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PHOTOGRAPHIC SILVER HALIDE EMULSIONS OF SYNTHETIC POLYMERS

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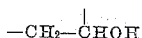
13 Claims. (Cl. 95-7)

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This invention relates to photographic silver halide emulsions.

In the manufacture of photographic silver halide emulsions, which are dispersions of crystalline, light-sensitive silver halides protected by hydrophilic colloids, the most commonly used protective colloid is gelatin. While gelatin has many advantages which contribute to its successful use in photographic emulsions, it has a number of undesirable properties. For example, it is brittle, unstable, susceptible to the action of mold, fungi and bacteria, especially under conditions of high humidity, and cannot be processed in warm water unless given special treatment. Furthermore, gelatin is derived from natural sources and hence is subject to considerable variations in its properties. In particular, the properties vary with the source of the raw material and the particular treatment to which it is subjected during isolation. Therefore, gelatin for use in photographic emulsions always requires careful and extensive purification procedures to make it satisfactory for use in this application.

Other polymeric materials have been proposed for use as the protective colloid in photographic emulsions in order to avoid the defects of gelatin. The most promising of these new materials are synthetic, hydroxylated polymers containing as recurring intralinear units the group

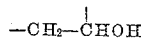


such as polyvinyl alcohol. However, such synthetic, hydroxylated polymers have the disadvantage of forming silver halide emulsions of small particle size and low photographic speed. Such emulsions have been subjected to conventional ripening processes in attempts to improve their photographic properties. Some of the procedures which have been tried involve boiling the emulsion for several hours under acidic conditions, and, when nitrogenous bases such as ammonia or ethylenediamine are present heating has been carried out at moderate temperatures, e. g., 50-60° C. or lower. These treatments, which have been based on conventional gelatin emulsion technology, where it has been established that ripening temperatures must be held below 50° C. when an alkaline material is present in order to avoid fogging of the emulsion and hydrolysis of gelatin, have not, however, been capable of producing synthetic, hydroxylated polymer emulsions with the high photographic speed desired for use as negative emulsions. This deficiency of the synthetic, hydroxylated polymers as binders in photographic emulsions has apparently retard-

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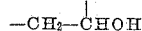
ed their commercial use in high speed emulsions up to the present time even though such binders, particularly polyvinyl alcohol, have been proposed for many years.

It has now been found that high speed photographic silver halide emulsions which are free from the disadvantages of gelatin emulsions, can be prepared by this invention which involves subjecting to temperatures of above 80° C. light-sensitive silver halides dispersed in a synthetic hydroxyl-containing polymer having a plurality of intralinear



groups as recurring units in the presence of a nitrogenous base in concentrations of between 0.1 and 2.5N. Several procedures can be used in carrying out the process of this invention, all of which involve treatment of the emulsions at temperatures of above 80° C. in the presence of the concentration of the nitrogen base specified above. This treatment of the emulsions at unconventionally high temperatures in the presence of the nitrogen base has been found to result in the formation of silver halide/hydroxylated polymer emulsions having the requisite large particle sizes to give high photographic speed.

One method, which involves precipitating the silver halides in the presence of a nitrogen base at high temperature, is especially suitable for the preparation of emulsions containing as the silver halide binder a synthetic, linear hydroxylated polymer containing a plurality of intralinear



groups having a minor amount of acetal substitution. In this process the precipitation of the silver halide is carried out in the presence of a concentration of a nitrogen base preferably ranging from 0.9 to 1.4N at a temperature of between 80° and 100° C. The precipitation of the silver halide may be carried out in any of several ways, among which are: (a) the simultaneous addition of the soluble silver salt and soluble halide solutions, e. g., an aqueous solution of silver nitrate and an aqueous solution of a mixture of ammonium bromide and potassium iodide, to a solution of the synthetic, hydroxyl-containing polymer; (b) the addition of the soluble silver salt solution to a solution containing both the soluble halide and the polyvinyl acetal binder; (c) the addition of soluble halide to the combined silver and synthetic, hydroxyl-containing polymer solutions; and, (d) the addition of the silver solution in

portions at different temperatures to a solution of a mixture of soluble halide and the synthetic, hydroxyl-containing polymer. In the precipitation procedures just described, the nitrogen base may be included in the silver salt, soluble halide, or hydroxyl-containing polymer solution. After the precipitation of the silver halide particles is complete, the emulsion is held at a temperature of 80° to 100° C. for a short period to complete the development of the desired silver halide grain size. Periods of time ranging from 1 to 30 minutes are generally sufficient for such heat treatment but periods up to two hours can be used. After cooling to about 30° C., the emulsion is coagulated, for example, by forcing the emulsion in a fine stream into a 15% aqueous sodium sulfate solution. The coagulum is then washed free of soluble salts after which it is redissolved by stirring it into a mixture of alcohol and water at a temperature of about 75° C. Additional synthetic hydroxyl-containing polymer solution is conveniently added at this time to bring the emulsion to a viscosity suitable for coating on a support such as paper or film. Other finishing ingredients, e. g., triethanolamine and C-cetylbetaine can also be incorporated in the emulsion at this stage.

Another method of carrying out the process of this invention involves the heat treatment of a previously precipitated emulsion. In this process the silver halide is precipitated in a solution of the synthetic, hydroxylated polymer in the presence of 0.9 to 1.4N nitrogen base at temperatures from about 20° to 30° C., and the resulting precipitate is then subjected to a ripening step at a temperature of between 80° and 125° C., preferably between 90° and 110° C., without removal of soluble salts and nitrogen base, or the addition of other materials. Ripening times ranging from 1 to 30 minutes at such temperatures are usually sufficient to develop silver halide grains of the desired particle size, but ripening times up to ten hours can be used. After ripening is completed, the emulsion is coagulated, washed, redissolved, and finished as in the preceding embodiment.

In still another exemplary method the silver halide/synthetic hydroxylated polymer emulsion is subjected to the heat treatment in the presence of the nitrogen base after the silver halide is precipitated, the emulsion coagulated, and the coagulum washed free of excess soluble salts. The washed coagulum is mixed with an amount of a nitrogen base, e. g., triethanolamine, ranging between 0.1 and 1.4N based on the total emulsion, and, if desired, a small amount of a surface-active agent, e. g., C-cetylbetaine, and the emulsion digested at temperatures up to 200° C., preferably at 150° to 200° C. In this embodiment of the invention, the lower concentrations of nitrogen base within the limits specified above are preferred. Digestion periods of 1 to 30 minutes at temperatures of 150° to 200° C. are usually sufficient to produce silver halide grains of the desired particle size, but when digestion temperatures of 80° to 150° C. are used times up to ten hours are required. After digestion is complete, the emulsion is cooled and brought to the desired coating viscosity by the incorporation of additional synthetic, hydroxylated polymer solution. At this stage the desired finishing agents can also be incorporated in the emulsion.

As evident from the above descriptions of the different embodiments of this invention, the process conditions can be varied considerably within

the specified limits. The optimum temperature and time to which the silver halide/synthetic hydroxylated polymer emulsion is to be subjected to develop the desired silver halide grain size, however, are somewhat interrelated and are also dependent on the concentration of the nitrogen base. In general, heating times ranging from one minute to ten hours can be employed. Usually heat treatments at the higher temperatures within the ranges specified above are carried out for the shorter times and in the presence of the lower concentrations of nitrogen base. By way of illustration, precipitation or ripening steps carried out at 80° to 90° C. in the presence of 0.9 to 1.4N ammonia are continued for several hours. However, when temperatures of 90° to 95° C. are employed with the same concentration of ammonia, periods of only 15 to 30 minutes are sufficient and when ammonia concentrations of 2.5N are used still shorter times are sufficient. At temperatures of 100° to 125° C. and with 0.9 to 1.4N ammonia, ripening periods of 5 to 15 minutes are usually employed. When the coagulated and washed emulsion is subjected to a digestion treatment at 150° to 200° C. in the presence of a nitrogen base in concentrations of 0.1 to 1.4N, periods of 1 to 30 minutes are satisfactory, the 30-minute digestion being necessary only with very low concentrations of base, e. g., 0.1 to 0.5N.

The process of this invention has the commercial advantage that it is capable of producing a silver halide/synthetic, linear, hydroxylated polymer emulsion having photographic speeds suitable for use as negative-type coatings. The negative-type, hydroxylated polymer emulsions produced by the process of this invention are unique in the photographic art. These emulsions are characterized by having silver halide grains with a root mean square diameter of from 0.6 to 3.0 microns.

The invention is illustrated further by the following examples in which the proportions of the ingredients are expressed in parts by weight unless otherwise specified and in which all radiations which will expose or fog the light-sensitive silver halides are excluded.

EXAMPLE I

A solution of a completely hydrolyzed vinyl acetate/ethylene copolymer of mole ratio 25:1 (prepared as described in Example II of U. S. P. 2,397,866) in aqueous ethanol is prepared in the polymer/ethanol/water weight ratio of 10/10/80. The following solutions are then prepared.

Solution A

3N aqueous silver nitrate solution	-----ml---	70
20% aqueous ammonium hydroxide	---ml---	42

Solution B

3N aqueous ammonium bromide solution	ml---	74
0.5N aqueous potassium iodide solution	ml---	12
Distilled water	-----m---	26
Above-described polymer solution	-----g---	140

Solutions A and B are heated to 95° C. and Solution A is added to B with stirring over a period of nine minutes. After precipitation of the silver halide is complete the emulsion is stirred for an additional five minutes at 95° C., then cooled and washed by dialysis (as described in Example I of U. S. application Ser. No. 726,961, filed February 6, 1947, by C. F. Glick), until the conductivity of the emulsion is 120 micromhos. Another 140

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grams of the above-described polymer solution is added with stirring to the dialyzed emulsion. To one-half of the emulsion is added six milliliters of a 20% aqueous solution of triethanolamine and 3.5 milliliters of a 3% aqueous solution of C-cetylbetaine. The emulsion is finally adjusted to proper coating viscosity by the addition of 10% aqueous ethanol, and then coated on cellulose nitrate film which has previously been given a subcoating of vinylpyridine polymer as described in U. S. P. 2,448,525. When dry, the resulting film is exposed to tungsten light through a step tablet, developed in a solution containing:

	Grams
N,N - diethyl - p - phenylenediamine hydrochloride	2.5
Sodium sulfite (anhydrous)	10.0
Sodium carbonate (monohydrated)	29.25
Potassium bromide	2.0
Water to make 1.0 liter.	

fixed for a period of ten minutes in a 25% sodium thiosulfate solution, washed and dried.

Sensitometric measurements show the emulsion of the above example has about eight times the speed of one prepared from the same ingredients but precipitated at 25° C., and ten times the speed of an unsensitized gelatin print film. The silver halide grain size of the emulsion of the above example is 0.6 micron root means square diameter. The grain size of the silver halide emulsion precipitated at 25° C. is only 0.25 micron. An emulsion prepared in the same way as that of Example I, except that precipitation is carried out at 78° C. instead of 95° C., contains silver halide grains having about the same root means square diameter as those precipitated at 25° C., and the emulsion has a speed about the same as the emulsion precipitated at 25° C.

EXAMPLE II

A photographic emulsion is prepared from the same ingredients and in the same manner as described in Example I except that the precipitation is performed at 25° C. One-half of the resulting emulsion is placed in a sealed container and heated with stirring at 110° C. for ten minutes. The ripened emulsion is cooled, washed by dialysis as described in Example I to a conductivity of 350 micromhos and finished by the addition of 70 grams of polymer solution and the coating aids as in Example I. The emulsion is coated on film base, exposed and processed as in Example I.

Sensitometric tests show that the emulsion of Example II, ripened at 110° C., has about 20 times the speed as the other half of the emulsion which was finished and coated on film base without the high temperature ripening step.

EXAMPLE III

A photographic emulsion containing a polyvinyl alcohol containing a minor amount of acetal substitution as the binder for the silver halide particles is prepared as follows. Fifty grams of a polyvinyl alcohol containing minor amounts of acetal groups of m-[p-(5-ethylcarbonato - 3 - methyl - 5 - pyrazolyl) - benzamido] - benzaldehyde (prepared as described in Example III of U. S. P. 2,476,988) is dissolved by heating 20 minutes at 80° C. in 190 milliliters of ethanol and 450 milliliters of water containing two milliliters of 10% KOH solution. The solution is filtered and made up to 667 grams with 30%

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aqueous ethanol. The following solutions are then prepared:

Solution A

5	3N aqueous AgNO ₃	ml.	60
	20% aqueous NH ₄ OH	ml.	60
	Distilled water	ml.	75

Solution B

10	3N aqueous NH ₄ Br	ml.	66
	0.5N aqueous KI	ml.	12
	Distilled water	ml.	42
	Ethanol	ml.	75

Solution C

15	Low-substituted polyvinyl acetal solution (described above)	g.	120
	Distilled water	ml.	120
	Ethanol	ml.	60

20 The solutions are maintained at 25° C. and Solutions A and B are added separately and simultaneously (B leading A slightly) to C with stirring within a period of eight minutes. Following completion of precipitation the emulsion is stirred for an additional ten minutes at the same temperature. Seventy-five milliliters of ethanol is then added. One-half of the emulsion is placed in a sealed container and heated with stirring at 95° C. for three minutes. Following ripening, 25 milliliters of ethanol is added and the emulsion is washed by dialysis as in Example I until the conductivity is 500 micromhos. One hundred and fifty-four grams of the low-substituted polyvinyl acetal solution is then mixed into the emulsion. To one-half of the emulsion is added 4.2 milliliters of a 20% aqueous solution of triethanolamine and 2.1 milliliters of a 2% aqueous solution of C-cetylbetaine. The emulsion is then adjusted to suitable coating viscosity and coated on film base as in Example I.

After drying, the photographic film coated with the emulsion of Example III is exposed and processed as in Example I except that following development the film is fixed in a solution consisting of:

		Grams
	Sodium thiosulfate.....	80
	Sodium sulfite (anhydrous).....	5
	Borax	6
50	Acetic acid (glacial).....	4
	Water to make 1 liter.	

After fixing, the film is washed and bleached in a solution containing 60 grams of potassium ferricyanide, 10 grams of boric acid, 5 grams of borax, and water to make one liter. After bleaching, the film is washed, fixed in 25% sodium thiosulfate solution, washed and dried. The film then carries a magenta image.

Sensitometric tests show the speed of the ripened emulsion of Example III to be about 500 times greater than that of an emulsion prepared in the same way with the single exception that the ripening step at 95° C. is omitted. The silver halide particles in the ripened emulsion of Example III have a root mean square diameter of 2.25 microns; whereas, the silver halide grain size of the unripened emulsion is only 0.1 to 0.2 micron root mean square diameter.

EXAMPLE IV

A photographic emulsion containing another polyvinyl alcohol having a minor amount of acetal substitution as binder for the silver halide particles is prepared as follows. Fifty grams of a low-substituted polyvinyl acetal of m-benzoyl-

acetamidobenzaldehyde (prepared as described in U. S. application Ser. No. 9330, filed February 18, 1948, now U. S. Patent 2,513,190), is dissolved by heating 25 minutes at 80° C. in 165 milliliters of ethanol and 285 milliliters of water. Two milliliters of a 10% aqueous KOH solution is added and heating is continued for five minutes longer after which the solution is cooled and made up to 500 grams with 30% aqueous ethanol. The following solutions are prepared for use in making the silver halide emulsions:

Solution A

3N aqueous AgNO ₃	ml.....	20
20% aqueous NH ₄ OH.....	ml.....	20
Distilled water.....	ml.....	25

Solution B

3N aqueous NH ₄ Br.....	ml.....	22
0.5N aqueous KI.....	ml.....	4
Distilled water.....	ml.....	14
Ethanol.....	ml.....	25

Solution C

Low-substituted polyvinyl acetal solution (described above).....	g.....	30
Distilled water.....	ml.....	45
Ethanol.....	ml.....	25

Solutions A and B are added separately and simultaneously (B leading A by two parts) to Solution C over a period of 14 minutes while stirring at 25° C. The emulsion is stirred 15 minutes after the completion of the precipitation and then 50 milliliters of ethanol is added. The emulsion is placed in a sealed container and ripened by stirring at 105° C. for 7½ minutes, cooled and washed by dialysis as in Example I. At the completion of the dialysis most of the emulsion has coagulated and has settled out. The coagulum is redissolved by heating 15 minutes at 65° C. with 150 milliliters of 25% aqueous ethanol, then an additional 100 grams of the low-substituted polyvinyl acetal solution is added and heating is continued 15 minutes longer. The emulsion is then prepared for coating and coated on film base as in Example I.

The dry film is exposed and processed as in Example III, giving a yellow image.

Sensitometric measurements show the speed of the emulsion to be about nine times that of an emulsion prepared from the same ingredients and in the same manner with the single exception that the ripening at 105° C. is omitted. The silver halide particle size of the ripened emulsion of Example IV is 1.48 microns root mean square diameter; whereas, the grain size of the unripened emulsion is only 0.23 micron root mean square diameter.

EXAMPLE V

A photographic emulsion having still another partial acetal of polyvinyl alcohol as the silver halide binder is prepared by a procedure similar to that described in Example IV. Thirty grams of a low-substituted polyvinyl acetal of m-(3-methyl-salicylamido)benzaldehyde (prepared as described in U. S. application Ser. No. 29,921, filed May 28, 1948, U. S. Patent 2,538,257) is dissolved by stirring at 80° C. for 25 minutes in 90 milliliters of ethanol and 210 milliliters of water. To this solution 9.5 milliliters of 10% aqueous KOH solution is added and the heating continued for an additional five minutes. The resulting solution is made up to 300 grams by the addition of 30% aqueous ethanol. The photographic

emulsion is prepared from the same solutions described in Example IV with the exception that the polyvinyl acetal solution of Solution C in Example IV is replaced with the same quantity of the above-described polyvinyl acetal solution. At the completion of the precipitation 75 milliliters of ethanol is added and the emulsion placed in a sealed container and ripened by heating for 7½ minutes at 105° C. with stirring. Fifty milliliters of ethanol is added after the ripening step and the emulsion is washed by dialysis as in Example I. The emulsion coagulates, and the coagulum is redissolved as described in Example IV, then finished and coated on film base in the manner described in that example. Exposure to light and processing as in Example IV yields a film having a cyan image.

Sensitometric measurements of the film of the above example show it to have about 450 times the speed of a film prepared from an unripened emulsion. The silver halide grain size in the emulsion of Example V is 0.65 micron root mean square diameter. The grain size of the unripened emulsion is only 0.11 micron root mean square diameter.

EXAMPLE VI

The following solutions are prepared:

Solution A

3N aqueous AgNO ₃	ml.....	35
20% aqueous ammonium hydroxide.....	ml.....	30

Solution B

3N aqueous NH ₄ Br.....	ml.....	37
0.5N aqueous KI.....	ml.....	6
Distilled water.....	ml.....	22

Solution C

10% aqueous polyvinyl alcohol (completely hydrolyzed low molecular weight polyvinyl acetate) solution.....	g.....	20
Distilled water.....	ml.....	80

Solutions A and B are added separately and simultaneously (B leading A by two parts) to Solution C at 25° C. while stirring over a period of six minutes. The emulsion is then ripened for 15 minutes at 100° C. in a sealed container. Following ripening, 100 grams of a 10% solution of a completely hydrolyzed high molecular weight polyvinyl acetate is added, and the emulsion is washed, prepared for coating as in Example I, and coated on film base. After drying, the film is exposed and processed as in Example I.

The film of Example VI has a photographic speed of 50 to 100 times that of a film coated with an emulsion prepared with the same type of polyvinyl alcohol binder but ripened under acidic conditions. The size of the silver halide grains in the emulsion of Example VI is 2.0 microns root mean square diameter. Furthermore, an emulsion prepared in the same manner as Example VI with the single exception that the ammonia is omitted from the silver nitrate solution has a silver halide grain size of only 0.04 micron root mean square diameter and this grain size remains unchanged on ripening at 100° C. for 15 minutes.

EXAMPLE VII

A photographic emulsion is prepared by precipitating silver halide at a high temperature in the polyvinyl acetal binder of Example IV. Ten grams of the low-substituted polyvinyl acetal of m-benzoyl-acetamidobenzaldehyde is stirred at 80° C. for 15 minutes in a mixture of 24 milliliters

of ethanol, 171 milliliters of water, and 1 milliliter of 7.5% aqueous NaHCO_3 solution. The following solutions are then prepared for use in forming the emulsion:

Solution A

3N aqueous AgNO_3 -----	ml.---	29
20% aqueous NH_4OH -----	ml.---	29
Water -----	ml.---	7

Solution B

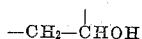
3N aqueous NH_4Br -----	ml.---	31
0.5N aqueous KI -----	ml.---	2
Water -----	ml.---	32

Solution C

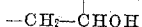
Low-substituted polyvinyl acetal solution described above)-----	g.---	103
Ethanol -----	ml.---	25

Solutions A and B are run separately and simultaneously into Solution C while stirring at 95° C. The emulsion is maintained at 95° C. for ten minutes after completion of precipitation. The emulsion is then coagulated by pumping it through a capillary into 15% aqueous Na_2SO_4 solution. The coagulum is broken up and washed in running water for one hour, after which it is redissolved by stirring at 75° C. for 15 minutes with 25 milliliters of ethanol made up to 100 milliliters with water. The remainder (103 grams) of the polyvinyl acetal solution is then added, and heating is continued for 15 minutes more. The emulsion is finished and coated on film base as described in Example IV. After drying, the photographic film is exposed and processed as in Example IV. Sensitometric tests of the resulting film show that the emulsion is approximately 1,000 times as fast as one prepared from the same ingredients and in a similar manner with the single exception that the precipitation of the silver halide was carried out at 20° C.

The examples have illustrated the process of this invention by referring to certain hydroxylated polymers as the polymeric binders for the silver halide particles; however, other synthetic, linear, hydroxylated polymers can be used. Synthetic hydroxylated polymers which are operable include film-forming polymers which contain as the predominant hydrophilic group a plurality of recurring vinyl alcohol,



units. Polyvinyl alcohol and its partially substituted esters, ethers and acetals are especially useful polymers of this type. Polyvinyl alcohol is a tough, water-white, polymeric material which is soluble in water. The more highly polymerized varieties are soluble in hot water, and the lower polymers are soluble in cold water. They are usually prepared by hydrolysis of polyvinyl esters, such as polyvinyl acetate, and polyvinyl isobutyrate, etc. The partially hydrolyzed esters which contain a large number of recurring vinyl alcohol,

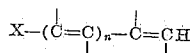


units are hydrophilic in character. The ethers can be made by incompletely etherifying completely or partially hydrolyzed polyvinyl acetate, etc. In addition to the synthetic hydroxylated polymers just described, there may be also used the partially and completely hydrolyzed vinyl ester, e. g., vinyl acetate, copolymers with ethylenically unsaturated compounds such as vinyl

chloride and styrene; and monoolefins, e. g., ethylene. Hydrolyzed ethylene/vinyl acetate copolymers are especially useful types of such copolymers. Hydrolyzed ethylene/vinyl acetate copolymers containing less than 10% ethylene are hydrophilic and form highly suitable polymeric binders in the process of this invention.

An indicated above the low-substituted polyvinyl acetals, i. e., polyvinyl alcohol having less than about 13% of its hydroxyl groups substituted as acetals, are especially preferred as the synthetic, hydroxyl-containing polymer binders of this invention. These acetals can be made by acetalization of polyvinyl alcohol and its completely hydrolyzed carboxylic esters. Examples of such acetals are polyvinyl alcohols whose hydroxyl groups are partially substituted as acetals by acetaldehyde, benzaldehyde, 2-thiophene aldehyde, m-acetamidobenzaldehyde, m-aminobenzaldehyde, succinaldehydic acid, butyraldehyde, and p-diethylaminobenzaldehyde.

Synthetic, hydroxylated polymers containing small amounts of color-forming acetal groups are especially suitable as the silver halide binder. These are more precisely defined as essentially colorless, synthetic, linear, hydroxylated polymers, 0.75 to 7.5% of whose hydroxyl groups are substituted as acetals by color-former nuclei with the structure



where X is a member of the group consisting of hydroxyl and primary and secondary amino radicals, n having a value of 0 or 1, and which may be 0.1 to 5.2% substituted as acetals by aldehydes containing carboxylic or sulfonic acid groups, said polymers containing at least 12.5 but less than 49 hydroxyl groups for every 100 chain atoms and between 1 and 35 color-forming groups for each 100 chain atoms and a polymer chain in excess of 200 carbon atoms. In addition to the specific polyvinyl acetals of this type mentioned in Examples III, IV, V and VII other polyvinyl acetal color-formers having a maximum of 7.5% of the hydroxyl groups substituted as acetals by the color-former nuclei which can be used include polyvinyl acetals of m-[p-(5-benzoxo-3-methyl-1-pyrazolyl)benzamido]benzaldehyde, as described in U. S. application Ser. No. 682,137, U. S. Patent 2,476,988; m-(p-chlorobenzoylacetamido)benzaldehyde, and 4-methyl-3-(benzoylacetamido)benzaldehyde, as described in U. S. application Ser. No. 9330, U. S. Patent 2,513,190; and other m-(methylsalicylamido)benzaldehydes, as described in U. S. application Ser. No. 29,921, U. S. Patent 2,538,257.

The light-sensitive silver salts mentioned in the examples are mixed crystals, i. e., iodobromides obtained from silver bromide and silver iodide. However, other light-sensitive silver salts may be employed if desired. The silver halides, e. g., silver chloride, silver bromide, and silver iodide, or mixtures of any of these, or mixed crystals containing two or more of these salts, are especially suitable.

In addition to the cellulose nitrate film base mentioned specifically in the examples as the support for the emulsions of this invention, other common photographic supports can be used if desired. For example, other cellulose derivatives, e. g., cellulose acetate, cellulose acetate butyrate, cellulose propionate, cellulose ethers, polyamides, polyvinyl chloride, polyvinyl acetal, paper, glass, metals, etc., can be used as supports for the emulsions.

The examples have illustrated the process of this invention by the use of ammonia as the preferred nitrogen-containing base which must be present during the high temperature treatment of the silver halide emulsions. However, other nitrogen bases which can act as silver solvents by forming complexes with the silver ion can also be used. Thus, ammonia and amines, including primary, secondary, tertiary, acyclic, cyclic, heterocyclic, mono, and polyamines can be used. Examples of specific operable amines include methylamine, ethylamine, diethylamine, triethylamine, benzylamine, triethanolamine, ethylenediamine, propylenediamine, cyclohexylamine, 2-methyl-cyclohexylamine, pyridine, piperidine, and morpholine.

The photographic emulsions of this invention may also contain the usual sensitizers such as cyanines and the carbocyanine salts and bases commonly used to extend the sensitivity of photographic emulsions.

The process of this invention has the great advantage over the hitherto known methods for producing photographic emulsions having synthetic, hydroxylated polymer binders of being capable of producing such emulsions which have the high speeds desired for fast photographic films, i. e., negative emulsions. Furthermore, the emulsions of this invention do not possess the previously mentioned disadvantages of conventional gelatin emulsions. The step of heating the synthetic, hydroxylated polymer/silver halide emulsion to the unusually high temperatures herein specified in the presence of a nitrogen base in the specified concentrations, makes possible the production of high-speed emulsions by development of sufficiently large silver halide grain size. Processes in which hydroxylated polymer emulsions are heated at high temperatures in the absence of the nitrogen base, or heated to the moderate temperatures of the gelatin emulsion art in the presence of a nitrogen base, are not capable of producing the necessary silver halide grain size for a truly rapid emulsion. For example, an emulsion containing the low-substituted polyvinyl acetal of Example VII precipitated at 85° C. has particles having a root mean square diameter of 0.46 micron; whereas, the particles in a similar emulsion precipitated at 70° C. have a root mean square diameter of 0.22 micron and the particles in another similar emulsion precipitated at 55° C. have a root mean square diameter of only 0.16 micron.

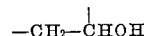
The synthetic, hydroxylated polymer/silver halide emulsions of this invention are useful for all applications in which gelatin/silver halide photographic emulsions are normally used, i. e., as light-sensitive coatings on paper, glass, films, etc., including both positive and negative types of film. The emulsions of this invention having a silver halide grain size of between 0.6 and 3 microns root mean square diameter are especially suitable as high-speed emulsions for negative-type films.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A process for increasing the speed of photographic silver halide emulsions which comprises subjecting an aqueous dispersion of light-sensitive silver halides in a synthetic hydrophilic

hydroxyl-containing polymer having a plurality of recurring intralinear



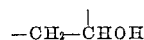
groups to a temperature between 80° and 200° C. in the presence of a nitrogenous base which forms a complex with a silver ion and acts as a silver solvent and is taken from the group consisting of ammonia, primary, secondary and tertiary aliphatic amines, cycloaliphatic amines, pyridine, piperidine and morpholine in a concentration of between 0.1 and 2.5N while excluding radiations which will expose the light-sensitive silver halides.

2. A process as set forth in claim 1 wherein said polymer is a low-substituted polyvinyl acetal wherein less than 13 percent of the hydroxyl groups have acetal substitution.

3. A process as set forth in claim 1 wherein said polymer is a hydrophilic hydrolyzed ethylene/vinyl acetate copolymer.

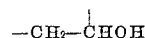
4. A process as set forth in claim 1 wherein said polymer is polyvinyl alcohol.

5. A process for increasing the speed of photographic silver halide emulsions which comprises precipitating light-sensitive silver halides in an aqueous dispersion of a synthetic hydrophilic hydroxyl-containing polymer having a plurality of recurring intralinear



groups at a temperature between 80° and 100° C. in the presence of a nitrogenous base which forms a complex with a silver ion and acts as a silver solvent and is taken from the group consisting of ammonia, primary, secondary and tertiary aliphatic amines, cycloaliphatic amines, pyridine, piperidine and morpholine in a concentration of between 0.9 and 1.4N while maintaining the mixture at such temperatures for a period of one minute to two hours.

6. A process for increasing the speed of photographic silver halide emulsions which comprises precipitating light-sensitive silver halides in an aqueous dispersion of a synthetic hydrophilic hydroxyl-containing polymer having a plurality of recurring intralinear



groups and then heating the resulting aqueous silver halide dispersion to a temperature between 80° and 125° C. in the presence of a nitrogenous base which forms a complex with a silver ion and acts as a silver solvent and is taken from the group consisting of ammonia, primary, secondary and tertiary aliphatic amines, cycloaliphatic amines, pyridine, piperidine and morpholine in a concentration of between 0.9 and 1.4N for a period of one minute to ten hours while excluding radiations which will expose the light-sensitive silver halides.

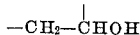
7. A process as set forth in claim 6 wherein said polymer is a hydrophilic hydrolyzed ethylene/vinyl acetate copolymer.

8. A process as set forth in claim 6 wherein said polymer is polyvinyl alcohol.

9. A process as set forth in claim 6 wherein said polymer is a low-substituted polyvinyl acetal wherein less than 13 percent of the hydroxyl groups have acetal substitution.

10. A process for increasing the speed of photographic silver halide emulsions which comprises precipitating light-sensitive silver halides in an aqueous dispersion of a synthetic hydro-

philic hydroxyl-containing polymer having a plurality of recurring intralinear



groups, coagulating the silver halide emulsion of said polymer, washing the coagulum and heating an aqueous dispersion of the washed coagulum to a temperature between 80° and 200° C. in the presence of a nitrogenous base which forms a complex with a silver ion and acts as a silver solvent and is taken from the group consisting of ammonia, primary, secondary and tertiary aliphatic amines, cycloaliphatic amines, pyridine, piperidine and morpholine in a concentration of between 0.1 and 1.4N for a period of one minute to ten hours while excluding radiations which will expose the light-sensitive silver halides.

11. A process as set forth in claim 10 wherein said polymer is a low-substituted polyvinyl acetal wherein less than 13 percent of the hydroxyl groups have acetal substitution.

12. A process as set forth in claim 10 wherein said polymer is a hydrophilic hydrolyzed ethylene/vinyl acetate copolymer.

13. A process as set forth in claim 10 wherein said polymer is polyvinyl alcohol.

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