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PREPARATION OF SILVER HALIDE GRAINS AND PHOTOGRAPHIC EMULSIONS

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ABSTRACT OF THE DISCLOSURE

Silver halide grains of controlled size are obtained by preparing a soluble silver halide-ammonia complex in water, with or without a carrier, and then depositing solution drops of controlled size into a chilled non-aqueous immiscible fluid. This results in the formation of discrete spheres of silver halide solution, which spheres are subsequently treated to remove the ammonia, and precipitate discrete grains of silver halide having a preselected size. Where a carrier is not present in the original solution, subsequent dispersion of the silver halide grains in a carrier, such as gelatin, forms a photographic emulsion. The practice of this invention is especially useful in producing silver halide grains of substantially uniform size for use in a light-sensitive emulsion having excellent contrast, and sensitivity. Where the silver halide particles are uniformly large the resulting emulsion is also capable of high-speed exposure.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to the preparation of silver halide grains, and to light sensitive silver halide emulsions, as well as to light sensitive photographic elements, such as paper, plates, or films containing such emulsions.

Description of the prior art

Ordinarily, silver halide photographic emulsions are formed by the gross reaction of a water-soluble halide with a water-soluble silver salt in the presence of water and a carrier, such as gelatin. Upon mixing, the soluble silver salt and soluble halide react immediately to form an insoluble silver precipitate. Following initial silver halide grain formation, the gelatin emulsion is normally noodled, washed, and then melted, with or without additional gelatin, to remove unreacted soluble salts and to control both the size and size distribution of the silver halide grains obtained. This classical process has the disadvantage of producing a photographic emulsion in which the silver halide grain size is relatively uncontrolled and spread over a large range. A narrow range of size distribution is desirable for a high-quality photographic emulsion exhibiting good contrast, and sensitivity.

Emulsions having a wide range of grain size have an average contrast. High contrast is obtained from grains having as nearly as possible the same size. It is not unusual for commercial process to have grain sizes of relative areas of 10 to 1, while negative emulsions often run to a range of relative areas of 100 to 1.

Sensitivity increases as the size of the grains increase. In order for a silver halide grain to undergo the chemical reaction which reduces it to silver upon exposure to light, each grain must be struck by a minimum number of photons of light in a short period of time. The smaller the grain, the more difficult it is for the requisite number of photons to impinge upon its surface in a short time. The larger the silver halide grain, the more readily it intercepts the requisite number of photons. It is thus seen that, at a given level of exposure, a large grained silver halide photographic emulsion will be completely exposed much more rapidly than a small grained silver halide emulsion. It is therefore desirable in some instances to have a photographic emulsion in which the silver halide grains are not only of uniform size, but also of large diameter.

SUMMARY OF THE INVENTION

It has now been discovered that silver halide grains of uniform size can be provided by a simple and inexpensive technique. In the present invention, an aqueous precipitate of silver halide, with or without a carrier, is formed. The silver halide grains are then rendered soluble in water by, for example, reacting the silver with ammonia to form a soluble silver ammonia complex. Subsequently, the complexed silver halide solution thus formed is dissipated into uniform-sized drops and caused to come into contact with a chilled non-aqueous liquid in which the silver halide solution is immiscible and forms frozen prills. The individual uniformly sized frozen silver halide solution droplets thus formed are then treated to reprecipitate a silver halide grain in each droplet of solution. In most instances, the silver halide grains thus formed will be substantially uniform in size with only one grain precipitating from each drop. The size of each grain will be a function of both the size of the drop from which it was precipitated and the silver halide concentration of that drop. Therefore, under this procedure, uniform silver halide grains of any size, from a fraction of a micron to larger than 20 microns, can be formed. If required, the resulting silver halide grains are then dispersed in gelatin or some other carrier to form a photographic emulsion exhibiting excellent contrast and sensitivity. The speed of the resulting emulsion is a function of the grain size.

The foregoing and other objects, features, and advantages of the invention will be apparent from the following description of the preferred embodiments of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, the preparation of silver halide grains for incorporation in photographic emulsions is carried out by preparing a relatively dilute aqueous solution of silver halide-ammonia complex. Other means of rendering silver halide soluble in aqueous solution may also be employed and are to be considered fully equivalent to ammonia. Regardless of the means employed to render silver halide soluble, it must be reversible so that silver halide can be precipitated from the solution.

After the silver halide solution is formed, droplets of the solution having controlled size and uniform silver halide concentration are formed and caused to enter a fluid in which the silver halide solution is immiscible. Suitable fluids include toluene, silicone oils, carbon-based oils and many other organic liquids. In the preferred embodiments, the immiscible liquids into which the silver halide droplets are dispersed is at a controlled temperature, at or below the freezing temperature of the silver solution, thereby causing the droplets not only to remain discrete, but to freeze into tiny prills. Where this latter approach is taken, the resulting frozen spheres can easily be segregated and handled for further processing to form individual silver halide grains. For example, where the silver halide is complexed with ammonia, the ammonia can be subsequently driven off under controlled time and temperature conditions so that the silver halide in each droplet precipitates to form a single grain of controlled size.

As previously noted, the size and composition of the silver halide grains formed in accordance with this invention are most easily controlled by selecting suitable reactants to form the silver halide, and controlling the con-

centration of the silver halide solution, as well as the size of the individual droplets. Any water soluble silver compound capable of reacting with a halide compound to produce an insoluble silver halide compound, and any halide compound capable of reacting with a silver compound to produce an insoluble silver halide compound may be used in the practice of this invention. In some instances the practice of this invention will be best served by the use of previously formed silver halide. Any source of ammonia, such as ammonium hydroxide, can be used.

To initially implement this procedure, droplets of silver halide solution may be formed in a discontinuous stream from, for example, burette. However, once desired composition, concentration, and droplet size is determined experimentally, it is relatively easy to prepare a fixture containing hundreds of ports, from each of which droplets of equal size and concentration are caused to issue discontinuously, but in a continuous operation. This latter technique, or adaptations of this latter technique make it possible for both laboratory and commercial quantities of controlled size silver halide grains to be formed. In a similar manner, the discrete prills formed by the technique of the present invention can be caused to precipitate the silver halide in each sphere as a single grain of controlled size, in most instances, by merely collecting them from the immiscible liquid and placing them under temperature conditions in which the ammonia complexing agent sublimes. By controlling the time and temperature of precipitation, the growth of a single crystal per prill can be assured. For example, by maintaining the prills frozen, but at a temperature just below their melting point, ammonia will slowly, but completely sublime, and thus provide formation of insoluble silver halide. In a larger volume technique, the droplets can be formed and then removed from the immiscible liquid continuously, through an outlet in the immiscible liquid container or by a conveyor system, for example, and then further conveyed in a continuous manner for whatever additional processing is necessary in order to allow the desired formation of the individual silver halide grains.

Subsequent to the formation of the individual silver halide grains, the grains are washed, if necessary, to remove any traces of salts or complexing ingredients and then dispersed in a carrier, such as gelatin. The dispersal of such presized and prewashed silver halide in gelatin can thus be accomplished rapidly, without the usual washing, melting, ripening, and noodling techniques since the silver halide grains are in themselves free of any undesirable salts or other ingredients, and since it is not necessary to control the grain size of the silver halide by the use of these techniques. Thus, once the silver halide particles are available, the actual formation of a photographic emulsion can be accomplished much more rapidly than by the use of classic techniques. Furthermore, the photographic emulsion thus obtained exhibits excellent contrast and sensitivity due to the uniformity of the silver halide particles.

Where silver halide grains of controlled size have been produced in accordance with the teaching of the present invention in a gelatin-containing environment, the grains and gelatin will already be associated in a mixture at the time the grain growth is completed. Therefore, all that remains to render the mixture usable as an emulsion will be to melt the prills, if necessary, and, if desired, add additional water, gelatin, or other constituents.

The following examples illustrate this invention:

EXAMPLE I

A classical silver halide gelatin emulsion was prepared by dispersing 31.2 grams of potassium bromide, 2.0 grams of potassium iodide, and 8 drops of concentrated ammonium hydroxide in 400 ml. of distilled water. A second solution containing 42.0 grams of silver nitrate and 400 ml. of distilled water was also prepared. The halide and silver solutions were then added to a solution of 20

grams of gelatin and 16 drops of concentrated ammonium hydroxide in 300 ml. distilled water. Addition of the halide and silver solutions was carried out over a period of 35 minutes with the gelatin solution being slowly stirred at all times. The temperature of the gelatin solution was maintained at 68° C. throughout the addition reaction. The resulting mixture was then poured into 3 liters of cold absolute methanol maintained at a temperature of 0° C. The precipitated mass was recovered by decantation, dissolved in 400 ml. of 0.025 M ammonium hydroxide and reprecipitated by cooling. The resulting gel was then noodled, poured into 1200 ml. of ice water, and stirred to remove unreacted salts. Following this washing, the mixture was stored for 1 hour, after which the water was decanted. This noodling and washing technique was repeated a total of 4 times. The resulting classical emulsion was free of fog and exhibited a density of 1.105 grams/ml.

A sample containing 49.9 grams of the silver halide gelatin emulsion, prepared above, was mixed with an additional 4.8 grams of gelatin and with 4.4 grams of concentrated ammonium hydroxide. The ammonia in the ammonium hydroxide caused the silver in the silver halide to form a water soluble complex. The resulting complexed solution was then placed in a burette which was insulated and warmed with heating tapes to keep the gelatin molten. The stopcock of the burette was opened to a fixed position to emit droplets having a volume of about 0.053 ml. from the nozzle of the burette. Below the nozzle of the burette there was suspended a vessel containing water immiscible silicone oil, the vessel itself being surrounded by a Dewar flask containing Dry Ice and acetone. While this extremely cold environment did not solidify the silicone oil, it did chill the oil to a temperature such that as the droplets of complexed silver halide gelatin solution descended through the silicone oil, they formed spheres which froze into discrete pellets or prills. Upon descending to the bottom of the container of chilled silicone oil, the prills maintained their identity and did not shatter or coalesce with one another.

The prills thus provided by this technique were divided into two portions and placed in separate, capped vials. One vial was placed in a refrigerator freezer at a temperature of 0° C. for 27 days. At this temperature and under these conditions, the ammonia slowly evaporated from each prill, causing the silver halide to reprecipitate and form a single grain at the same rate. The second vial was held at room temperature for a period of 27 days. Under these conditions the prills quickly melted and lost their identity. Following this 27-day period, each sample was coated on a separate glass plate with a single layer of grains. The size-frequency distribution of the grains on each plate was then determined by making photomicrographs at a magnification of 4000 times and measuring the diameter of each particle. The particle size range for both the frozen and room temperature reprecipitated emulsions each were found to cover a range of approximately two microns. However, the size distribution of the silver halide grains in the two emulsions was startlingly different. The sample that was slowly reprecipitated in the freezer exhibited 92% of the particles in the one micron range of 0.8 to 1.8 microns. The sample which was reprecipitated quickly, at room temperature, exhibited only 74% of its grains in the 1.1 micron range of .7 to 1.8 microns. However, even this latter sample showed a surprisingly narrow range of grain sizes as compared with the original classical emulsion prior to its treatment in accordance with the present invention. The original classical emulsion which was not processed in accordance with the teachings of this invention showed an overhwelming majority of particles in the size range of about 0.1 micron, or less, and yet inconsistently included a large number of grains on the order of 1 micron and more so that the overall range distribution was on the order of 100 to 1 in terms of area.

Employing statistical terms, the classical emulsion was bimodal, having separate distribution curves clustered in both the 0.1 micron and 1 micron range. The emulsions provided by the present invention had a Gaussian distribution, with the slowly precipitated species having a narrower half width.

It is therefore seen that using the technique of the present invention results in larger grains having more uniform distribution of size, with the distribution of size being even further improved where reprecipitation is controlled by time and temperature techniques.

Silver halide gelatin emulsions made in accordance with the present invention were coated on paper of the type used in preparing ordinary photographic paper. After customary processing, they were found to give prints of good quality, showing good contrast, and high sensitivity.

EXAMPLE II

A complexed silver halide solution containing approximately 0.02% silver bromide, and ammonia, but no gelatin, was prepared in a manner similar to Example I. Droplets of the complexed solution in water were then released from a burette in drops of 0.053 ml. into a chilled water immiscible toluene bath. The frozen spheres were collected without thawing and stored in a freezer at 0° C. in a loosely capped vial. After 40 days, substantially all of the particles lay in the range of 0.5 to 1.2 microns. Subsequent dispersal of the particles in a carrier to form an emulsion, and coating of the emulsion on a substrate, resulted in a light sensitive article displaying excellent contrast and sensitivity characteristics, and capable of high speed exposure.

In the practice of the present invention, the silver halide concentration can range from about 0.01 to 15%, by weight, of the prill-forming solution, with the preferred range being 0.01 to about 8%, by weight. While the examples shown include gelatin in the prill-forming solution, the present invention may be carried out successfully in hte complete absence of gelatin or with as much as about 30% gelatin or other carrier, by weight. The preferred range of carrier is about 0 to 15%.

The drop size and concentration of the situations are interdependent and are chosen to provide the minimum amount of silver halide material required by one grain of the desired size as determined experimentally or as calculated based upon the density of the silver halide compound.

The solvent of choice in preparing the silver halide ammonia complex solutions is water. The cooling fluid must be immiscible with water, capable of remaining liquid at temperatures necessary to freeze the complexed silver halide solution and is preferably easily available and inexpensive. The viscosity of the water immiscible material should be selected such that the droplets of complexed silver halide solution will descend at such a speed that they become solid before they contact one another. Falure to do this will result in the still liquid particles contacting one another and coalescing, to eventually form undesirably large grains.

By the practice of the present invention, silver halide gelatin emulsions can be obtained in which the grain size is substantially uniform, thus yielding photographic articles of excellent contrast and good sensitivity. The technique of the present invention is also useful in providing large-grained emulsions, and as such is a new form of ripening in which a small-grained emulsion has its grain size increased.

While the present invention is primarily directed at the production of silver halide grains of uniform size, its teaching is not necessarily limited to this mode of operation. In some instances, for example, a precisely controlled range of particle sizes is desired. The present invention can be utilized to provide a controlled range of particle sizes by several techniques. Several different sizes of particles can be prepared and blended, for example. In another approach, droplets of different sizes over a controlled size range can be prepared simultaneously and processed to produce grains covering a controlled size range. In any event, the teachings of the present invention can be applied to the preparation of silver halide grains of controlled size, as well as to the preparation of grains of uniform size.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. The process of producing silver halide grains of substantially controlled size comprising:
   - mixing silver halide with sufficient ammonia to completely dissolve the silver halide by forming a soluble complex with the silver;
   - producing drops of substantially controlled size from said complex solution;
   - placing said drops of complexed solution into an immiscible fluid, said fluid being maintained at a temperature to cause each drop of said solution to freeze and form a discrete prill;
   - removing said prills from said immiscible fluid; and then
   - placing said prills under conditions of temperature and environment to cause the ammonia to disassociate from the silver so that the silver halide in substantially each prill precipitates as a grain of controlled size.

2. The method of claim 1 wherein the silver halide in each drop constitutes about 0.01 to about 15%, by weight, of the drop.

3. The method of claim 1 wherein the silver halide portion of each drop constitutes 0.01 to about 8%, by weight, of the drop.

4. The process of claim 1 wherein a carrier is present in the solution prior to the formation of drops of controlled size.

5. The process of claim 4 wherein the carrier is gelatin.

6. The process of claim 1 wherein a carrier is associated with the silver halide prior to the formation of the soluble silver ammonia complex.

7. The process of claim 1 wherein the silver halide grains produced are of substantially uniform size, and in which the drops of controlled size are of substantially uniform size.

8. The process of producing silver halide grains of substantially controlled size comprising:
   - mixing together in aqueous solution a soluble silver compound capable of reacting with a halide compound to produce silver halide, a halide compound capable of reacting with silver to produce silver halide, and ammonia in an amount to form a soluble silver ammonia complex with the silver present;
   - producing drops of substantially controlled size from said complex solution;
   - placing said drops of complexed solution into an immiscible fluid, said fluid being maintained at a temperature to cause each drop of said solution to freeze and form a discrete prill;
   - removing said prills from said immiscible fluid; and then
   - placing said prills under conditions of temperature and environment to cause the ammonia to disassociate from the silver so that the silver halide in substantially each prill precipitates as a grain of controlled size.

9. The method of producing a light-sensitive photographic emulsion including silver halide grains of substantially controlled size comprising:

mixing silver halide with sufficient ammonia to completely dissolve the silver halide by forming a soluble complex with the silver;

producing drops of substantially controlled size from said complex solution;

placing said drops of complexed solution into an immiscible fluid, said fluid being maintained at a temperature to cause each drop of said solution to freeze and form a discrete prill;

removing said prills from said immiscible fluid;

placing said prills under conditions of temperature and environment to cause the ammonia to evaporate so that the silver halide in substantially each prill precipitates as a grain of controlled size; and then

associating said grains of substantially controlled size with a carrier to form an emulsion.

10. The method of producing a light-sensitive photographic element including silver halide grains of substantially controlled size comprising:

mixing silver halide with sufficient ammonia to completely dissolve the silver halide by forming a soluble complex with the silver;

producing drops of substantially controlled size from said complex solution;

placing said drops of complexed solution into an immiscible fluid, said fluid being maintained at a temperature to cause each drop of said solution to freeze and form a discrete prill;

removing said prills from said immiscible fluid;

placing said prills under conditions of temperature and environment to cause the ammonia to disassociate from the silver so that the silver halide in substantially each prill precipitates as a grain of controlled size;

associating said grain of substantially controlled size with a carrier to form an emulsion; and then

coating the resulting emulsion on a substrate.

11. The method of claim **10** wherein a carrier is present in the solution prior to the formation of drops of substantially controlled size, and association of the resulting grains of substantially controlled size, after their formation, with additional carrier is a matter of choice.

12. The article produced by the process of claim **11.**

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