

2,833,650

PHOTOGRAPHIC EMULSIONS

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19 Claims. (Cl. 96—114)

This invention relates to photography and more particularly to photographic emulsions in which the binding agent comprises an addition polymer containing extralinear amide groups and extralinear betaine and/or glycol groups. Still more particularly, it relates to emulsions of light-sensitive silver halide in a water-permeable colloid binder comprising an aforesaid polymer. The invention also relates to photographic elements having at least one layer composed of such an emulsion.

This invention relates to light-sensitive photographic emulsions which are equally useful for black and white as well as for color photography. More particularly it relates to silver halide photographic emulsions in which synthetic polyamides containing betaine and/or glycol groups (as described in U. S. application Ser. Nos. 415,161, 415,162 and 415,163, filed March 9, 1954), are used instead of all or part of the gelatin which is ordinarily the carrier, binder and protective colloid for the light-sensitive agent.

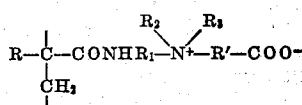
Heretofore, gelatin has been employed as the carrier, for the light-sensitive silver halide in commercial high-speed negative type photographic emulsions. However, this substance has numerous disadvantages and it has long been sought to obtain a substitute therefor which possesses the advantages of gelatin with a minimum of its disadvantages. Many materials have been proposed for this purpose including natural and synthetic colloids and polymers having hydrophilic properties. The previously proposed materials have the serious disadvantage that photographic emulsions with speeds equivalent to those of high-speed negative type gelatino-silver halide emulsions cannot be made in them.

An object of this invention is to provide silver halide emulsions in synthetic colloids which are free from the disadvantages of gelatin and related natural protein colloid emulsions. Another object is to provide such emulsions which have speeds at least as high as those obtainable with gelatin. Yet another object is to provide emulsions of silver halide in synthetic addition polymers that are uniform, stable, resistant to bacteria and from thin layers which are flexible over a wide range of temperatures. A further object is to prepare such emulsions which can be admixed with an additional amount of the same or another polymeric colloid and/or gelatin. A still further object is to prepare such emulsions in which polymeric and other non-diffusing color formers are readily dispersible and the developed photographic layers are free from haze and other disadvantages. Still other objects will be apparent from the above description of the invention.

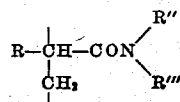
The photographic emulsions of this invention, in their broader aspects, consist essentially of a dispersion of light-sensitive silver halide in a water-permeable colloid binding agent wherein at least 2% by weight of such agent is an addition copolymer having hydrophilic properties composed of a substantial number of recurring intralinear units (a) of at least one of the types taken

from the group consisting of those having Formula I and those having Formula I' and (b) at least one type of a unit having Formula II (each of said formulae being given below). The remaining proportion of the binding agent can be a different copolymer of the same type and/or a different compatible water-permeable colloid, preferably gelatin, polyvinyl alcohol, or a polyvinyl acetal having hydrophilic colloid properties, including p-hydroxybenzaldehyde polyvinyl acetal, sodium o-sulfobenzaldehyde polyvinyl acetal and polyvinyl acetals containing color former nuclei linked to the polyvinyl alcohol by an acetal linkage.

Copolymers containing one each of the types of units having Formula I and II and their preparation are described in Shacklett U. S. application Ser. No. 415,163, filed March 9, 1954. These copolymers are composed of recurring intralinear units of the formulae:

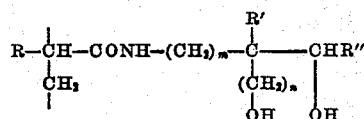


wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent, aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated divalent, aliphatic hydrocarbon radical of 1 to 4 carbon atoms, and



wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl. These copolymers may contain one, two or more different units of the type of Formula I and one, two or more different units of the type of Formula II. In these copolymers, units of type I are present in an amount of 5 to 80 mol percent and the copolymers have a molecular weight of at least 5,000.

Copolymers containing one each of the types of units having Formula I' and II and their preparation are described in Shacklett U. S. application Ser. No. 415,162, filed March 9, 1954, and the applications referred to therein. These copolymers are composed of recurring intralinear units of the Formula II above and intralinear units of the formula:



wherein R is a member taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, R' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, R'' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, m is a cardinal number from 0 to 4, and n is a cardinal number 0 to 1 and the sum of m and n equals at least 1. Units of type I' constitute 10 to 70 mol percent of the copolymers, which have molecular weights of at least 5,000.

Copolymers containing three intralinear units, namely those of Formulae I, I' and II and their preparation are described in Shacklett U. S. application Ser. No. 415,161, filed March 9, 1954, and in the applications referred to therein. In these three-component copolymers, units I, I' and II are in the proportions 5 to 60, 5 to 60 and 30

to 90 mol percent, respectively, and the copolymers have a molecular weight of at least 5000.

The photographic emulsions of light-sensitive silver halide in the two-component or three-component copolymers described above are made by precipitating silver halide in an aqueous solution or dispersion of such copolymer. This is accomplished by admixing an aqueous solution containing a water-soluble silver salt, e. g., nitrate sulphamate or citrate, with an aqueous solution containing a water-soluble halide, e. g., ammonium bromide, ammonium chloride, potassium bromide, chloride or iodide, or mixtures of two or more of such salts. The resulting aqueous emulsion or dispersion of silver halide is then ripened in the same manner as gelatino-silver halide emulsions, the copolymer is coagulated and the soluble salts are removed by separating the liquid from the coagulum, e. g., by decantation. The coagulum is then washed with water to remove soluble salts, e. g., alkali metal or ammonium nitrate and halide.

Redispersion of the coagulum in an additional amount of an aqueous solution of the same copolymer or a different copolymer described above or another suitable protective colloid, e. g., gelatin, polyvinyl alcohol or a polyvinyl acetal, or a mixture of two or more of such colloids, is followed by the addition of the usual photographic emulsion adjuvants including sensitizing agents, e. g., sensitizing dyes, sulfur sensitizers, metal sensitizers, and reduction sensitizers which give rise to a completed photographic emulsion ready for coating upon a suitable support, e. g., a hydrophobic film support, paper, metal sheet, or glass plate.

The photographic elements, e. g., films, papers and plates obtained by the methods just described may be exposed, developed, fixed, and washed in the usual baths to produce photographic images in both black and white and color photography.

The invention will be further illustrated but is not intended to be limited by the following examples, wherein the parts stated are parts by weight, unless otherwise indicated.

Example 1

A photographic emulsion was prepared by precipitating, by means of aqueous silver nitrate, ammonium bromide and potassium iodide solutions, 141.6 parts of silver iodobromide (in which the ratio of silver iodide to silver bromide was 1 to 23.7) in the presence of 11 parts in aqueous solution of the copolymer of methacrylamide and N,3-methacrylamidopropyl-N,N-dimethyl- β -aminopropionate betaine prepared from a solution of 76.5 parts of methacrylamide and 24.2 parts of the betaine, as described in paragraph 1 of Example 5 of U. S. application Ser. No. 415,163, filed March 9, 1954, with the exception that the solvent for the polymerization was a mixture of 750 parts of water and 197 parts of isopropyl alcohol and the temperature of the polymerization solution was 60° C., and the relative viscosity of a 1% aqueous solution of the resulting copolymer at pH 7 and 30° C., was 1.82. After precipitation, Ostwald "ripening" was carried out in the presence of excess bromide ion and ammonia. Thereafter, 199 parts of gelatin was added and dissolved in the mixture. The emulsion was then cooled to form a firm gel, broken up and washed with water to remove soluble compounds. The washed gel was melted, and digested with the additions of water, sensitizing and dispersing agents, hardeners, etc., being made, after which the finished emulsion was coated on a cellulose acetate support and dried.

A similar emulsion was made in the identical manner with the exception that 11 parts of gelatin was substituted for the 11 parts of the copolymer used during the precipitation and "ripening" stage. The finished emulsion was also coated on cellulose acetate and dried. When samples of the two films were exposed in a negative type 1B sensitometer, developed, fixed,

washed, and dried under identical conditions, the relative photographic speed of the film containing the copolymer was 132 compared with the gelatin control film whose relative speed was 100 and was equal to that which is characteristic of currently available high-speed negative type photographic films frequently referred to as "press" films.

Example 2

The procedure of Example 1 was repeated with the exception that a copolymer of methacrylamide and N,3-methacrylamidopropyl-N,N-dimethyl- β -aminopropionate betaine, prepared from a solution of 68.0 parts of methacrylamide and 48.4 parts of betaine, as described in paragraph 2 of Example 5 of U. S. application Ser. No. 415,163, filed March 9, 1954, except that the solvent for the polymerization was a mixture of 750 parts of water and 197 parts of isopropyl alcohol, the temperature of polymerization was 70° C., the time of polymerization was 20 hours and the relative viscosity of a 1% aqueous solution of the resulting copolymer at 30° C. and pH 7 was 1.87, was used instead of the copolymer of Example 1.

A similar emulsion containing gelatin as the sole binding agent was prepared and coated as described in Example 1. Samples of the two films were exposed and processed as described in Example 1. The relative speed of the film containing the copolymer was 200 compared with that of the gelatin control film which was 100.

Example 3

The procedure of Example 1 was repeated with the exception that a copolymer of methacrylamide and N,2-methacrylamidoethyl-N,N-dimethyl- β -aminopropionate betaine prepared from a solution of 76.5 parts of methacrylamide and 22.8 parts of the betaine, as described in Example 1 of U. S. application Ser. No. 415,163, filed March 9, 1954, the relative viscosity of whose 1% aqueous solution at 30° C. and pH 7 was 1.86, was used instead of the copolymers described in Example 1. A similar emulsion having gelatin as the sole binding agent was prepared and coated as described in Example 1. Samples of the two films were exposed and processed as described in Example 1. The photographic speeds of the two films were the same and were equal to that which is characteristic of currently available high-speed negative type photographic films frequently referred to as "press" films.

Example 4

The procedure of Example 1 was repeated with the exception that a copolymer of methacrylamide and N,2-methacrylamidoethyl-N,N-dimethyl- β -aminopropionate betaine prepared as described in Example 1 of U. S. application Ser. No. 415,163, filed March 9, 1954, except that the solvent was a mixture of 1000 parts of water and 314 parts of ethyl alcohol, and the relative viscosity of a 1% aqueous solution of the polymer at 30° C. and pH 7 was 3.08, was used instead of the copolymer described in Example 1.

A similar emulsion containing gelatin as the sole binding agent was prepared and coated as described in Example 1. Samples of the two films were exposed and processed as described in Example 1. The photographic speeds of the two films were the same and were equal to that which is characteristic of currently available high-speed negative type photographic films frequently referred to as "press" films.

Example 5

The procedure of Example 1 was repeated with the exception that a three-component copolymer of methacrylamide, N,3-methacrylamidopropyl-N,N-dimethyl- β -aminopropionate betaine, and N,2,3-dihydroxypropyl-methacrylamide, prepared by the method described in Example 5 of U. S. application Ser. No. 415,161, filed

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March 9, 1954, with the following changes: 600 parts of water and 157.2 parts of isopropyl alcohol were placed in the polymerization vessel instead of 800 parts of water, 48.4 parts of N,3-methacrylamidopropyl-N,N-dimethyl- β -aminopropionate betaine was used instead of 45.6 parts of N,2-methacrylamidoethyl- β -aminopropionate betaine, the hydrolysis of the dioxolane was carried out in a mixture of 150 parts of water and 39.3 parts of isopropyl alcohol, the yield of the resulting copolymer was 101 parts and the relative viscosity of a 1% aqueous solution thereof at 30° C. and pH 7 was 2.61, was used instead of the copolymer described in Example 1.

A similar emulsion containing gelatin as the sole binding agent was prepared and coated as described in Example 1. Samples of the two films were exposed and processed as described in Example 1. The relative speed of the film containing the copolymer was 229 compared with the gelatin control film whose relative speed was 100 and was equal to that which is characteristic of currently available high-speed negative type photographic films.

Example 6

A photographic emulsion was prepared by precipitating by means of aqueous silver nitrate, ammonium bromide and potassium iodide solutions, 141.6 parts of silver iodobromide (in which the ratio of silver iodide to silver bromide was 1:23.7) in the presence of 11 parts in aqueous solution of the copolymer of methacrylamide and N,2-methylacrylamidoethyl-N,N-dimethyl- β -aminopropionate betaine prepared as described in Example 3 above. After precipitation, Ostwald "ripening" was carried out in the presence of excess bromide ion and ammonia. Thereafter, an additional portion of 40 parts of the same copolymer was added as a 10% aqueous solution and the polymer after thorough mixing, was precipitated by the addition of a large excess of acetone. The precipitated copolymer containing the silver halide was washed with aqueous methanol, then redissolved in a 10% aqueous solution of 169 additional parts of the same copolymer, and digested with the conventional additions of water, sensitizing, and dispersing agents, etc. being made after which it was coated on a paper support and dried.

A similar emulsion was made in gelatin as the sole binding agent as described in Example 1 above and this emulsion was also coated on paper and dried. When samples of these two papers were exposed in a negative type 1B sensitometer, developed, fixed, washed and dried under identical conditions the relative photographic speed of the product made with gelatin was 200 compared with that made with the copolymer which was 100, and was characteristic of currently available high-speed negative type photographic emulsions.

Example 7

The procedure of Example 6 was repeated with the exception that a copolymer of methacrylamide and N,3-methacrylamidopropyl-N,N-dimethyl- β -aminopropionate betaine of the same composition as that described in Example 2 above was used instead of the copolymer described in Example 6.

The photographic speed of the product of this experiment was somewhat lower than that of Example 6, being that of a low-speed negative type emulsion.

Example 8

The procedure of Example 6 was repeated with a mixed polyvinyl acetal of orthosulfobenzaldehyde and N-m(3-methylsalicylamido)benzaldehyde similar to that described in U. S. Patent No. 2, 489,655, but containing 20 to 30% of each of the two aldehyde residues, used to replace those portions of the polymer described in Example 6 that were employed after the "ripening" of the silver halide was completed. Because this polyvinyl acetal

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is gellable by use of borate ion as a cross-linking agent, this emulsion was coated on a support having a layer containing a borate ion as described in U. S. Patent 2,534,326.

A similar emulsion was made in which the precipitating and "ripening" of the silver halide was done in the presence of 11 parts of gelatin rather than in the copolymer described in Example 6. The remainder of the procedure was as described in that example. When samples of these two films were exposed in a sensitometer, and processed according to the procedure described by Jennings et al., Journal of the Society of Motion Picture and Television Engineers, volume 55, pages 469 through 471, November 1950, they had the same photographic speed, and the saturation and hue of their photographic images were indistinguishable.

Example 9

The procedure of Example 6 was repeated with the exception that the copolymer used during precipitation and "ripening" of the silver halide was the one used for this purpose in Example 1 and the copolymer used for that purpose in Example 5 was used in place of both portions of copolymer after Ostwald "ripening" as described in Example 6. Because the polymer of Example 5 was borate-gellable, this emulsion was coated on a borate-subbed support such as that described in Example 8.

An all gelatin emulsion of the type described in paragraph 2 of Example 1 was also prepared. When samples of these two films were exposed in a type 1B sensitometer and developed, fixed, washed, and dried the same way, the relative photographic speed of the all-gelatin film was shown to be 141 as compared with the relative speed of the polymer film of 100.

Example 10

The procedure of Example 7 was repeated with the exception that a copolymer of methacrylamide and N,2,3-dihydroxypropyl-methacrylamide, prepared as described in Table 1, Experiment 2 of Example 1 of U. S. application Ser. No. 415,162, filed March 9, 1954, except that the solvent for the polymerization consisted of a mixture of 375 parts of water and 98.3 parts of isopropyl alcohol, and the relative viscosity of 1% aqueous solutions of the resulting polymer at 30° C. and pH 7 was 1.21, was used instead of the copolymer described in Example 6.

The photographic speed of the product obtained in this experiment was essentially the same as that obtained in Example 8.

Example 11

The procedure of Example 10 was repeated with the exception that the methacrylamide copolymer described in Example 5 was used instead of that mentioned in Example 10. The photographic speed of the product obtained here was similar to that reported in Example 7.

Example 12

A photographic emulsion was prepared by precipitating by means of aqueous silver nitrate, ammonium bromide, potassium bromide and potassium iodide solutions from aqueous solution, 140.8 parts of silver iodobromide (in which the ratio of silver iodide to silver bromide was 1:50.1) in the presence of 24 parts in aqueous solution of a copolymer of methacrylamide and N,2-methacrylamidoethyl-N,N-dimethyl- β -aminopropionate betaine, prepared as described in Example 1 of U. S. application Ser. No. 415,163, filed March 9, 1954. After precipitation, Ostwald "ripening" was carried out in the presence of excess bromide ion and ammonia. Thereafter, 182.5 parts of gelatin was added and dissolved in the mixture. The emulsion was then cooled to form a firm gel, broken up and washed with water to remove soluble compounds. The washed gel was melted, and digested with the conventional addi-

tions of water, sensitizing and dispersing agents, hardeners, etc., being made after which it was coated on a cellulose acetate support and dried.

A similar emulsion was made in the identical fashion with the exception that 24 parts of gelatin was substituted for the 24 parts of the copolymer used during the precipitation and "ripening" stage and this emulsion was also coated on a cellulose acetate support and dried. When samples of the two films were exposed in a positive type 1B sensitometer, developed, fixed, washed and dried under identical conditions, the relative photographic speed of the film containing the copolymer was 213 compared with the gelatin control whose relative speed was 207 and was equal to that which is characteristic of currently available highest speed cine positive films.

Still other soluble polyamides of the type disclosed in U. S. application Ser. Nos. 415,161, 415,162 and 415,163 can be employed as protective colloid, bulking and binding agent for the silver halide in place of or in addition to those described in the foregoing examples. Among such compounds may be mentioned:

Poly(methacrylamide co N,2,3-dihydroxypropylacrylamide co N,2-acrylamidoethyl-N,N-dimethyl-β-amino-propionate betaine)

Poly(methacrylamide co N,2,3-dihydroxypropylacrylamide co N,3-methacrylamidopropyl-N,N-dimethyl-aminoacetate betaine)

Poly(methacrylamide co N,2,3-dihydroxypropylmethacrylamide co N,2-acrylamidoethyl-N,N-dimethylaminoacetate betaine)

Poly(methacrylamide co N,2-methacrylamidoethyl-N,N-dimethylaminoacetate betaine)

Poly(methacrylamide co N,3-methacrylamidopropyl-N,N-dimethylaminoacetate betaine)

Poly(methacrylamide co N,2-methacrylamidoethyl-N,N-diethylaminoacetate betaine)

Poly(methacrylamide co N,3-methacrylamidopropyl-N,N-diethylaminoacetate betaine)

Poly(methacrylamide co N,3-acrylamidopropyl-N,N-dimethyl-β-aminopropionate betaine)

Poly(methacrylamide co N,2-acrylamidoethyl-N,N-dimethyl-β-aminopropionate betaine)

Poly(methacrylamide co N,2-acrylamidoethyl-N,N-dimethylaminoacetate betaine)

Poly(methacrylamide co N,3-acrylamidopropyl-N,N-diethylaminoacetate betaine), and

Poly(methacrylamide co N,2,3-dihydroxypropylacrylamide)

In all of the above examples in which a hydroxylated polymer was used, great improvement in the toughness, permanence, resistance to abrasion was obtained by cross-linking the copolymer by treatment with solutions of the titanium compounds described in U. S. application Ser. No. 433,286, filed May 28, 1954.

The invention is not limited to the specific light-sensitive materials described in the above detailed examples. On the contrary, various other simple and mixed silver halides may be used as the light-sensitive materials in like manner. Mixtures of silver bromide, chloride and/or iodide can be made by adding mixtures of soluble salts of these halides in like manner. Other useful soluble halides include potassium bromide, potassium iodide, sodium, potassium and ammonium iodides, chlorides and bromides, etc. Other useful soluble silver salts include silver sulfamate, silver sulfate, silver citrate and silver acetate.

During the digestion stage or prior thereto, various types of sensitizing agents, e. g., sulfur sensitizers, such as allylthioureas, thiocyanates, thiosulfates, allylthiocyanates, and other organic or inorganic sulfur sensitizers can be added. In addition, various metal sensitizers may also be added, such as those normally used in gelatin emulsions and known to those skilled in the art of photographic emul-

sion manufacture. In addition, various types of optical sensitizing dyes which modify the spectral characteristics of the resulting emulsions can be added. Suitable sensitizing dyes are described in U. S. Patents 2,010,388, 2,079,376, 2,202,990, 2,202,991, 2,202,992, 2,278,461, 2,265,908, etc. Similarly desensitizing dyes can be used when it is desired to make fogged emulsions for direct positives.

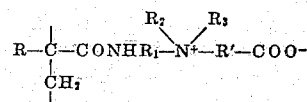
Various types of color forming aldehydes may be used in forming the polyvinyl acetals used in certain specific embodiments of this invention. Suitable such aldehydes and polyvinyl acetals are described in U. S. Patents 2,476,986, 2,476,987, 2,476,988, 2,472,910, 2,518,704, 2,538,259, 2,513,190, 2,513,189. Noncolor forming aldehydes may also be used in preparing these polyvinyl mixed acetals such as, for example, ortho-sulfo-benzaldehyde, benzaldehyde, p-hydroxybenzaldehyde, etc.

The synthetic polyamides described above are completely free from sulfur, metal, and other sensitizing materials, yet allow the preparation of silver halide grains of such type that these sensitizing materials can be added at or prior to the digestion stage in the emulsion manufacture and still exert their full sensitizing effects.

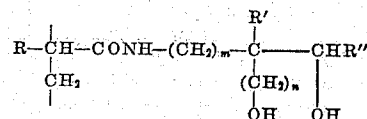
An important advantage of the invention is that it provides photographic emulsions having the high-speed characteristics desirable in negative films. Another advantage is that silver halide emulsions of uniform characteristics can be made readily. A further advantage is that the use of the synthetic polyamides described above admit of the precipitation and growth of silver halide grains which are potentially as sensitive to light as the high-speed negative emulsions made with gelatin. Still other advantages will be apparent from the above description of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

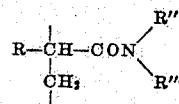
1. An emulsion of light-sensitive silver halide in a water-permeable colloid binding agent wherein at least 2% by weight is an addition copolymer having hydrophilic properties composed solely of a substantial number of recurring intralinear units of (a) at least one type of unit taken from the group consisting of those of formulae:



wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent, aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated divalent, aliphatic hydrocarbon radical of 1 to 4 carbon atoms, and



wherein R is a member taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, R' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, R'' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, m is a cardinal number from 0 to 4, n is a cardinal number from 0 to 1 and the sum of m and n equals at least 1 and (b) at least one type of unit of the formula:



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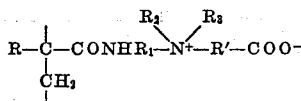
wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, said unit (a) being present in an amount of at least 5 mol percent.

2. An emulsion as set forth in claim 1 wherein substantially 100% of the binding agent is selected from the group of copolymers recited in claim 1.

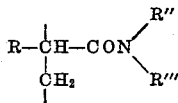
3. An emulsion as set forth in claim 1 wherein the rest of the binding agent is gelatin.

4. An emulsion as set forth in claim 1 wherein the rest of the binding agent is a polyvinyl acetal.

5. An emulsion of light-sensitive silver halide in a water-permeable colloid binding agent wherein at least 2% by weight is an addition copolymer having hydrophilic properties composed solely of a substantial number of intralinear units of the formulae:



wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent, aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated divalent, aliphatic hydrocarbon radical of 1 to 4 carbon atoms, and



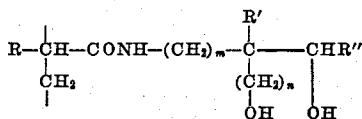
wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, wherein the first type of unit is present in the amount of 5 to 80 mol percent.

6. An emulsion as set forth in claim 5 wherein substantially 100% of the binding agent is selected from the group of copolymers recited in claim 5.

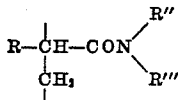
7. An emulsion as set forth in claim 5 wherein the rest of the binding agent is gelatin.

8. An emulsion as set forth in claim 5 wherein the rest of the binding agent is a polyvinyl acetal.

9. An emulsion of light-sensitive silver halide in a water-permeable colloid binding agent wherein at least 2% by weight is an addition copolymer having hydrophilic properties composed solely of a substantial number of intralinear units of the formulae:



wherein R is a member taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, R' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, R'' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, m is a cardinal number from 0 to 4, n is a cardinal number from 0 to 1 and the sum of m and n equals at least 1, and



wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, wherein the first type of unit is present in the amount of 10 to 70 mol percent.

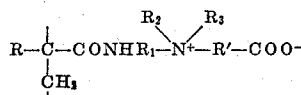
10. An emulsion as set forth in claim 9 wherein substantially 100% of the binding agent is selected from the group of copolymers recited in claim 9.

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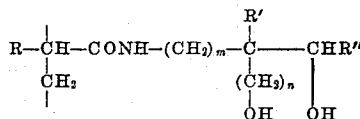
11. An emulsion as set forth in claim 9 wherein the rest of the binding agent is gelatin.

12. An emulsion as set forth in claim 9 wherein the rest of the binding agent is a polyvinyl acetal.

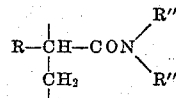
13. An emulsion of light-sensitive silver halide in a water-permeable colloid binding agent wherein at least 2% by weight is an addition copolymer having hydrophilic properties composed solely of a substantial number of intralinear units of the formulae:



15 wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent, aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated divalent, aliphatic hydrocarbon radical of 1 to 4 carbon atoms, and



wherein R is a member taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, R' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, R'' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, m is a cardinal number from 0 to 4, n is a cardinal number from 0 to 1 and the sum of m and n equals at least 1, and



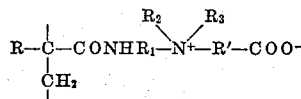
wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, wherein the types of units are in the proportions of 5 to 60, 5 to 60 and 30 to 90 mol percent respectively.

14. An emulsion as set forth in claim 13 wherein substantially 100% of the binding agent is selected from the group of copolymers recited in claim 13.

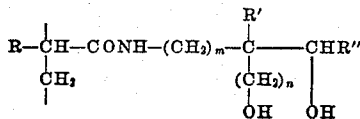
15. An emulsion as set forth in claim 13 wherein the rest of the binding agent is gelatin.

16. An emulsion as set forth in claim 13 wherein the rest of the binding agent is a polyvinyl acetal.

17. The process which comprises precipitating light-sensitive silver halide in an aqueous solution containing an addition copolymer having hydrophilic properties composed solely of a substantial number of recurring intralinear units of (a) at least one type of unit taken from the group consisting of those of formulae:



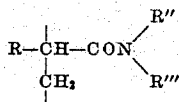
wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent, aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated divalent, aliphatic hydrocarbon radical of 1 to 4 carbon atoms, and



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wherein R is a member taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, R' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, R'' is a member taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms, m is a cardinal number from 0 to 4, n is a cardinal number from 0 to 1 and the sum of m and n equals at least 1 and (b) at least one type of unit of the formula:



wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, said unit (a) being present

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in an amount of at least 5 mol percent, ripening the emulsion, coagulating the emulsion, washing the coagulum and admixing additional water-permeable colloid with the washed emulsion.

18. A process as set forth in claim 17 wherein said colloid is gelatin.

19. A process as set forth in claim 17 wherein said colloid is a polyvinyl acetal.

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