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GELATIN-ANION SOAP COMPLEX DISPERSION IN POLYVINYL ALCOHOL PHOTOGRAPHIC EMULSIONS

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This invention relates to photographic emulsions and more particularly, it relates to radiation sensitive silver halide emulsions comprising silver halide dispersed in a gelatin-anion soap complex, said complex being dispersed in a synthetic polymer binder. Still more particularly this invention relates to processes for making these photographic emulsions.

Gelatin has been used for many years as a protective colloid for light-sensitive silver halides because it has many desirable characteristics for this purpose. It has the ability to keep the silver halide grains finely dispersed and inherently has the ability of imparting non-optical sensitization to the grains. Gelatino-silver halide emulsion layers also have good permeability to processing solutions.

However, gelatin has many features which are troublesome in the manufacture of photographic emulsions and the coated emulsion layers. Being a natural product it is subject to deterioration by micro-organisms. It also requires extensive testing from batch to batch because of non-uniformity. Gelatin layers are also very sensitive to changes in atmospheric conditions, especially humidity and temperature changes. This sensitivity to variations in humidity and temperature which manifests itself in one aspect by dimensional instability of the coated layer is also one of the greatest drawbacks to the use of gelatin in modern emulsions which are utilized for cine-positive films. Such films are often subjected to the heat of high-intensity arc lamp projectors which are commonly in use in out-door theaters. It has been the custom in conventional emulsion manufacture to set the gelatin emulsion, after the silver halide grains have been formed therein, by cooling to cause gelation and then noodling the emulsion and washing the noodles to remove the unwanted excess soluble salts. Under such conditions, it is impractical for the gelatin concentration in the aqueous solution to exceed 8 to 15%. This limitation is quite troublesome to the emulsion maker for obvious reasons. The necessity for using very dilute systems also presents considerable difficulty in coating and drying and requires very elaborate and costly equipment for this purpose.

More recently, the technique of removing unwanted soluble salts has been accomplished by coagulation washing. This is a method whereby certain chemicals are added to a gelatin silver halide dispersion containing a small ratio of gelatin to silver halide whereby chemical complexes are formed with the gelatin which are sensitive to pH changes. By lowering the pH the gelatin complex containing the silver halide grains coagulates and settles out of the liquid medium and the supernatant liquid containing the soluble salts is decanted. The coagulum may be washed as many times as is necessary with water and then redispersed in an aqueous medium by raising the pH and in turn adding the redispersed coagulum to an aqueous solution of gelatin.

Emulsion makers for years have attempted to find a synthetic material which would be suitable as a colloid carrier and dispersing agent for silver halide grains and which would overcome the deficiencies of gelatin. Such emulsions must possess the sensitometric characteristics and permeability to the usual photographic processing

solutions comparable to emulsions comprising gelatin as the sole binder. Polyvinyl alcohol and its various chemical analogues have been the subject of research for decades in an attempt to use them as the sole or partial replacement of gelatin as the colloid binder in photographic emulsions. Polyvinyl alcohol as a direct and complete substitute for gelatin has some practical advantages. Polyvinyl alcohol for example has higher mechanical strength and durability. Being a synthetic product it may be produced with more uniform properties from batch to batch than in the case of gelatin which is extracted from animal products from different geographical locations. Attempts have been made to mix gelatin and polyvinyl alcohol in an amount of 1–20% of gelatin based on the weight of polyvinyl alcohol in an effort to obtain the advantages of each colloid and to minimize the deficiencies of each. Very little in the way of practical results has been obtained in this manner. This is mainly because gelatin of the quality and molecular weight required for photographic use is incompatible with polyvinyl alcohol having a molecular weight of sufficient magnitude to function adequately as a colloid binder. Other attempts to solve the problem have been to form chemical derivatives of gelatin by reacting it with, for example, a sulfonyl chloride. Such derivatives with the silver halide grains dispersed therein may be coagulated in an aqueous medium and washed by lowering the pH as described above with the gelatin complexes. Such derivatives may be redispersed by raising the pH to above 6.0 and mixing an aqueous solution of the material with an aqueous solution of polyvinyl alcohol as the main binder. However, the reactions involving the formation of such derivatives are usually quite rigorous and tend to reduce the beneficial dispersing characteristics of gelatin for silver halide grains and for this and other reasons the method of using gelatin derivatives has not been found to be practicable.

An object of this invention is to provide photographic emulsions and a method for their preparation which are very dimensionally stable and have high resistance to deterioration under conditions of exposure to intense heat of high intensity arc light projectors.

Another object is to provide photographic emulsions and a method for their preparation wherein the principal colloid carried is polyvinyl alcohol.

A further object is to provide photographic emulsions and a method for their preparation which are compatible with water soluble polyvinyl alcohol solutions without the use of organic solvents in the system. Other objects will appear hereinafter.

These and other objects are accomplished by the present invention which is a method of preparing a photographic emulsion which comprises dispersing silver halide in an aqueous gelatin solution, adding thereto an anion soap thereby forming a gelatin-anion soap complex containing dispersed silver halide grains and dispersing the said complex in a water soluble polyvinyl alcohol binder in aqueous solution.

It has now been found that high quality photographic emulsions can be made using a water-soluble polyvinyl alcohol polymer containing a large number of intralinear $-CH_2CHOH$ groups as the colloid carrier by dispersing silver halides in a small quantity of aqueous gelatin by the double decomposition of a soluble silver salt and a soluble halide or mixture as is well known in the art. After ripening the precipitated silver halide grains in the usual manner, a small quantity of an anion soap is then added to form a gelatin-anion soap complex in the manner taught in Waller et al., U.S. 2,489,341. The complex thus formed may be precipitated and coagulation-washed by the methods taught by Waller et al., to remove the unwanted soluble salts. After washing, the sedi-

mented complexes containing the originally suspended silver halide are re-dispersed in an aqueous solution of a water-soluble polyvinyl alcohol binder. The pH is adjusted by suitable means to approximately 7.0. Suitable sensitizers may then be added, and the emulsion digested in the usual manner, since such emulsions readily respond to chemical sensitization. After digestion, final adjuvants such as antifoggant, hardeners, etc. are added and the emulsion is coated on a suitable support.

Polyvinyl alcohols of low, medium or high viscosity may be used. Such compounds are usually made by hydrolyzing polyvinyl acetate, and to obtain the required water solubility, it is necessary that at least 80% of the ester groups be hydrolyzed. Many advantages reside in preparing a silver halide emulsion in the above manner. Gelatin-anion soap complexes having silver halide grains dispersed therein are completely compatible with water soluble polyvinyl alcohol in aqueous solutions and provide emulsion layers of good clarity. Such emulsions are readily adapted to the various manipulations carried out in the emulsion making art. Such emulsions are easily hardened by the water-soluble titanyl complexes formed by reacting a tetraalkyl titanate with an α-hydroxy carboxylic acid. Such compounds are disclosed and claimed in Shacklett U.S. Patent 2,870,181, January 20, 1959.

Anion soaps which are suitable for use as complexing agents include a large variety of water-soluble compounds which are surface-active compounds in which the reduction in surface tension resultant on their addition to water is due to the anion; these are described in detail in Waller et al., U.S. 2,489,341. Sodium dodecyl sulfate is one member of the class which has been found to be particularly suitable. It readily forms complexes with gelatin and is commercially available at relatively low cost. In general, the quantity of the anion soap required to effect a satisfactory gelatin-anion soap complex depends on many factors since the exact nature of the reaction between the anion soap and the gelatin is not clear. Some of the factors are gelatin concentrations, pH value of the solution and the nature of the anion soap itself. It is not possible, therefore, to define exactly the best conditions for all sets of circumstances, but the optimum conditions for any particular case can readily be ascertained by trial, usually from .75 to 1.25 parts by weight of anion soap per part of gelatin is used.

As a general procedure one may precipitate the silver halides to form a silver iodobromide in a 0.40 to 0.60% aqueous gelatin solution in an amount of from 7 to 20 grams of gelatin to one mol of silver halide. The emulsion is ripened at from 45° to 50° C. for from 5 to 40 minutes. An aqueous anion-soap solution (e.g. containing 5% by weight of said anion soap based on the weight of the water) is then added to provide approximately an amount of anion soap equivalent to the amount of gelatin present although this may be varied over a wide range, e.g. 75% to 125% by weight per unit weight of gelatin. Ripening may be continued from 1 to 5 minutes longer depending upon the photographic characteristics desired in the emulsion, but can be omitted in some cases. An acid, which is innocuous to the emulsion, e.g. acetic acid, is added to lower the pH to about 5. The amount of acid required will of course vary depending on the pH of the emulsion since at this point it contains a substantial quantity of ammonia or electrolyte in the form of soluble salts resulting from the silver halide precipitation. The addition of acid brings about the coagulation of the gelatin-anion soap complex. The emulsion is then cooled to about 15 to 20° C. and the coagulum allowed to settle. The supernatant liquid is then removed by decantation or siphoning and the coagulum is washed with a 1 to 2% solution of sodium chloride which may contain a small quantity of acid (e.g. acetic acid). Within practical limits, the amount of washing solution is not critical nor is the number of times that the coagulum is washed. It is only necessary to wash the coagulated emulsion sufficiently to remove the unwanted soluble salts. To the coagulum there is added one liter of distilled water and the mixture is stirred at 43° C. for five minutes. At this point, deionized polyvinyl alcohol in the form of a 3.5 to 5% solution equivalent to 70 to 200 grams per mol of silver salt, is added, the pH is raised to 7.5 with sodium hydroxide, and the emulsion is stirred for 5 to 20 minutes to disperse the coagulum. The temperature is raised to from 49° to 60° C., sulfur and metal sensitizers are added and the emulsion is digested for 20 to 60 minutes. The emulsion is then cooled to about 40° to 45° C., the usual coating aids, antifoggants, etc. are added, the pH adjusted to from 8 to 10 with a suitable amine or alkali metal hydroxide, and the emulsion is coated on a suitable support in an amount to give a coating weight of 50–150 mg. of silver halide per square decimeter.

The emulsions may also be made by precipitating the silver halides in an aqueous gelatin solution and ripening as described above and then washing by coagulating the gelatin dispersion with a water soluble, acid soluble organic polymer as described in Moede, U.S. 2,772,165, i.e. the water soluble, acid soluble partial acetal of polyvinyl alcohol and the sodium salt of o-sulfobenzaldehyde described in McQueen, U.S. 2,462,527 and Umberger and Grumbine, U.S. 2,609,290. The pH is adjusted to below the isoelectric point of the gelatin, preferably below 4.5 and a pH between 2 and 3 is particularly preferred. The coagulum is then redispersed by a readjustment of the pH to above 6, preferably between 6 and 7, and the anion soap is then added as described above to form the gelatin-anion soap complex. The resulting dispersion is mixed with the deionized polyvinyl alcohol solution.

The photographic emulsions of the invention in general contain 70 to 200 grams of polyvinyl alcohol or other vinyl alcohol polymer and 7 to 20 grams of gelatin per mole of silver halide.

The invention will now be further illustrated by, but is not intended to be limited to, the following examples. The emulsions are prepared and maintained under conditions such that actinic light will not expose the silver halide grains.

Example I

A cine positive silver iodobromide emulsion containing 30 grams of gelatin and approximately 2% silver iodide and 98% silver bromide based on the total weight of silver halides was made by precipitating the silver halides in a 0.59% aqueous gelatin solution in an amount to give a ratio of gelatin to silver halide of about 1:9. The emulsion was ripened at about 49° C. for about 17 minutes. At the end of this time, an aqueous solution of sodium dodecyl sulfate was added while maintaining the temperature at 49° C. in an amount to give a ratio of gelatin to sodium dodecyl sulfate of 1:1.25. The emulsion was stirred to obtain a good mixture and then enough acetic acid (about 150 ml.) was added to lower the pH to about 4.5. The emulsion was cooled 15° C. and the coagulum carrying the suspended silver iodobromide grains and formed by the addition of sodium dodecyl sulfate and acetic acid was allowed to settle for six minutes. The supernatant liquid was carefully decanted from the coagulum which was washed with about 5 liters of a 2% sodium chloride solution under agitation for about 3 minutes. The supernatant liquid was then removed by decantation. Distilled water was added to bring the total weight up to 1000 grams and then 3000 grams of 3½% deionized high molecular weight polyvinyl alcohol (98–100% hydrolysis grade) was added to the mixture. The pH was adjusted to 7.0 with sodium hydroxide and the coagulum was redispersed by stirring for 10 minutes. The temperature was raised to 60° C. and sensitizers were added. The emulsion was digested for 50 minutes at 60° C. The emulsion was cooled to 43° C. and final additions were made which included an antifoggant and 200 ml. of a 3% aqueous solution of titanium lactate. The pH was ad-

justed to 9.5 with sodium hydroxide solution and the emulsion was coated on a film support made in the manner disclosed in Weaver U.S. 2,534,326 and dried by procedures well known in the art. An all-gelatin emulsion prepared in the same manner but using gelatin in place of polyvinyl alcohol with the same halide ratio and content was used as a control in the following photographic tests. The coated elements were exposed and developed in the following developer.

	Grams
Methyl-p-aminophenol hydrosulfate	3.0
Hydroquinone	9.0
Sodium sulfite (anhydrous)	50.0
Potassium carbonate	50.0
Potassium bromide	4.5
Water to make 1 liter.	

Following development, the films were fixed, washed and dried in the conventional manner. The results of the sensitometric tests in terms of relative speed and gamma are shown in the following table.

Emulsion	Relative Speed	Gamma	Fog
Gelatin (Control)	12	2.5	0.03
Polyvinyl alcohol emulsion	25	3.3	0.15

In referring to an all-gelatin emulsion made in a conventional manner we mean dispersing the silver halides in gelatin, coagulation-washing and then redispersing by warming in an aqueous gelatin solution. The polyvinyl alcohol emulsion as compared with the control had very high resistance to dimensional change, blistering, and deterioration under the influence of high intensity arc light projection.

Example II

A cine positive silver iodobromide emulsion was made in the manner described in Example I except that the silver halides were precipitated in a 0.43% aqueous gelatin solution in a ratio of gelatin to silver halide of 1:14. The emulsion was ripened at 49° C. for 15 minutes and then ammonium hydroxide (50 ml. of 20% NH_3 solution) was added and ripening continued for 30 seconds longer. There was then added 50 ml. of a 5% aqueous solution of sodium dodecyl sulfate. Ripening was continued for 2 minutes and then acetic acid was added to lower the pH to 5. The emulsion was cooled to 18° C. and the resulting coagulum was allowed to settle. The supernatant liquid was carefully decanted from the coagulated curds. The curds were washed with 5 liters of an acidified 2% solution of sodium chloride. One liter of distilled water was added to the curds and the mixture was stirred for 5 minutes. At this time 210 grams of deionized high molecular weight polyvinyl alcohol (PVA) was added in the form of a 3.5% aqueous solution. Enough dilute sodium hydroxide solution was added to raise the pH to 7.5 and the coagulum was redispersed by stirring for 5 minutes. The temperature was raised to 60° C. during which gold and sulfur sensitizers were added. The resulting emulsion was digested for 40 minutes. The digested emulsion was cooled to about 43° C., final additions as set forth in Example I were added, and the pH was adjusted to 10 with diisopropylamine. The final emulsion ready for coating was completely homogeneous indicating complete compatibility of the gelatin complex with polyvinyl alcohol. The film was coated on the film support referred to in Example I in a manner to give a coating weight of 72 mg. AgBr/dm.^{2}. The film was dried in the conventional manner. The film and an all-gelatin cine positive emulsion film as a control were exposed and processed in the manner described in Example I and gave the following sensitometric results.

Emulsion	Relative Speed	Gamma	Fog
Control	100	2.39	.02
PVA emulsion	87	2.35	.02

The polyvinyl alcohol emulsion showed very high resistance to dimensional change, blistering and deterioration under the influence of high intensity arc light projection.

Example III

Example II was repeated in every detail except the final emulsion was coated to give a coating weight of 80 mg/dm.^{2}. This may be accomplished by either viscosity change, coating speed change or both, all of which are well known to those skilled in the art. The coated element was exposed and processed as described in Example I and the sensitometric results were as follows:

Emulsion	Relative Speed	Gamma	Fog
All gelatin control	100	2.37	.01
PVA emulsion	132	2.24	.05

The polyvinyl alcohol (PVA) emulsion had very high resistance to blistering and deterioration under the influence of high intensity arc light projection.

Example IV

Two emulsions were made according to the procedure of Example II except that in place of 210 grams of deionized high molecular weight polyvinyl alcohol (PVA) there was added in the form of a 3.5% aqueous solution 168 grams and 273 grams respectively. The rest of the treatments of digestion, coating, drying, processing etc. were the same as Example I. The sensitometric results were as follows:

Emulsion	Relative Speed	Gamma	Fog
Control	100	2.09	.07
168 g. PVA	88	1.39	.07
273 g. PVA	96	1.27	.07

Both polyvinyl alcohol emulsions showed good resistance to dimensional change, blistering and deterioration under the influence of high intensity arc light projection.

Example V

A silver iodobromide emulsion was made in the manner described in Example I containing approximately 85 grams of silver halides and 10 grams of gelatin. The silver halides constituted about 96.4 mol percent bromide and 3.6 mol percent iodide. To this emulsion, which amounted to about 740 grams including the water, there was added 100 ml. of distilled water containing 10 ml. of glacial acetic acid and 12 ml. of a 9% solution of a water-soluble, acid-soluble partial acetal of polyvinyl alcohol and the sodium salt of o-sulfobenzaldehyde consisting of 5 grams of sulfonate sulfur per 100 grams of polymer. The temperature was adjusted to about 15° C. and 65 ml. of 3 N H_2SO_4 was added to lower the pH to 2.8–3.0. The resulting coagulum was allowed to settle in the manner described in Moede U.S. Patent 2,772,165. After removing the supernatant liquid by decantation the curds were washed twice with 8 liters of distilled water to remove the soluble salts. Five hundred grams of the washed curds were redispersed in 2400 ml. of distilled water containing 30 grams of gelatin by adjusting the pH to 6.3. The temperature was adjusted to 35° C. To assure complete dispersion stirring was carried on for about 20 minutes and the pAg was adjusted to about 8.6 with

3 N potassium chloride solution. Gold and sulfur sensitizers in excess were then added and the emulsion was digested for 30 minutes at 63° C. The emulsion was cooled to 27° C. and the pH was lowered to 4.5 with 25 ml. of 10% acetic acid solution which brought about the coagulation of the suspended matter. After decanting the supernatant liquid the resulting coagulum was washed once with distilled water to remove excess sensitizers. To the curds free of supernatant liquid there was added 400 ml. of a 5% aqueous solution of sodium dodecyl sulfate. The pH was adjusted to 6.3 with aqueous sodium hydroxide and the curds were redispersed by stirring for 5 minutes at about 38° C. The total weight of the emulsion was adjusted to 1000 grams with water. Three-hundred gram portions of this emulsion were each mixed with (I) 450 grams of a 15% aqueous gelatin solution and (II) 450 grams of a 15% aqueous solution of deionized high molecular weight polyvinyl alcohol. The emulsions after thorough mixing were coated on polyester film supports, dried at room temperature and exposed and tested as described in Example I. The results are shown in the following table.

Emulsion	Relative Speed	Gamma	Fog
Gelatin emulsion (control)	100	1.5	.05
Polyvinyl alcohol emulsion	125	1.9	.15

The polyvinyl alcohol emulsion showed much higher resistance to dimensional change, blistering and deterioration under high intensity arc light projection.

The deionization of the polyvinyl alcohols of the foregoing examples was made by passing the PVA through a mixed bed ion exchange column.

Any silver halide emulsion may be made by the process. For example, silver bromochloride emulsions for use in graphic arts films may be made in the manner described above and are of value because of their dimensional stability. The emulsions of the invention are also useful in the manufacture of radiographic films.

The process of the invention is also useful in making emulsions which are optically sensitized with cyanine, carbocyanine and merocyanine dyes of the usual types which are known to be optical sensitizers for gelatin photographic emulsions. The process of the invention may also be used in preparing color photographic emulsions in multilayer structures wherein color couplers or color formers, bleach-out dyes and other dyes and dye-formers are incorporated in the emulsion layers. The emulsions may be coated on any suitable support such as paper, hydrophobic organic polymer film supports including those disclosed in Alles et al., U.S. 2,627,088, and cellulose ester supports, e.g. cellulose acetate films. They may also be coated on glass, metal, cardboard, etc. Special anchoring layers may be necessary for some supports but these are well-known to technicians skilled in the manufacture of photographic materials.

As indicated above, there are a large number of anion soaps which are useful in the invention. The classification of these compounds is discussed in the book Kolloidchemische Grundlagen der Textilveredlung by Dr. E. Valko, 1937, at pages 519–522, to which reference is made for the meaning of the expression "anion soaps." Generally the class also includes soluble salts of long-chain alkyl carboxylic acids, e.g. soluble salts of fatty acids containing eight or more carbons as, for example, lauric, oleic, ricinoleic, linoleic, stearic and palmitic. These compounds, however, are much less satisfactory than long chain alkyl sulfates and sulfonates. Soluble salts of long-chain alkyl sulfonic acids, soluble salts of sulfated higher fatty alcohols in which the alkyl group contains at least 8 carbons and many other sulfonated and sulfated aliphatic and aromatic compounds which are water soluble and contain from 10 to 20 carbon atoms are suitable complexing agents.

The invention provides a method of making emulsions wherein the principal colloid carrier is a vinyl alcohol polymer, e.g. polyvinyl alcohol. Such emulsions have outstanding advantages over gelatin silver halide emulsions and have resistance to deterioration by microorganisms. They are very dimensionally stable and have high resistance to deterioration under conditions of exposure to the intense heat of high intensity arc light projectors. The processes of the invention also offer a convenient means of varying the silver halide to binder ratio which is quite important in certain photographic elements requiring a high concentration of silver.

The emulsions of the invention are also adapted to be made in highly concentrated form and even in substantially dry form for shipment and use at a later time by adding a sufficient amount of water for coating by any of the techniques known in the art, i.e. skim coating, extrusion coating and spray coating. One important advantage of the processes of the invention is that gelatin-complexes can be made which are water-soluble, and compatible with water-soluble polyvinyl alcohol solutions and do not require organic solvents in the system. Still other advantages will be apparent from the foregoing description and following claims.

We claim:

1. A method of preparing a photographic emulsion which comprises dispersing silver halide in an aqueous gelatin solution, adding thereto an anion soap thereby forming a gelatin-anion soap complex containing dispersed silver halide grains and dispersing said complex in a water soluble polyvinyl alcohol binder in a predominantly aqueous solution, said polyvinyl alcohol binder prepared by hydrolyzing a polyvinyl ester to an extent of at least 80 percent.

2. A method of preparing a photographic emulsion which comprises dispersing silver halide in an aqueous gelatin solution, adding thereto an anion soap thereby forming a gelatin-anion soap complex containing dispersed silver halide grains, coagulating the said complex thus formed and redispersing the said complex in a water soluble polyvinyl alcohol binder in a predominantly aqueous solution, said polyvinyl alcohol binder prepared by hydrolyzing a polyvinyl ester to an extent of at least 80 percent.

3. A method of preparing a photographic emulsion which comprises dispersing silver halide in an aqueous gelatin solution, adding an anion soap thereby forming a gelatin-anion soap complex containing dispersed silver halide grains, coagulating the said complex thus formed by adjusting the pH of the emulsion to less than 7, separating the coagulated complex, redispersing the said complex in a water soluble polyvinyl alcohol binder in a predominantly aqueous solution, said polyvinyl alcohol binder prepared by hydrolyzing a polyvinyl ester to an extent of at least 80 percent and concurrently readjusting the pH to about 7.

4. Method according to claim 3 wherein the anion soap is sodium dodecyl sulfate.

5. Method according to claim 3 wherein the aqueous gelatin solution contains from 7 to 20 grams of gelatin per mole of silver halide.

6. Method according to claim 3 wherein the aqueous polyvinyl alcohol binder solution contains from 70 to 200 grams of polyvinyl alcohol and 7 to 20 grams of gelatin per mole of silver halide.

7. A method of preparing a photographic emulsion which comprises dispersing silver halide in an aqueous gelatin solution, coagulating said dispersion by the addition of a water soluble, acid soluble partial acetal of polyvinyl alcohol and the sodium salt of o-sulfobenzaldehyde, adjusting the pH to below 4.5, redispersing the coagulum by readjusting the pH to above 6, adding thereto an anion soap thereby forming a gelatin-anion soap

complex containing dispersed silver halide grains and dispersing said complex in a water soluble polyvinyl alcohol binder in a predominantly aqueous solution, said polyvinyl alcohol binder prepared by hydrolyzing a polyvinyl ester to an extent of at least 80 percent.

8. A photographic emulsion comprising silver halide dispersed in a gelatin-anion soap complex, said complex being dispersed in a polyvinyl alcohol binder in a predominantly aqueous solution, said polyvinyl alcohol binder prepared by hydrolyzing a polyvinyl ester to an extent of at least 80 percent.

9. An emulsion as described in claim 8 wherein the anion soap is sodium dodecyl sulfate.

10. An emulsion as described in claim 8 wherein the gelatin is present in an amount from 7 to 20 grams per mole of silver halide present.

11. An emulsion as described in claim 8 wherein the polyvinyl alcohol is present in an amount from 70 to 200 grams and said gelatin in an amount from 7 to 20 grams per mole of silver halide present.

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