	16.6
Do	2-piperidinoethylamine	do	do	131-132	93.5	62.9	9.4	15.7	62.8	9.4	15.8
Do	3-piperidino-1-aminopropane	do	do	103-104	93.5	64.0	9.7	14.9	64.0	9.7	14.8
Do	3-morpholino-1-aminopropane	do	do	96-97	91.5	59.4	8.9	14.8	59.6	8.8	14.8
Do	2-(1-methylpyrrolidin-2-yl) ethylamine	do	do	92-94	74.0	62.9	9.4	15.7	62.8	9.7	15.6
Do	N-methylpiperazine	Diethyl ether	do	72-75	62.0	-----	-----	-----	-----	-----	-----
2-isopropenyl-4,4-dimethyl-5-oxazolone	do	do	do	115.9	64.0	-----	-----	-----	-----	-----	-----
2-vinyl-4,4-dimethyl-5-oxazolone	3-(N-methylpiperazino)-1-aminopropane	Hexane	do	113-114	95.5	60.8	9.5	18.9	60.7	9.9	18.5

¹ Very high boiling point.

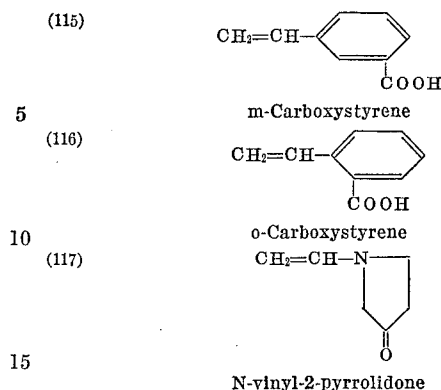
The instant polymers may be homopolymers or interpolymers having, in addition to the repeating units defined above, any compatible repeating unit or various repeating units which are not detrimental to photographic silver halide emulsions and which allow the resultant polymer to be soluble in water. Examples of typical comonomers which may be employed in forming the polymers suitable for use in the present invention include the following ethylenically-unsaturated monomers:







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Polymerization of the indicated monomers is achieved by conventional free radical polymerization techniques.

The following non-limiting examples illustrate the preparation of polymers within the scope of the present invention.

EXAMPLE I

9:1 copolymer of N-isopropylacrylamide/2-acrylamido-3-methyl-N- $[\beta$ -(dimethylamino)ethyl] butyramide.

A 30.6 g. of N-isopropylacrylamide and 7.29 g. of 2-acrylamido-3-methyl-N- $[\beta$ -(diethylamino)ethyl]butyramide were dissolved in 300 ml. of distilled water and 5 ml. of isopropanol. The pH was adjusted to 6.4 with nitric acid and then 0.05 g. of potassium persulfate and 0.05 g. of sodium bisulfite were added. The polymerization was carried out at room temperature for 3 hours. The thus-formed polymer was precipitated into acetone, washed, dried and redissolved for use in making an emulsion.

EXAMPLE II

A 1:1 copolymer of acrylamide/2-acrylamido-3-methyl-N- $[\beta$ -(dimethylamino)ethyl] butyramide was prepared according to the procedure of Example I.

EXAMPLE III

A 1:1 copolymer of N-isopropylacrylamide/2-methacrylamido-3-methyl-N- $[\beta$ -(dimethylamino)ethyl]butyramide was prepared according to the procedure of Example I.

EXAMPLE IV

A 1:1 copolymer of acrylamide/2-methacrylamido-3-methyl-N- $[\beta$ -(dimethylamino)ethyl]butyramide was prepared according to the procedure of Example I.

EXAMPLE V

A 4:1 copolymer of acrylamide/2-acrylamido-3-methyl-N- $[\beta$ -(dimethylamino)ethyl]butyramide was prepared according to the procedure of Example I.

EXAMPLE VI

A 1:1 copolymer of N-isopropylacrylamide/2-acrylamide was prepared according to the procedure of Example I.

EXAMPLE VII

A 4:1 copolymer of methacrylic acid/2-methacrylamido-3-methyl-dimethylaminoethyl butyramide was prepared according to the procedure of Example I.

EXAMPLE VIII

A 1:1 copolymer of acrylamide/N- $[\beta$ -(dimethylamino)ethyl]-2-acrylamido-2-methyl propionamide was prepared according to the procedure of Example I.

EXAMPLE IX

A 4:1 copolymer of acrylamide/N- $[\beta$ -(dimethylamino)ethyl]-2-acrylamido-2-methylpropionamide was prepared according to the procedure of Example I.

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EXAMPLE X

A 5:2 copolymer of acrylamide/N-[β -(dimethylamino)ethyl]-2-acrylamido-2-methyl-propionamide was prepared according to the procedure of Example I.

EXAMPLE XI

A 1:1 copolymer of acrylamide/2 - acrylamido-2-methyl - N - [2-pyrrolidinoethyl]-propionamide was prepared according to the procedure of Example I.

EXAMPLE XII

A 1:1 copolymer of acrylamide/3'-(dimethylamino)propyl-2-acrylamido - 2 - methylpropionate was prepared according to the procedure of Example I.

EXAMPLE XIII

A 38:1 copolymer of acrylamide/N-[β -(dimethylamino)ethyl] - 2 - acrylamido-2-methyl-propionamide was prepared by dissolving 13.5 g. of acrylamide and 1.14 g. of the diamide in 80 ml. of dimethylformamide with 0.01 g. of azobisisobutyronitrile. The mixture was heated to 60° C. for 18 hours. The thus-formed polymer was precipitated into acetone, washed, dried and redissolved for use in making an emulsion.

EXAMPLE XIV

A 3:4 copolymer of acrylamide/N - [β - (dimethylamino)ethyl] - 2 - acrylamido-2-methyl-propionamide was prepared according to the procedure of Example XIII.

EXAMPLE XV

A 10:1 copolymer of acrylamide/N-[β -(dimethylamino)ethyl] - 2 - acrylamido-2-methyl-propionamide was prepared according to the procedure of Example XIII.

EXAMPLE XVI

A 1:1 copolymer of acrylamide/2-acrylamido-2-methyl-N-[N' - methyl - N'' - piperazinopropyl]propionamide was prepared by dissolving in 27.6 ml. water and 0.9 ml. isopropanol 1.78 g. of acrylamide, and 7.4 g. 2-acrylamido - 2 - methyl - N - [N' - methyl - N'' - piperazinopropyl] propionamide. Polymerization was carried out at 65° C. for 66 hours in an evacuated sealed tube using 0.0459 g. azobisisobutyronitrile initiator. The solution of medium viscosity was precipitated into acetone, washed, dried and redissolved for use in an emulsion.

EXAMPLE XVII

A 1:1 copolymer of acrylamide/ β -(tert-butylamino)-ethyl-2-acrylamido-2-methylpropionate nitrate was prepared employing the procedure of Example I.

EXAMPLE XVIII

A 1:1 copolymer of acrylamide/2 - acrylamino-2-methyl-N-[piperidinopropyl]propionamide was prepared according to the procedure of Example XVI.

EXAMPLE XIX

A 1:1 copolymer of acrylamide/2 - acrylamino-2-methyl - N - [3-morpholinopropyl]propionamide was prepared according to the procedure of Example XVI.

EXAMPLE XX

A 9:5 copolymer of acrylamide/2-acrylamido-2-methyl-N - [N'-methyl-2'-pyrrolidinoethyl]propionamide was prepared according to the procedure of Example XVI.

EXAMPLE XXI

A 12:5 copolymer of acrylamide/2 - acrylamido-2-methyl-N-[N,N' - dimethyl-2-aminopropyl]propionamide was prepared according to the procedure of Example XVI.

EXAMPLE XXII

A 18:5 copolymer of N'-[methyl]-N-[(2-methylacrylamido-2-methyl) - propionyl] piperazine/methacrylamide was prepared according to the procedure of Example XVI.

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The following general procedure may be used for preparing photographic emulsions using the polymers of the instant invention as the colloid binders.

A water-soluble silver salt, such as silver nitrate, may be reacted with at least one water-soluble halide, such as potassium, sodium, or ammonium bromide, preferably together with potassium, sodium or ammonium iodide, in an aqueous solution of the above-described polymer. The emulsion of silver halide thus-formed contains water-soluble salts, as a by-product of the double decomposition reaction in addition to any unreacted excess of the initial salts. To remove these soluble materials, the emulsion may be centrifuged and washed with distilled water to a low conductance. The emulsion may then be redispersed in distilled water. To an aliquot of this emulsion may be added a known quantity of a solution of bodying or thickening polymer, such as polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. du Pont de Nemours & Company, Wilmington, Del., designated Type 72-60). A surfactant, such as dioctyl ester of sodium sulfosuccinic acid, designated Aerosol OT (commercially available from American Cyanamid Company, New York, N.Y.), may be added and the emulsion slot coated onto a base of cellulose triacetate sheet 5 mls. thick having a coating of 30 mg./sq. ft. of hardened gelatin.

Alternatively, the soluble salts may be removed by adding to the emulsion a solution of polyacid such as 1:1 ethylene:maleic acid copolymer and lowering the pH to below 5, thereby bringing about precipitation of the polyacid carrying the silver halide grains along with the precipitate, and then to wash and resuspend the resulting precipitate by redissolving the polyacid at pH 6-7.

The emulsions may be chemically sensitized with sulfur compounds such as sodium thiosulfate or thiourea, with reducing substances such as stannous chloride; with salts of noble metals such as gold, rhodium and platinum; with amines and polyamines; with quaternary ammonium compounds such as alkyl α -picolinium bromide; and with polyethylene glycols and derivatives thereof. The emulsions of the present invention require only 5% as much gold for chemical sensitization as do gelatin emulsions.

The polymers employed as the binders in the emulsions of the present invention may be cross-linked according to conventional procedures. As an example, polymers containing amine groups may be cross-linked with zirconium salts under alkaline conditions wherein amine-containing polymer is coated with a zirconium salt, for example, zirconium sulfate, and the pH is raised cross-linking the polymer.

The emulsions of the present invention may also be optically sensitized with cyanine and merocyanine dyes more easily than are gelatin emulsions. Cyanine dyes tend to aggregate less on the polymers of the instant invention than with gelatin providing less light filtering and speed loss. Where desired, suitable antifoggants, toners, restrainers, developers, accelerators, preservatives, coating aids, plasticizers, hardeners and/or stabilizers may be included in the composition of the emulsion.

The emulsions of this invention may be coated and processed according to conventional procedures of the art. They may be coated, for example, onto various types of rigid or flexible supports, such as glass, paper, metal, and polymeric films of both the synthetic type and those derived from naturally occurring products. As examples of specific materials which may serve as supports, mention may be made of paper, aluminum, polymethacrylic acid, methyl and ethyl esters, vinylchloride polymers, polyvinyl acetal, polyamides such as nylon, polyesters such as polymeric film derived from ethylene glycol-terephthalic acid, and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate propionate, and acetate butyrate. These novel emulsions of the instant invention have been found to adhere to supports in a most satisfactory manner.

The polymers employed in the practice of the instant invention may contain from 5–100 mole percent of the repeating units represented in Formula A. The specific amount employed may be selected by the operator depending upon the grain particle size and habit desired.

Emulsions within the scope of the present invention may also be prepared employing polymers such as:

N-[β -(diethylamino)ethyl]-2-acrylamido-3-methyl-butyn-
amide):N-methyl-N-[2-acrylamido-2-methyl-
propionyl]-piperazine

and

methacrylamide:N-methyl-N-[2-acrylamido-2-methyl-
propionyl]-piperazine copolymer.

By selecting appropriate comonomers, the instant copolymers may be made to be compatible with all water-soluble bodying polymers. Emulsions made from these novel polymers, may be bodied with any water-soluble polymers, overcoming the disadvantage encountered with gelatin which is only compatible with a very few polymers in a most limited pH range. As examples of specific materials which may serve as bodying polymers are polyvinyl alcohol, polyacrylamide, polyalkylacrylamides, polyvinyl pyrrolidone, poly(β -hydroxyethyl acrylate), polyethylene imine and cellulose derivatives such as hydroxypropyl cellulose and methyl cellulose. It has been found that using only a small amount of one or more of the instant polymers, large amounts of photosensitive silver halide grains may be obtained.

An emulsion made from one of these polymers of the instant invention may therefore be bodied with a water-soluble polymer such that the polymeric constitution of the resulting emulsion comprises a relatively large percentage of the bodying polymer.

By selecting appropriate comonomers, copolymers with selected diffusion characteristics may be prepared.

The instant polymers containing acidic comonomers may be pH flocculated in order to remove the soluble salts formed as a byproduct of the double decomposition reaction between the water-soluble silver salt and the water-soluble halide, in addition to any unreacted excess of the initial salts. As an example, an acid copolymer may be precipitated by lowering the pH below 5 and then washed and resuspended by raising the pH to above 7.

The instant invention will be further illustrated by reference to the following nonlimiting examples in which the preparation of the emulsion was carried out in the following general manner.

Procedure A

A solution of 4.15 g. of the dry copolymer in 266 ml. of distilled water was adjusted to pH 6.30 with dilute nitric acid and maintained at a temperature of 55° C. To this solution, 44.0 g. of dry potassium bromide and 0.50 g. of dry potassium iodide were added.

A solution of 55 g. of silver nitrate in 500 ml. of distilled water was prepared. From this silver nitrate solution, 100 ml. was rapidly added with continuous agitation to the polymer-halide solution and an additional 396 ml. was added over a period of 22 minutes. Thereafter, the emulsion was ripened for 30 minutes at 55° C., and then rapidly cooled to below 20° C.

Procedure B

In an alternative procedure for preparing the emulsion, the pH of the polymer solution was adjusted to 3.0; the amount of dry potassium bromide used was 88.0 g. and the amount of dry potassium iodide used was 1.0 g. In addition, the emulsion was ripened for 60 minutes instead of for 30 minutes.

The emulsion mixture in both procedures was centrifuged and washed with water to a low conductance. The emulsion was then redispersed in distilled water. To an

aliquot of this emulsion was added a known quantity of a solution of bodying or thickening polymer of polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. du Pont de Nemours & Company, Wilmington, Del., designated Type 72–60). A surfactant, such as Aerosol OT, was added and the emulsion was slot coated onto a base of cellulose triacetate sheet 5 mils thick having a coating of 30 mg./sq. ft. of hardened gelatin (Celfa, commercially available from Instar Supply Company, New York, N.Y.). This film so prepared was air dried, exposed on a sensitometer, and processed with a processing solution and an image-receiving sheet from a Type 42 film assembly (Polaroid Corporation, Cambridge, Mass.). The negative and image-receiving element were maintained in superposed position for 15 seconds, after which they were stripped apart. The photographic characteristics of the resulting positive print were measured on an automatic recording densitometer.

The following table summarizes silver halide grain sizes obtained in emulsions prepared with polymers of the present invention.

TABLE 2

Polymer	Grain size (microns)	
	Range	Average
Dimethylaminoethyl-2-acrylamido-2-methylpropionamide	0.2–2.0	0.5
3'4 Acrylamide, dimethylaminoethyl-2-acrylamido-2-methylpropionamide	0.3–2.1	1.0
1:1 Acrylamide, dimethylaminoethyl-2-acrylamido-2-methylpropionamide	0.4–1.4	0.8
4:1 Acrylamide, dimethylaminoethyl-2-acrylamido-2-methylpropionamide	0.5–3.7	1.8
38:1 Acrylamide, dimethylaminoethyl-2-acrylamido-2-methylpropionamide	0.3–2.2	1.3
Dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.2–2.0	0.5
1:1 Acrylamide, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.4–2.8	1.5
6:1 Acrylamide, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.2–2.0	0.8
1:1 N-isopropylacrylamide, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.1–2.0	0.9
9:1 Acrylamidoacetamide, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.1–1.5	0.6
8:1:1 Methacrylamidoacetamide, methacryloylglycine, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.2–2.0	0.8
2:1:2 Acrylamide:acryloylvaline, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.1–0.8	0.3
4:3:3 Acrylamide:acryloylvaline, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.2–1.0	0.5
2:2:1 Acrylamide:acryloylvaline, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.1–1.5	0.8
2:2:1 Methacrylamide:methacryloylvaline, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.2–2.0	1.0
4:3:3 Methacrylamide:methacryloylvaline, dimethylaminoethyl-2-acrylamido-3-methylbutyramide	0.1–2.0	0.5
5:1 Acrylamide: β -(tert-butylamino)-ethylacrylamido-2-methylpropionate	0.2–1.1	0.4
7:7:1 Acrylamide: β -(diethylamino)ethyl-2-acrylamido-2-methylpropionate	0.4–1.6	0.7
N-[β -(diethylamino)ethyl]-2-acrylamido-2-methylpropionamide	0.2–1.1	0.5
1:77:1 Acrylamide, 2-acrylamido-2-methyl-N-[2'-(diisopropylamino)ethyl]propionamide		0.4
12:5 Acrylamide, 2-acrylamido-2-methyl-N-[2-(dimethylamino)-prop-1-yl]propionamide	0.2–2.4	1.0
4:8:1 Acrylamide:3'-(dimethylamino)-prop-1'-yl-2-acrylamido-3-methylpropionate	0.4–4.5	1.5
1:1 Acrylamide:2-acrylamido-2-methyl-N-[2-pyrrolidino)ethyl]propionamide	0.2–0.9	0.4
2:6:1 Acrylamide, 2-acrylamido-2-methyl-N-[2'-(piperidino)-ethyl]propionamide	0.2–0.8	0.4
1:1 Acrylamide, 2-acrylamido-2-methyl-N-[piperidinopropyl]propionamide	0.2–0.8	0.4
9:5 Acrylamide, 2-acrylamido-2-methyl-N-[2-(1'-methylpyrrolidinyl)ethyl]propionamide	0.2–1.4	0.6
1:08:1 Acrylamide, 2-acrylamido-2-methyl-N-[3'-morpholino)propyl]propionamide	0.3–1.2	0.7
1:1 Acrylamide, 2-acrylamido-2-methyl-N-[N'-methyl-N'-piperazinopropyl]propionamide	0.2–1.1	0.6

The following table shows densitometer readings obtained on negatives prepared from emulsions within the scope of the present invention.

TABLE 3

Grain growing polymer	Bodying polymer	Silver/ polymer ratio	Silver, mg./ ft. ²	Dmax.	Dmin.	ΔD
21:1 acrylamide/N-[B-(dimethylamino)ethyl]-2-acrylamido-2-methylpropionamide	None	∞	81.5	0.81	0.15	0.66
Do	Polyvinyl alcohol	0.91	105.5	1.62	0.09	1.53
10:1 acrylamide/dimethylamino-ethyl-2-acrylamido-2-methylpropionamide	None	∞	52.5	0.65	0.00	0.65
4:1 acrylamide/dimethylamino-ethyl-2-acrylamido-2-methylpropionamide	do	∞	143.3	0.90	0.00	0.90
6:1 acrylamide/2-acrylamido-3-methyl-N-[β-(dimethylamino)ethyl]butyramide	do	∞	29.6	1.14	0.29	0.85

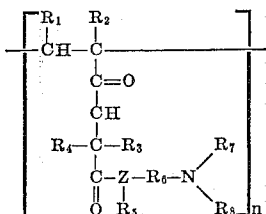
In certain photographic applications, it may be desirable to replace part, but not all, of the gelatin in the photosensitive emulsion. In view of the characteristics of these polymers described above, and further, in view of their compatibility with gelatin in substantially all proportions, it will be obvious that these polymers are ideally suited for such work.

The term "photosensitive" and other terms of similar import are herein employed in the generic sense to describe materials possessing physical and chemical properties which enable them to form usable images when photo-exposed by radiation.

Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative only and not in a limiting sense.

What is claimed is:

1. A photosensitive silver halide emulsion wherein the emulsion binder comprises a polymer having in its structure repeating units of the formula:



wherein R_1 , R_3 and R_4 each are selected from the group consisting of hydrogen, lower alkyl and halogen; R_2 is selected from the group consisting of hydrogen, lower alkyl, halogen and cyano; Z is selected from the group consisting of oxygen and nitrogen; when Z is oxygen R_5 is an electron pair and when Z is nitrogen R_5 is selected from the group consisting of hydrogen and lower alkyl; R_6 is selected from the group consisting of lower alkyl and lower cycloalkyl groups; R_7 and R_8 each are selected from the group consisting of hydrogen, lower alkyl, lower cycloalkyl, and any combination of R_5 , R_6 , R_7 and R_8 may be chemically joined to form a 3-7 atom ring structure, and n is a positive integer greater than 1.

2. The product as defined in claim 1 wherein substantially all of said emulsion binder comprises said polymer.

3. The product as defined in claim 1 wherein said polymer comprises 5-100 mole percent of said repeating segments.

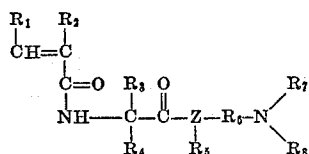
4. The product as defined in claim 1 wherein said silver halide emulsion is a silver iodobromide emulsion.

5. The product as defined in claim 1 wherein said emulsion includes at least one chemical sensitizing agent.

6. The product as defined in claim 1 wherein said emulsion includes at least one optical sensitizing agent.

7. The product as defined in claim 1 wherein said polymer is a homopolymer.

8. The product as defined in claim 1 wherein said polymer comprises a copolymer of a first monomer of the formula:



and a second ethylenically unsaturated monomer.

9. The product as defined in claim 8 wherein said first monomer is dimethylaminoethyl-2-acrylamido-2-methylpropionamide.

10. The product as defined in claim 8 wherein said first monomer is dimethylaminoethyl-2-acrylamido-3-methylbutyramide.

11. The product as defined in claim 8 wherein said first monomer is β -(dimethylamino)-ethyl-2-acrylamido-2-methylpropionate.

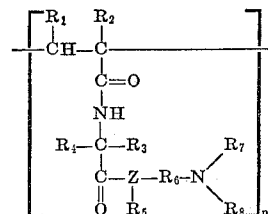
12. The product as defined in claim 8 wherein said first monomer is 2-acrylamido-2-methyl-N-[2'-(piperidino)-ethyl]-propionamide.

13. The product as defined in claim 8 wherein said comonomer is acrylamide.

14. The product as defined in claim 8 wherein said comonomer is N-isopropylacrylamide.

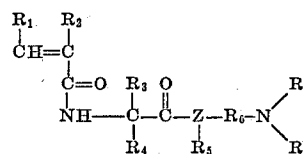
15. The product as defined in claim 8 wherein said comonomer is acrylamidoacetamide.

16. A method of preparing a photosensitive silver halide emulsion which comprises reacting a water-soluble silver salt with a water-soluble halide salt in an aqueous solution containing a polymer having in its structure repeating units of the formula:



wherein R_1 , R_3 and R_4 each are selected from the group consisting of hydrogen, lower alkyl and halogen; R_2 is selected from the group consisting of hydrogen, lower alkyl, halogen and cyano; Z is selected from the group consisting of oxygen and nitrogen; when Z is oxygen R_5 is an electron pair and when Z is nitrogen R_5 is selected from the group consisting of hydrogen and lower alkyl; R_6 is selected from the group consisting of lower alkyl and lower cycloalkyl groups; R_7 and R_8 each are selected from the group consisting of hydrogen, lower alkyl, lower cycloalkyl, and any combination of R_5 , R_6 , R_7 and R_8 may be chemically joined to form a 3-7 atom ring structure, and n is a positive integer greater than 1.

17. The method as defined in claim 16 wherein said polymer comprises a copolymer of a first monomer of the formula:



and a second ethylenically unsaturated monomer.

18. The method as defined in claim 17 wherein said first monomer is dimethylaminoethyl-2-acrylamido-2-methylpropionamide.

19. The method as defined in claim 17 wherein said first monomer is dimethylaminoethyl-2-acrylamido-3-methylbutyramide.

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20. The method as defined in claim 17 wherein said first monomer is β -(dimethylamino)-ethyl - 2 - acrylamido-2-methylpropionate.

21. The method as defined in claim 17 wherein said first monomer is 2-acrylamido-2-methyl-N-[2'-(piperi- 5 dino)-ethyl]-propionamide.

22. The method as defined in claim 17 wherein said comonomer is acrylamide.

23. The method as defined in claim 17 wherein said comonomer is N-isopropylacrylamide.

24. The method as defined in claim 17 wherein said comonomer is acrylamidoacetamide.

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10 RONALD H. SMITH, Primary Examiner

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