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METHOD OF PREPARING PHOTOGRAPHIC EMULSIONS

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This invention relates to the preparation of photographic emulsions having silver halide as the sensitive element in which the silver halide is prepared in dispersed form in a gelatin derivative. The gelatin derivative-silver halide dispersion is coagulated and washed. This invention also includes the products obtained thereby and the emulsions obtained by re-dispersing the washed silver-halide grains using gelatin or gelatin derivative as the vehicle therefor.

The most common method of preparing silver-halide dispersions is by reacting a water-soluble salt, such as silver nitrate and a water-soluble halide, such as potassium bromide in an aqueous solution of gelatin. There is formed thereby a dispersion of the silver halide in an aqueous solution of gelatin, which solution also contains salts resulting as a by-product of the reaction. In processes of making silver-halide dispersions and emulsions using the natural product gelatin the emulsion maker has in the past been limited in the scope of his operations by the physical properties peculiar to that material. These physical properties have necessitated the use of concentrations of silver halide and of gelatin in photographic emulsion formulae which are not the most desirable for all photographic products. For instance, emulsions of high concentration of silver halide have been difficult to prepare. Limitations have been imposed on the emulsion maker regarding the conditions of dilution during emulsion making since emulsions with too high water content are difficult and undesirable to coat and dry. In addition, the technician has been obliged to limit the minimum concentration of gelatin in the washing operation in which soluble salts are removed.

It has been considered desirable in the case of photographic emulsions, particularly those to be coated on water impermeable supports, that the soluble salts present in the emulsion be reduced in concentration. It has been the practice previously where gelatin has been used as the protective colloid to remove the soluble materials therefrom by setting the gel dispersion, noodling, and washing the noodles by osmosis in cold water. Under such conditions a minimum gelatin concentration of approximately 4% is useful under practical conditions and this limitation has hampered the operations of the emulsion maker in his preparation of emulsions by this method.

One of the objects of our invention is to prepare dispersions of silver halides from which water-soluble by-products may be readily removed. Another object of our invention is to provide a convenient and practical method of preparing silver-halide dispersions in which the dispersing colloid need be but a small percentage of the total composition. A further object of our invention is to provide a method of washing silver-halide dispersions in which substantially all of the liquid may be removed, thus making for

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complete removal of the water-soluble impurities therein. A still further object of our invention is to provide a method of preparing silver-halide dispersions in dry form whereby those dispersions can be readily transported in a compact condition. Other objects of our invention will appear herein.

Our invention is based upon the discovery that gelatin derivatives are useful as peptizers for dispersions of silver halide and that those derivatives are acid coagulable and will envelop the silver grains when so precipitated. The method of our invention avoids the limitations which have previously characterized the preparation of silver-halide dispersions and is valuable for expanding the possible conditions for the manufacture of photographic silver-halide emulsions of different speeds, contrast, and other photographic characteristics. In addition, our invention offers a simple means of preparing emulsions of high silver concentration, this being especially valuable in the manufacture of photographic films bearing large quantities of silver per unit area.

Gelatin derivatives are prepared by reacting gelatin with a reagent, such as a sulfonyl chloride, a carboxylic acid chloride, a carboxylic acid anhydride, an aromatic isocyanate, or a 1,4 diketone at a pH of 8–11 or more imparted by the addition of a suitable base, such as sodium hydroxide or ammonium hydroxide, preferably at a temperature of 20–60° C. The reaction between the gelatin and the reagent employed therewith takes place within a very few minutes, and the resulting product may be employed directly in our invention without separating it from the solution in which it is formed, or it may be separated from the mass and employed in purified form. We have found that these gelatin derivatives when employed as dispersing agents for silver halide have the property of enveloping the silver-halide grains upon acidulation of the mass and that the resulting insoluble material consisting of silver-halide grains enveloped by the gelatin derivatives may be washed free of salts or any other water-soluble materials which may be present therein. To effect coagulation it is desirable to acidify the mass to a pH of approximately 4.5 or less. When inert salts are present at relatively high concentration, the pH range for this acid coagulation phenomenon may extend as low as 3. If, however, the salt concentration is less, the pH range for the acid coagulation is less broad, depending upon the percentage of salt which is present. At low salt concentration it is desirable that the pH be held within the range of approximately 3.5 to 4.5 to obtain the optimum coagulation of the dispersion of silver halide in the gelatin derivative.

Our invention may be carried out either by preparing the silver halide in an aqueous solution of the gelatin derivative, or the silver halide may be prepared in an aqueous solution of gelatin as the peptizer, and the gelatin thus present may

be converted into the derivative prior to acidifying and washing. Where the gelatin derivative is employed as the protective colloid that material is employed in substantially the same quantity as that of the gelatin usually used in preparing silver halide emulsions. Also, the silver halide may be prepared by any of the normal methods for emulsification of the silver halides, for example, by introducing a stream of an aqueous solution of silver nitrate and a stream of an aqueous solution of an alkali metal halide, such as potassium bromide, into a vigorously agitated aqueous solution of the gelatin derivative. After the silver halide has been formed and after any ripening operations which may be considered advisable, acid is added in a sufficient amount to lower the pH to less than 4.5, the range of pH depending upon the amount of salt present as explained above. The amount of acid is such that the gelatin derivative becomes insoluble in the reaction mixture and coagulates and settles carrying with it the silver-halide grains which are present. The coagulum may now be separated from the liquid by any one of several techniques. In the simplest form this supernatant mother liquor may be removed from the receptacle in which the mass is contained by means of a siphon and the coagulum may be rinsed with water to remove excess insoluble salts. The coagulum after this washing operation consists of silver halide, the gelatin derivative, any other water-insoluble materials which are present, and a small amount of residual soluble salt dissolved in water trapped in the coagulum.

For some types of emulsions, this coagulum may be used directly without further washing, for instance, in the preparation of emulsions for the coating of paper or other permeable supports. For the preparation of emulsions for the coating of film or glass plates, however, it may be desirable to reduce further the content of soluble salts which may be present. This may be done by any one of several methods. For instance, the coagulum may be rinsed by treatment with cool water, preferably with the pH adjusted to the range of the isoelectric point of the gelatin derivative. The number of rinses which are necessary to reduce the salt content of the coagulum to the desired point may be determined by experiment, but usually is within the range of 1 to 4 changes of water. As an alternative washing method, the coagulum may be redispersed in water at an elevated temperature using water and a small amount of alkaline material, such as sodium hydroxide or ammonium hydroxide so that the pH of the mixture remains of the order of 6 or higher. The temperature of the solution is raised to approximately 40° C., and the whole is stirred for a few minutes to effect redispersion of the coagulum. The gelatin derivative and silver grains may then again be precipitated by the addition of an appropriate acid solution to reduce the pH of the solution to the coagulation point of the derivative. The coagulum will again settle, and the separation from the original mother liquor is effected as before. This coagulation and redispersion operation may be repeated as many times as is necessary, but for normal purposes one redispersion and coagulation is sufficient. As a third method of washing, the coagulum may be redispersed in water at a pH below the isoelectric point of the derivative, for example, at pH 3.0 or lower and slightly elevated temperature. The low pH may be obtained by the addition of a quantity of an appropriate acid, such as sulfuric acid. Recoagulation may then be effected by the addi-

tion of a suitable base such as ammonium hydroxide, to raise the pH of the solution to the coagulation point of the derivative. The coagulum will settle, and the separation from the supernatant liquor is carried out as before.

The coagulum which has been washed by any one of the three general methods outlined above may then be redispersed to form photographic emulsions suitable for the subsequent finishing and coating operations by treating with the required quantity of water, normal gelatin and base to raise the pH of the whole to the range of 5 or 6 or greater. If desired, gelatin derivative instead of normal gelatin may be employed as the vehicle in the formation of the photographic emulsion. The mixture of coagulum, water, gelatin and any other desired reagents is stirred at approximately 40° C. for a time sufficient to effect a complete redispersion of the coagulum, usually requiring ten to twenty minutes. The emulsion obtained has properties comparable to those of the best types of washed emulsions and responds readily to chemical sensitization or after ripening and optical sensitization of the types employed upon photographic emulsions generally. The emulsions prepared in accordance with our invention may be coated onto a support using the techniques which are standard in the emulsion coating art.

An alternative method for the use of the gelatin derivative in the preparation of silver-halide dispersions affords equal advantage. The aromatic isocyanate and sulfonyl chloride derivatives of gelatin are especially adapted for preparing silver-halide dispersions by this method. In this method the silver-halide dispersion is prepared in normal gelatin solution according to standard techniques for the preparation of the silver halide and any ripening which may be desired is carried out. At this point the pH of the mass is adjusted to a value of approximately 8 to 11 or more with a suitable base, such as sodium hydroxide or ammonium hydroxide, and the reagent for formation of the gelatin derivative is added in suitable physical form, usually dissolved in a solvent. After a suitable time has elapsed for the reaction between the reagent and the gelatin (five minutes is ordinarily adequate) the pH of the mass may then be lowered to the coagulation region. After the formation of the coagulum by the reduction of the pH, the silver-halide gelatin derivative coagulum may be washed to remove insoluble salts by either of the two methods outlined above.

The use of gelatin derivatives by either of the two methods outlined above presents considerable advantage over other techniques described in the literature for washing of emulsions by coagulation methods. It has been well-known for years that gelatin silver-halide emulsions could be coagulated by the addition of sufficient quantities of suitable organic solvents, such as methanol, ethanol, or acetone. Such a procedure, however, has proved to be expensive and cumbersome because of the very large quantities of organic solvent which must be used per unit of emulsion. The gelatin coagulates and becomes insoluble in the solvent medium through the well-known effect of organic solvents to coagulate proteins generally.

In the preparation of gelatin silver-halide emulsions by the use of gelatin derivatives the physical characteristics of water-solubility as related to pH are of vital importance. We have found that gelatin derivatives prepared by reacting standard photographic gelatins under conditions of elevated pH with aromatic sulfonyl

chlorides, carboxylic acid chlorides, carboxylic acid anhydrides, aromatic isocyanates, or 1,4-diketones possess the characteristic of water solubility at pH values above approximately 4.5 and below approximately 4.0, providing, of course, salts are absent. In the pH range of approximately 4 to 4.5 these derivatives are relatively water-insoluble. The pH range of insolubility in water is broadened by the presence of neutral electrolytes. For instance, the derivative obtained by reacting benzene sulfonyl chloride with gelatin is insoluble in aqueous solutions over a pH range extending from 3 to 4.5 if a concentration of potassium nitrate of at least 0.1 normal is present. It may be noted, therefore, that in the initial coagulation in the cycle of washing emulsion by coagulation considerable neutral electrolyte is usually present in the form of potassium nitrate resulting from the double decomposition reaction between silver nitrate and a soluble halide, such as potassium bromide. In addition to this salt it is common practice that some soluble halide also be present. Under such conditions the adjustment of pH in the first coagulation is not particularly critical. We prefer to add sufficient photographically inert acid to reduce the pH of the emulsion to approximately 3.0 in the presence of such concentrations of salt. It is obvious that when the mother liquor is removed from the coagulum first formed that the largest proportion of soluble salts is also removed. If the coagulum is redispersed in distilled water for washing by raising or by lowering the pH, the second coagulation takes place at a much lower salt concentration and, therefore, the pH adjustment necessary will be more critical. For this purpose we prefer to operate in the range of 3.8 to 4.2.

For the acid which is to be employed for reducing the pH to the coagulation point, any acid may be employed which will give the desired pH in the mass and which will not deleteriously affect the photographic material. Dilute aqueous sulfuric acid has been found to be particularly useful for this purpose. Nevertheless, other acids are useful and will suggest themselves to those skilled in the art. For instance, acetic acid or phosphoric acid are useful for this purpose if for some reason sulfuric acid is not available.

In the preparation of gelatin derivatives the gelatin in aqueous solution is treated with a solution of the reagent in a suitable solvent, preferably one which is water miscible. Some reagents which are useful in this connection are acetone, dioxane, isopropyl alcohol, and the like. Some of the compounds which are suitable for use in preparing gelatin derivatives useful in the process of our invention are as follows:

Sulfonyl chlorides

Benzene sulfonyl chloride
p-Methoxybenzene sulfonyl chloride
p-Phenoxybenzene sulfonyl chloride
p-Bromobenzene sulfonyl chloride
p-Toluene sulfonyl chloride
m-Nitrobenzene sulfonyl chloride
m-Sulfobenzoyl dichloride
Naphthalene- β -sulfonyl chloride
p-Chlorobenzene sulfonyl chloride
3-nitro-4-aminobenzene sulfonyl chloride
m-Carboxy-4-bromobenzene sulfonyl chloride
1-chlorosulfonyl-2-hydroxy-3-naphthoic acid quinoline-3-sulfonyl chloride
m-Carboxybenzene sulfonyl chloride
2-amino-5-methylbenzene-sulfonyl chloride

Carboxylic acid chlorides

Phthalyl chloride
p-Nitrobenzoyl chloride
Benzoyl chloride
Ethyl chlorocarbonate
Furoyl chloride
Methacrylyl chloride

Acid anhydride

Phthalic anhydride
Benzoic anhydride
Succinic anhydride
Maleic anhydride
Isatoic anhydride
Methacrylic anhydride

Isocyanates

Phenyl isocyanate
p-Bromophenyl isocyanate
p-Chlorophenyl isocyanate
p-Tolyl isocyanate
p-Nitrophenyl isocyanate
 α -Naphthyl isocyanate
 β -Naphthyl isocyanate

1,4-Diketones

Acetonyl acetone
Dimethyl acetonyl acetone
Diethyl diacetyl succinate

It is apparent that considerable advantage will accrue by the use of this method in that the concentration of silver halide in the final emulsion may be adjusted to any desired value without reference to the quantities of water, silver halide, and gelatin used in the initial emulsification reaction. Thus, concentrated emulsions may readily be prepared.

We have also found further advantage to result from an application of these techniques. The possibility of preparing for storage and shipment dried emulsions has been widely discussed and a few methods for attainment of this end have been revealed. In general, such methods have involved evaporation of water from standard emulsions or reduction of water content of finished emulsions by treatment with concentrated salt solutions or organic solvents. Such methods have been cumbersome and economically unprofitable. Recently the preparation of silver halide as a dry particulate emulsion by a method involving the use of anion soaps has also been revealed.

We have found that the coagulum prepared by the use of gelatin derivatives is especially suitable for preparation of dried emulsions since it may be obtained in a state nearly free of excess water and, therefore, the drying operation is simplified and rendered less expensive. The coagulum may be obtained in the suitable physical form for the purpose, and the dried emulsion may readily be redispersed in water containing appropriate alkali. In this connection we have found that the washed coagulum prepared from the dicarboxylic acid anhydride derivatives, such as phthalic anhydride, is especially useful. These derivatives and their preparation are described and claimed in our application, Serial No. 768,474 filed of even date, now Patent No. 2,525,753.

We have also found that the coagulation operation may be carried out either after the preparation of silver halide to remove water-soluble salts or after a heat treatment with appropriate chemical sensitizers so that coagulated

silver-halide grains are obtained before or after having been brought to optimum photographic speed. These grains may be dried at either stage in the cycle without harming their properties when finally made up in the emulsion.

The gelatin derivatives which may be employed in accordance with our invention may be either derivatives of a high viscosity gelatin or, if desired, they may be derivatives of gelatin which has been hydrolyzed or reduced in viscosity. Our invention is not critical as to the gelatin which is employed in preparing the derivatives to be used in our invention or process including gelatin derivatives generally in the preparation of washed emulsions by coagulation washing methods.

The following examples illustrate our invention:

Example 1.—100 g. of silver nitrate were dissolved in 900 cc. of distilled water at 25° C. 80 g. of potassium bromide, 1 g. of potassium iodide and 25 g. of gelatin were dissolved in another 900 cc. of distilled water. The temperature was adjusted to 50° C. and the silver nitrate solution was added to the bromide-gelatin solution over a period of approximately ten minutes with vigorous stirring. The temperature was maintained at 50° C. The mass was then stirred for ten minutes at 50° C. and then cooled to 40° C. The pH was adjusted to 9.5 by the addition of dilute ammonium hydroxide and 3 cc. of benzene sulfonyl chloride in 40 cc. of dry acetone were added. The mass was stirred at 40° C. for five minutes. Sulfuric acid was then added to adjust the emulsion pH to 3, and the gelatin derivative which had formed coagulated taking with it the silver halide. The mother liquor was decanted off, and the silver halide dispersion was washed twice with distilled water at 20° C. There was then added to the mass 150 g. of gelatin in solution in 1500 cc. of distilled water, and the mass was stirred at 40° C. Ammonia was added to bring the emulsion pH to 6.5, and stirring was continued until all of the solid matter was completely dispersed in the liquid. The resulting emulsion was then processed and coated as is usual for photographic emulsions.

Example 2.—The use of the *m*-carboxy benzene sulfonyl derivative of gelatin for making silver-halide dispersions: The gelatin derivative was prepared by dissolving 100 g. of gelatin in 900 cc. of distilled water at 40° C. The solution was then adjusted to a pH of 10 with 10% aqueous sodium hydroxide, and there was then added 10.5 g. of *m*-carboxybenzene sulfonyl chloride in 50 cc. of dry acetone over a 2-hour period. The temperature and pH was maintained by the application of heat and the occasional addition of alkali. The pH was then adjusted to 7.0, the gelatin derivative was set by chilling, sliced, washed, and dried.

To a solution of 80 g. of potassium bromide, 1 g. of potassium iodide, and 25 g. of the gelatin derivative prepared as described in 900 cc. of distilled water at 50° C., a solution of 100 g. of silver nitrate in 900 cc. of distilled water also at 50° C. was slowly added over a period of ten minutes. The temperature of the resulting emulsion was maintained at 50° C. for another ten minutes. The emulsion was then cooled to 35° C. and dilute sulfuric acid was added thereto to reduce the pH to 3.0. A coagulum of silver halide and the gelatin derivative formed and was allowed to settle out whereupon the liquid was

decanted therefrom. A volume of distilled water approximately equal to the original volume was added; the mass was heated to 35° C. and the pH was adjusted while stirring to 6.0–8.0. The coagulum redispersed whereupon dilute sulfuric acid was added to give a pH of 3.8–4.2. The coagulum was again caused to settle to the bottom of the container and the supernatant liquid was decanted. The emulsion was made up to the desired weight by the addition of water and gelatin. A uniform dispersion of the coagulum was obtained by stirring at 40° C. and a pH of approximately 7.0. After appropriate digestion the emulsion showed normal sensitometric characteristics when coated on plates.

Example 3.—Use of the benzoyl chloride derivative of gelatin in making silver-halide dispersions: The gelatin derivative was prepared by dissolving 100 g. of gelatin in 1100 cc. of water at 40° C., adjusting the pH to 9.5–10.0 with 20% sodium hydroxide and adding 15 g. of benzoyl chloride over a short period (3–20 minutes). The pH was maintained at about 10.0 by occasional addition of alkali. The reaction was continued at 40° C. for one hour, the pH of the mixture was lowered to 6–7 with dilute sulfuric acid, and the gelatin derivative was chill set, sliced, and dried.

There was mixed together in 900 cc. of distilled water at 50° C., 800 g. of potassium bromide, 1 g. of potassium iodide, and 25 g. of the gelatin derivative. A solution of 100 g. of silver nitrate in 900 cc. of distilled water also at 50° C. was added thereto over a period of ten minutes. The temperature of the resulting emulsion was maintained at 50° C. for another ten minutes, following which the emulsion was cooled to 35° C. and a quantity of dilute sulfuric acid sufficient to lower the pH of the emulsion to 3.0 was added. When the coagulum had settled, the supernatant liquid was decanted and the coagulum was rinsed with three changes of cold water. There was then added 125 g. of gelatin and distilled water to bring the weight of the mass to 5.5 lbs. The pH was adjusted to 6–7 with dilute ammonium hydroxide, and 0.25–0.5 g. of potassium bromide was added. The emulsion was finished by heating at 65° C. for 20–40 minutes and was then coated onto glass plates where the emulsion layer was dried and tested sensitometrically by exposure in a sensitometer and development in a photographic developer. The emulsion showed normal sensitometric characteristics.

Example 4.—Use of the furoyl chloride derivative of gelatin in preparing silver-halide dispersions: The gelatin derivative was prepared in a manner similar to that of Example 3 except that only 7.5 g. of alpha-furoyl chloride was used instead of 15 g. of benzoyl chloride.

The emulsion was prepared as in Example 3 using this furoyl halide derivative of gelatin as the peptizing agent. After the silver-halide grains had been thoroughly washed, the emulsion was cooled to 35°, the pH was lowered to 3 with dilute sulfuric acid, the coagulum was washed, rinsed with three changes of cold water and then made up with the desired quantities of gelatin and water. The coagulated silver-halide grains and gelatin derivative were readily dispersed at a pH of 6–7. The emulsion was made up with an aqueous solution of gelatin. The pH was adjusted and potassium bromide was added as described herein. The emulsion was finished by heating at 65° C. for a short

time and was coated on film support which was dried and tested photographically. The emulsion showed normal sensitometric characteristics.

Example 5.—The use of the phthalic anhydride derivative of gelatin in making silver-halide dispersions: The gelatin derivative was prepared by the method described in Example 3 except that 5 g. of phthalic anhydride in 35 cc. of dry acetone was used instead of the benzoyl chloride. The silver-halide dispersion was prepared by adding to a solution of 80 g. of potassium bromide 1 g. of potassium iodide and 25 g. of the gelatin derivative in 900 cc. of distilled water at 50° C., a solution of 100 g. of silver nitrate in 900 cc. of distilled water at 50° C. all over a period of ten minutes. The temperature of the resulting mass was then maintained at 50° C. for another ten minutes. The silver-halide dispersion was then cooled to 35° C. and dilute sulfuric acid was added thereto to bring the pH to 3. The clear supernatant liquid formed upon standing was decanted. There was then added a volume of distilled water approximately equal to the original volume of the emulsion and stirring was continued at 35° C. and a pH of 3–3.5 until the coagulum was dispersed. Dilute ammonium hydroxide was then added to adjust the pH to 3.8–4.2 at which point the gelatin derivative and silver halide settled to the bottom of the container. After decanting the liquid the silver-halide dispersion was made up with gelatin and water and with proper finishing gives an emulsion having normal sensitometric characteristics.

Instead of being made up directly into an emulsion the washed coagulum consisting of silver-halide grains and the gelatin derivative may be dried. When it is desirable to use the dried coagulum, it may be employed by soaking in water for a time whereupon it may be readily dispersed at a pH of approximately 6 or 7.

Example 6.—The use of the maleic anhydride derivative of gelatin as the peptizer in making silver-halide dispersions: The maleic anhydride derivative of gelatin was prepared in the same manner as described in Example 3 except that 4 g. of maleic anhydride was employed in reacting upon the gelatin instead of the benzoyl chloride. The emulsion was prepared by mixing a solution of 80 g. of potassium bromide, 1 g. of potassium iodide and 25 g. of gelatin in 900 cc. of distilled water at 50° C. and adding over a period of ten minutes a solution of 100 g. of silver nitrate in 900 cc. of distilled water at the same temperature. The temperature of the dispersion was maintained at 50° C. for an additional ten minutes, was then cooled to 35° C. and dilute sulfuric acid was added to impart a pH of 3.0. The coagulum settled to the bottom of the container, the supernatant liquid was decanted, and a volume of water equal to the original volume was added. The temperature was adjusted to 35° C. and while stirring the pH was adjusted to 6–8 with dilute ammonium hydroxide. The coagulum was thus redispersed in water. Dilute sulfuric acid was added to impart a pH of 3.8–4.2 whereupon the coagulum again settled. The liquid was decanted, and the silver-halide dispersion was mixed with an aqueous gelatin. The resulting emulsion was coated on film base and tested for photographic characteristics. Normal sensitometric characteristics were obtained therefrom on finishing.

Example 7.—Use of the phenyl ureido derivative of gelatin in preparing silver-halide disper-

sions: A silver-halide dispersion was prepared by preparing a solution of 80 g. of potassium bromide, 1 g. of potassium iodide and 25 g. of gelatin in 900 cc. of distilled water at 50° C. There was then added to this solution over a period of ten minutes a solution of 100 g. of silver nitrate in 900 cc. of distilled water, also at 50° C. The resulting dispersion was maintained at 50° C. for ten minutes. The mass was then cooled to 40° C., the pH of the emulsion was adjusted to approximately 9.0 with dilute ammonium hydroxide, and a solution of 2.5 g. of phenyl isocyanate in 30 cc. of dry acetone was added thereto and stirred in for approximately five minutes while maintaining the pH of the emulsion at about 9.5 by periodical additions of dilute ammonium hydroxide. The pH of the emulsion was then adjusted to 3 by the addition of dilute sulfuric acid. The silver halide and gelatin derivative were thereby caused to settle, and the clear, supernatant liquid was decanted. The coagulum was dispersed in an equal volume of distilled water at 40° C. at a pH of approximately 3.0. The pH was then raised to 3.8–4.2 with dilute ammonium hydroxide whereupon the coagulum again formed and settled and the liquid was decanted. A photographic emulsion was made up using this coagulum with the required amounts of gelatin and water as described in the preceding examples. The photographic emulsion upon testing was found to have normal sensitometric characteristics on finishing.

If desired, instead of preparing the silver halide in the gelatin solution, the gelatin derivative prepared may be employed as the dispersing colloid during the silver halide precipitation. The coagulation procedures in both cases are identical.

Example 8.—Use of the p-tolyl ureido derivative of gelatin in making silver-halide dispersions: A gelatin derivative was prepared in the same manner as described in Example 3 except that 7.5 g. of p-tolyl isocyanate was employed instead of the benzoyl chloride. The silver halide was prepared in a solution of this gelatin derivative in the same manner as described in Example 3. After maintaining the dispersion at 50° C. for ten minutes, it was cooled to 35° C., and the pH of the emulsion was adjusted to 3.0 with dilute sulfuric acid. When the coagulum had settled, the clear, supernatant liquid was decanted therefrom. An equal volume of distilled water was added, and the mass was stirred at 35° C. at a pH of 3–3.5 until the coagulum had dispersed. Re-coagulation was then effected by adding dilute ammonium hydroxide to impart a pH of 3.8–4.2. The dispersion thus obtained was employed in preparing a photographic emulsion by mixing gelatin and water therewith as described in Example 3 whereupon the emulsion was tested as described there. It was found that normal sensitometric characteristics were present in this emulsion.

*Example 9.—*A gelatin derivative was prepared in the same manner as in Example 3 except that diethyl diacetyl succinate was added before raising the pH to 10, and the reaction time was six hours, the diethyl diacetyl succinate being employed instead of benzoyl chloride. The silver-halide dispersion was prepared as described in that example using the diethyl succinate derivative of gelatin as the dispersing colloid. After the temperature of the dispersion had been maintained at 50° C. for ten minutes, the emulsion was cooled to 35° C. and dilute sulfuric acid was added to impart a pH of 3. When the co-

agulum had settled, the clear, supernatant liquid was decanted and the coagulum was washed with three changes of cold water, taking care to break up the large masses to permit thorough washing. This coagulum was then employed to prepare a photographic emulsion by mixing therewith the desired quantities of gelatin in water and stirring until the whole was dispersed with the pH raised to 7 with dilute ammonium hydroxide. The emulsion was tested as described in the preceding examples and showed satisfactory sensitometric data as to speed, fog, and contrast, following suitable digestion.

It is to be understood that in all of the procedures described herein for the preparation of silver-halide dispersions that the preparation of the silver halide is carried out under darkened conditions so as to preserve the light-sensitivity of that material.

We claim:

1. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of a gelatin derivative whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, which derivative is selected from the group consisting of the aromatic sulfonyl chloride derivatives of gelatin, the carboxylic acid chloride derivatives of gelatin, the carboxylic acid anhydride derivatives of gelatin, the aromatic isocyanate derivatives of gelatin and the 1,4 diketone derivatives of gelatin, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH, whereby silver halide-gelatin derivative grains are formed, and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

2. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of an aromatic sulfonyl chloride derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

3. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of a carboxylic acid chloride derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

4. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of a carboxylic acid anhydride derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin deriva-

tive grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

5. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of an aromatic isocyanate derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

6. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of 1,4 diketone derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

7. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of the benzene sulfonyl chloride derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

8. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of the benzoyl chloride derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

9. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of the phthalic anhydride derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

10. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of the tolyl isocyanate derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, co-

agulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed and subsequently separating the silver halide-gelatin derivative grains thus formed from the liquid portion of the mass.

11. A method of preparing a gelatino-silver halide emulsion which comprises preparing a silver halide dispersion by mixing together a water-soluble silver salt and a water-soluble halide in an aqueous solution of a phthalic anhydride derivative of gelatin whose presence renders the dispersion obtained coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative by adjusting to said pH whereby silver halide-gelatin derivative grains are formed, separating the thus-formed silver halide-gelatin derivative grains from the liquid portion of the mass and subsequently mixing those grains with gelatin and water as a protective colloid for the silver halide whereby a photosensitive emulsion is formed.

12. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of a gelatin derivative whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, which derivative is selected from the group consisting of the aromatic sulfonyl chloride derivatives of gelatin, the carboxylic acid chloride derivatives of gelatin, the carboxylic acid anhydride derivatives of gelatin, the aromatic isocyanate derivatives of gelatin and the 1,4 diketone derivatives of gelatin, coagulating the dispersion of silver halide in gelatin derivative by adjusting to said pH whereby silver halide-gelatin derivative grains are formed, separating those grains from the liquid portion of the mass, redispersing the grains thus obtained in water at an elevated pH followed by adjusting the pH of the solution to that which will coagulate the silver halide dispersion which pH is within the range of 3-4.5, and separating the thus-formed silver halide-gelatin derivative grains from the liquid portion of the mass.

13. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble halide salt and a water-soluble silver salt in an aqueous solution of a phthalic anhydride derivative of gelatin, whose presence renders the dispersion thus obtained coagulable at a pH within the range of pH 3-4.5, coagulating the dispersion of silver halide in gelatin derivative by adjusting to said pH whereby silver halide-gelatin derivative grains are formed, separating those grains from the liquid portion of the mass, redispersing those grains in water at an elevated pH followed by adjusting the solution to a pH which will coagulate the silver halide dispersion, which pH is within the range of 3-4.5 and separating the thus-formed silver halide-gelatin derivative grains from the liquid portion of the mass.

14. A method of preparing a gelatino-silver halide emulsion which comprises preparing a silver halide dispersion by mixing together a water-soluble silver salt and a water-soluble halide in an aqueous solution of a gelatin derivative whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5,

which derivative is selected from the group consisting of the aromatic sulfonyl chloride derivatives of gelatin, the carboxylic acid chloride derivatives of gelatin, the carboxylic acid anhydride derivatives of gelatin, the aromatic isocyanate derivatives of gelatin and the 1,4 diketone derivatives of gelatin, coagulating the dispersion of silver halide-gelatin derivative by adjusting to said pH whereby silver halide-gelatin derivative grains are formed, separating the thus-formed grains from the liquid portion of the mass and subsequently mixing those grains with water and gelatin as a protective colloid for the silver halide whereby a photosensitive emulsion is formed.

15. In a method of preparing washed silver halide dispersions, the steps which comprise mixing together a water-soluble silver salt and a water-soluble halide salt in an aqueous solution of a maleic anhydride derivative of gelatin whose presence renders the dispersion coagulable at a pH within the range of 3-4.5, coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed, and subsequently separating the thus-formed grains from the liquid portion of the mass.

16. A method of preparing a washed gelatino-silver halide photographic emulsion which comprises preparing a silver halide dispersion by mixing together a water-soluble silver salt and a water-soluble halide in an aqueous solution of a gelatin derivative whose presence renders the dispersion coagulable at a pH within the range of pH 3-4.5, which derivative is selected from the group consisting of the aromatic sulfonyl chloride derivatives of gelatin, the carboxylic acid chloride derivatives of gelatin, the carboxylic acid anhydride derivatives of gelatin, the aromatic isocyanate derivatives of gelatin and the 1,4 diketone derivatives of gelatin coagulating the dispersion of silver halide in gelatin derivative thus formed by adjusting to said pH whereby silver halide-gelatin derivative grains are formed, separating the thus-formed grains from the liquid portion of the mass, redispersing those grains in water at a dispersing pH therefor, followed by adjusting the pH of the solution to that which will coagulate the silver halide dispersion, said pH being within the range of 3.8-4.2, separating those grains from the liquid portion of the mass and mixing them with water and gelatin as a protective colloid for the silver halide whereby a photosensitive emulsion is formed.

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