

Dec. 10, 1968

G. F. FRAME ET AL

3,415,650

METHOD OF MAKING FINE, UNIFORM SILVER HALIDE GRAINS

Filed Nov. 25, 1964

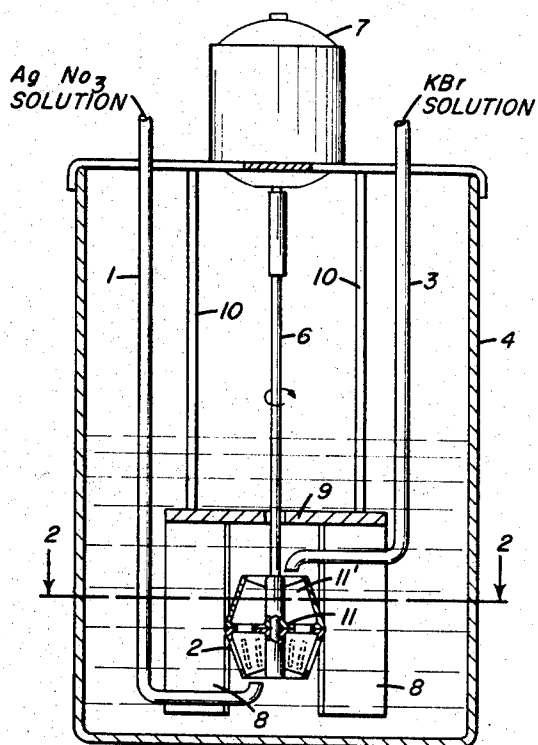


FIG. 1

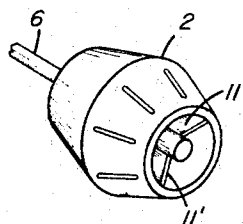


FIG. 3

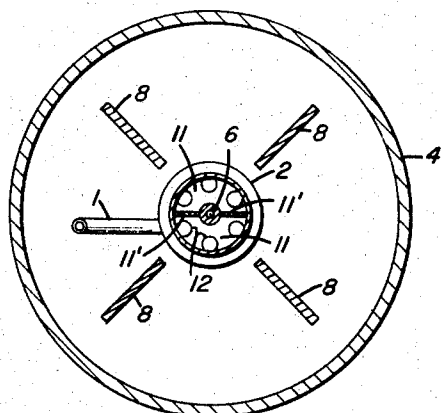


FIG. 2

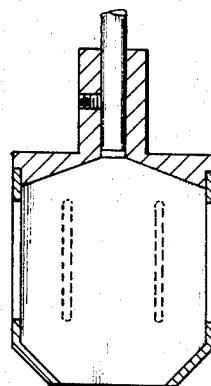


FIG. 4

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Filed Nov. 25, 1964, Ser. No. 413,807

18 Claims. (Cl. 96—94)

ABSTRACT OF THE DISCLOSURE

In making silver halide emulsions, the initial silver halide precipitation is carried out in a reaction zone beneath the surface of peptizer solution introducing a soluble silver and halide salt into a mixing chamber through which peptizing solution circulates. The silver halide reactants form silver halide precipitates in the reaction chamber which are expelled by centrifugal force.

This invention relates to a process for the preparation of silver halide crystals exhibiting improved physical characteristics. More particularly, this invention relates to the preparation of silver halide crystals which exhibit fine mean grain size. In a specific aspect, this invention relates to the preparation of silver halide crystals of fine grain size and uniformly by precipitating silver halide under certain prescribed conditions.

In the preparation of silver halide type photographic emulsions it is often desirable to have the silver halide grains in finely divided form. This is ordinarily accomplished by a double decomposition reaction in an aqueous solution of a colloid, called an aqueous peptizer solution, for example, aqueous gelatin solution. In preparing one type of photographic emulsion, i.e., a double jet emulsion, a water soluble silver salt and a water soluble halide solution are added simultaneously to the aqueous peptizer solution. When silver halide grains are precipitated according to such prior art procedures, the grain size tends to vary widely, particularly in fine grain emulsions. This is particularly true in large scale operations, for example, those employing at least 30 liters of solution. This non-uniformity of silver halide grains imparts adverse photographic characteristics which deleteriously affects the quality of photographic materials prepared from such emulsions. It is evident, therefore, that a method for providing silver halide crystals of fine grain size and good uniformity according to the aforementioned double decomposition reaction will greatly enhance the art.

Accordingly, it is an object of this invention to provide a method for preparing silver halide grains of improved physical properties.

Another object of this invention is to provide a method for preparing silver halide grains exhibiting improved uniformity of size.

Another object of this invention is to provide a method for preparing silver halide crystals which combine fine grain size with good uniformity of size.

Another object of this invention is to provide a method which is particularly effective in making silver halide grains of uniform size in large quantities, for example, at least 30 liter batches.

Still another object of this invention is to provide a method of making silver halide grains of uniform size which method is particularly advantageous in the preparation of double jet emulsions.

Still another object of this invention is to provide a method which substantially eliminates the formation of large non-uniform grains which tend to reduce light contrast and sharpness in photographic emulsions.

Still another object of this invention is to provide a simple, direct and economically feasible method for the preparation of silver halide grains having improved size uniformity.

Other objects of this invention will become apparent from an examination of the specification and claims that follow.

In accordance with this invention, it has been found that silver halide crystals of fine grain size and uniformity can be prepared by precipitating the grains under certain prescribed conditions, as described herein. In practicing this invention, silver halide grains are precipitated in a fluid reaction zone in which the reacting components enter at high velocity. After the grains are precipitated, they are expelled from the reaction zone by centrifugal force beneath the surface of an aqueous peptizer solution which is adjacent to and in fluid contact with the reaction zone, whereby there is obtained fine silver halide grains of good uniformity.

A significant feature of this invention is that photographic emulsions containing the silver halide grains prepared according to this invention are substantially free of non-uniform large grains. Such emulsions exhibit good high light contrast and sharpness.

An apparatus which is effective to prepare silver halide grains, as described herein, is illustrated by the attached drawings in which FIG. 1 is a side elevation in section, FIG. 2 is a cross-sectional view taken along line 2—2, FIG. 3 is a perspective view of the slotted mixing device shown in FIG. 1 and FIG. 4 is a side elevation in section of a modification of the slotted mixing device shown in FIG. 1.

In accordance with one aspect of this invention, aqueous silver nitrate solution is introduced from a remote source by a conduit 1 which terminates close to and adjacent to an inlet zone of a mixing device 2. Substantially simultaneously with the introduction of aqueous silver nitrate solution, and in opposing direction, aqueous potassium bromide solution is introduced from a remote source by a conduit 3 which terminates close to and adjacent to an inlet zone of the mixing device 2. The mixing device 2 is vertically disposed in a vessel 4 and is attached to the end of a shaft 6, driven at high speed by any suitable means, such as motor 7. The lower end of the rotating mixing device is spaced up from the bottom of the vessel 4 but beneath the surface of aqueous peptizer solution, in this case, aqueous gelatin solution, contained in the vessel. Baffles 8, sufficient in number to inhibit vortical rotation of the contents of vessel 4, are located around the mixing device 2 and are stabilized by frame 9 which is attached to supports 10 that can be affixed to the housing of motor 7 or to a saddle, clamp or other suitable means which secures the motor to vessel 4.

The mixing device 2, can be referred to herein simply as a mixing head. This mixing device contains horizontal and vertical baffles 11 and 11', respectively, and rotates at high speed. The horizontal baffles have openings 12 through which liquid introduced into the top of the mixing device passes. The high velocity of aqueous peptizer solution moving through the mixing device causes a suction at the inlet zones so that the aqueous solutions of silver nitrate and potassium bromide directed there go rapidly into the mixing chamber to precipitate silver halide, i.e., to form discrete particles of silver bromide.

In operation, the mixing head is rotated at high speed by shaft 6 which is driven at a speed of at least 1,000 r.p.m., generally about 3,000 to about 4,000 r.p.m., and preferably, about 3,400 to about 3,600 r.p.m. The mixing head is generally activated a short time, for example, 30 seconds to several minutes before the aqueous silver nitrate and potassium bromide solutions are fed. These

solutions, as well as aqueous peptizer, enter the mixing chamber at high velocity through the inlet zones.

The reactants, i.e., the aqueous silver halide and potassium bromide solutions are intimately mixed in the chamber of the mixing device in a zone of high velocity turbulent flow to precipitate silver bromide grains. The silver halide grains are expelled, by centrifugal force, through slots in the side wall of the mixing device 2. When the mixing device 2 is rotated at high velocity substantially all, i.e., at least about 99%, of the silver halide grains are less than 0.5 micron in diameter. The grains are also quite uniform in size, with at least about 80% of the grains being within about .03 micron of each other in diameter, even where rather large quantities, e.g., 30 liters or more, of solution are used. The size of the grains can be determined by any means suitable for this purpose, for example, microscopic measurement. When the mixing head is rotated at low velocity, the average grain size is substantially larger than 0.5 micron, for example, 0.8 micron and larger.

In order to precipitate silver halide grains, i.e., to form discrete particles of silver halide, an aqueous solution of a water soluble silver salt such as silver nitrate is contacted with an aqueous solution of at least one water soluble halide such as hydrogen, alkali metal, alkaline earth, ammonium or like halides, as exemplified by potassium bromide, sodium bromide, ammonium chloride, calcium chloride as well as mixtures of such halides. These solutions are advantageously run into the dynamic reaction zone described herein substantially simultaneously over a period of less than about 20 minutes, generally 3 to about 10 minutes, and preferably about 6 minutes or less. Where silver nitrate solution is to be reacted with alkali metal halide in agitated gelatin solution, the halide present in the gelatin solution before silver nitrate solution is fed should not exceed more than 10%, by weight, of total halide to be introduced. The aqueous solutions of dispersing agent or peptizer which can be employed in practicing this invention include, for example, gelatin or some other colloidal material such as colloidal albumin, cellulose derivative, or a synthetic resin such as a polyvinyl compound, an acrylamide polymer, or the like, although gelatin is preferred. Silver halides prepared according to the method described herein include, for example, silver bromide, silver iodide, silver chloride or mixed silver halides such as silver chlorobromide or silver bromoiodide.

In practicing this invention, it is generally desirable to introduce the reactant solutions into the high velocity mixing zone in opposing directions although the reactants can be introduced in the same direction, if desired. The temperature employed can vary over a rather wide range, but it is generally desirable to operate at a temperature of not more than about 180° F., with the lower temperature of operation being determined by that at which the solution remains liquid.

In practicing this invention, the aqueous solutions of silver salt, halide and peptizer are introduced into a high velocity reaction zone characterized in that the reactants enter, and precipitated silver halide exits, at high velocity. The flow of liquid within this reaction zone is turbulent flow since the velocity changes constantly in magnitude and direction. This provides intimate contact between the reactants to form the solid discrete particles of insoluble silver halide which are expelled from the reaction zone directly into the peptizer solution which surrounds it.

As seen from the attached drawings, particularly FIG. 1, the high velocity reaction zone can be a rotating mixing device having inlets at each end or, as shown in FIG. 4, it can have an inlet at only one end. The mixing device can be positioned within a vessel of aqueous peptizer solution with its axis of rotation oriented in any direction, although it is generally oriented along the vertical axis of the vessel in which it is confined. The

mixing device can be centrally located in the vessel containing aqueous peptizer or it can be off-set. This mixing device, therefore, forms a high speed reaction zone which is separated from the bulk of the surrounding peptizer liquid by fixed boundaries but, through its inlet zones, is in continuous liquid contact with the peptizer solution within which it is confined.

In operation, the peptizer solution is circulated through the reaction zone and along with precipitated silver halide, it is expelled from the reaction zone by centrifugal force, i.e., both are expelled outward from the center of rotation of the reaction chamber. The expelled liquid and solid particles pass rapidly through the slots or other shape openings in the side wall of the mixing head directly into the surrounding bulk liquid to agitate it. Operating in this manner, silver halide grains of good uniformity and small size dispersed in peptizer are obtained. The resulting dispersion can then be digested, ripened, sensitized and other addenda added, as is customary in the art, following which, the emulsion is coated on a suitable photographic support.

As already pointed out, the peptizers employed in this invention include any peptizers for silver halide. However, the peptizer solutions which are most often employed are the protein silver halide peptizer solutions such as gelatin solutions. In order to obtain fine grain silver halides of good uniformity, the grains should be expelled from the reaction zone beneath the surface of the peptizer solution.

The photographic emulsions prepared with the fine grain silver halides of this invention can be coated on a wide variety of support. Typical supports include those generally employed for photographic elements, as exemplified by cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and related films or resinous materials as well as glass, paper, metals, wood and the like. Supports such as paper which are coated with α olefin polymers, particularly polymers of α -olefins containing 2-10 carbon atoms, as for example, polyethylene, polypropylene, ethylene-butylene copolymers and the like, can also be employed.

The emulsions can also contain additional additives, particularly those known to be beneficial in photographic emulsions as exemplified by antifoggants, sensitizers, speed increasing materials, gelatin hardeners, plasticizers and the like.

This invention can be further illustrated by the following examples of preferred embodiments thereof although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLE 1

Using the invention described herein, rather than the conventional procedures of preparing silver halide dispersions with multiple blade stirrers combines a more uniform grain size with fine grain size. To illustrate:

(A) A gelatin solution is prepared by adding 100 parts of gelatin to 5080 parts of distilled water in a vessel and heated to 150° F. Separately 543 parts of silver nitrate are dissolved in 3810 parts of distilled water and heated to 130° F. 67 parts of potassium bromide and 210 parts of sodium chloride are dissolved in 3810 parts of distilled water, which solution is then heated to 150° F.

The gelatin solution in the vessel is stirred vigorously with an impeller confined within the solution. The impeller has four blades, each of which extends about 1½ inches from the shaft which is driven at about 500 r.p.m. The silver nitrate and potassium halide solutions are added simultaneously to the stirred gelatin solution over a period of approximately 6 min. The addition of the potassium halide solution is started approximately 10 seconds prior to the silver nitrate addition. A suspension of

silver halide grains in the liquid in the container results. This suspension is heated at 150° F. for 10 minutes, cooled to 125° F. and 952 parts of gelatin is added. The emulsion is set, noodled and washed. The emulsion is melted at 105° F. A soluble gold salt and a labile sulfur compound are added and the emulsion is sulfur and gold sensitized by heating for several minutes at 155° F. The resulting fine grain chlorobromide emulsion is coated on a glass plate.

(B) Gelatin, silver nitrate and potassium halide solutions are prepared as described in (A). An emulsion is prepared therefrom except that the apparatus, as pictured in FIG. 1 and described hereinabove, is used to form the dispersion of precipitated silver halide in the peptizing solution. The silver nitrate solution is fed through one conduit and the aqueous solution of potassium bromide and sodium chloride is fed through the other. The chamber in the mixing device 2 has a height of approximately 1.3 inches. The center diameter of the chamber is about 1.5 inches and the walls of the chamber taper towards each end to form concentric open ends, each of which has a diameter of about 1 inch. The mixing device is driven at 3,500 r.p.m. As shown in FIG. 1 the silver nitrate and the halide solutions are run into the reaction chamber in opposing directions. The emulsion prepared from the resulting silver halide grains is sensitized and coated as described in procedure A above. The grains prepared in (A) have a mean grain size of 0.8 micron while those prepared in (B) have a mean grain size of 0.3 micron. By microscopic examination the grains prepared in (B) are shown to be much more uniform than those prepared in (A).

Samples of each are exposed on an intensity scale sensitometer and developed in Kodak Developer D-19b for 4 min. at 70° F., whereupon they are fixed, washed and dried. The fine grain size of the emulsion made in (B) is shown by the fact that it is 0.8 to 1.2 log *E* slower than that prepared in (A). These results show that this invention gives smaller more uniform silver halide grains than are prepared by conventional prior art methods.

EXAMPLE 2

(A) A gelatin solution is prepared by adding 568 parts of gelatin to 5610 parts of distilled water in a vessel and heated to 105° F. Separately, 427 parts of silver nitrate are dissolved in 2310 parts of distilled water and the solution is heated to 95° F. 2464 parts of potassium bromide are dissolved in 2310 parts of distilled water and the solution heated to 95° F. The gelatin solution in the container is stirred vigorously with an impeller having four blades extending 1½ inches from the shaft which is driven at about 500 r.p.m., as in Example 1. The silver nitrate and potassium halide solutions are added simultaneously to the stirred gelatin solution over a period of approximately 10 minutes. The resulting suspension is set, noodled and washed. The grains are washed and remelted at 105° F. The emulsion is sensitized and coated using the procedure of Example 1.

(B) Gelatin, silver nitrate and potassium halide solutions are prepared as described in (A). An emulsion is prepared therefrom except that the mixing device, as pictured in FIG. 1, and more particularly described in Example 1, part (B), is used to form the dispersion of precipitated silver halide in the peptizing solution. The emulsion prepared from the resulting silver halide grains is sensitized and coated as described in (A) above. Upon inspection with an electron microscope, the grains prepared in (A) are shown to have larger and less uniform grains than those prepared in (B). Samples of each are exposed on an intensity scale sensitometer and developed in Kodak Developer K-19b for 4 min. at 70° F., whereupon they are fixed, washed and dried. The fine grain size of the emulsion made in (B), as compared to (A), is shown by the fact that it is 0.5 to 0.6 log *E* slower than that prepared in (A).

Thus, in accordance with this invention there is provided a method for preparing silver halide crystals of fine grain size and uniformity. Photographic emulsions containing these crystals are substantially free from the large grains which are found in many fine grain emulsions such as Lippmann type emulsions. The emulsions prepared using the precipitation method disclosed herein are particularly useful in making highly sensitive plates and in direct electron recording films where the presence of large grains is very objectionable.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. The method which comprises precipitating silver halide grains by reaction of soluble silver salt and soluble halide salt reactants in a fluid reaction zone characterized in that said reactants enter at high velocity, and expelling, by centrifugal force, said grains from said reaction zone into an aqueous peptizer solution beneath the surface of said solution, said solution being adjacent to and in fluid contact with said reaction zone.

2. The method which comprises precipitating silver halide grains by reaction of soluble silver salt and soluble halide salt reactants in a fluid reaction zone characterized in that said reactants enter at high velocity, and expelling, by centrifugal force, said grains from said reaction zone into an aqueous peptizer solution beneath the surface of said solution, said reaction zone being confined within, and in liquid contact with said solution.

3. The method which comprises precipitating silver halide grains by reaction of soluble silver salt and soluble halide salt reactants in a fluid reaction zone of high velocity turbulent flow and expelling, by centrifugal force, said grains from said reaction zone into an aqueous peptizer solution beneath the surface of said solution, said solution being adjacent to and in fluid contact with said reaction zone.

4. The method which comprises precipitating silver halide grains by reaction of soluble silver salt and soluble halide salt reactants in a fluid reaction zone of high velocity turbulent flow, which reaction zone is confined within an aqueous peptizer solution, and expelling, by centrifugal force, said grains from said reaction zone beneath the surface of said peptizer solution which is in fluid contact with said reaction zone.

5. The method which comprises introducing an aqueous solution of a water soluble silver salt and an aqueous solution of a metal halide into a fluid reaction zone characterized in that reactants enter at high velocity, reacting said solutions within said zone to form insoluble silver halide grains, and expelling, by centrifugal force, said grains from said reaction zone into an aqueous peptizer solution beneath the surface of said solution, said reaction zone being confined within, and in fluid contact with said solution.

6. The method which comprises introducing, in opposing directions, an aqueous solution of a water soluble, silver salt and an aqueous solution of a water soluble metal halide into a fluid reaction zone characterized in that reactants enter at high velocity, reacting said solutions within said zone to form insoluble silver halide grains, and expelling, by centrifugal force, said grains from said reaction zone into an aqueous peptizer solution beneath the surface of said solution, said reaction zone being confined within, and in fluid contact with said solution.

7. The method which comprises reacting, in a fluid reaction zone of high velocity turbulent flow, an aqueous solution of a water soluble silver salt with an aqueous solution of a water soluble metal halide to form water insoluble silver halide grains, and expelling, by centrif-

ugal force, said grains from said reaction zone beneath the surface of an aqueous peptizer solution which is adjacent to and in liquid contact with said reaction zone.

8. The method which comprises precipitating silver halide grains by reaction of soluble silver salt and soluble halide salt reactants in a fluid reaction zone of high velocity turbulent flow, said reaction zone being confined within an aqueous protein peptizer solution, and expelling, by centrifugal force, said grains from said reaction zone beneath the surface of said peptizer solution which is in fluid contact with said reaction zone.

9. The method which comprises precipitating silver halide grains by reaction of soluble silver salt and soluble halide salt reactants in a fluid reaction zone of high velocity turbulent flow, said reaction zone being confined within an aqueous gelatin peptizer solution, and expelling, by centrifugal force, said grains from said reaction zone beneath the surface of said peptizer solution which is in fluid contact with said reaction zone.

10. The method which comprises precipitating silver chlorobromide grains by reaction of soluble silver salt and soluble halide salt reactants in a fluid reaction zone of high velocity turbulent flow, said reaction zone being confined within an aqueous gelatin solution, and expelling, by centrifugal force, said grains from said reaction zone beneath the surface of said peptizer solution which is in fluid contact with said reaction zone.

11. The method which comprises precipitating silver halide grains by reaction of soluble silver salt and soluble halide salt reactants in the presence of an aqueous gelatin solution in a fluid reaction zone of high velocity turbulent flow, said reaction zone being confined within an aqueous gelatin solution, and expelling, by centrifugal force, said grains from said reaction zone into the confining aqueous gelatin solution beneath the surface of said solution, said reaction zone being in fluid contact with said confining solution.

12. The method of claim 5 in which the metal halide is an alkali metal halide.

13. The method of claim 5 in which the water soluble silver salt is silver nitrate and the water soluble metal halide is potassium bromide.

14. The method which comprises substantially simultaneously introducing an aqueous silver nitrate solution with an aqueous metal halide solution of potassium bromide and sodium chloride into a fluid reaction zone characterized in that the solutions enter at high velocity, reacting said solutions within said zone to form insoluble silver chlorobromide grains, and expelling, by centrifugal

force, said grains from said reaction zone into an aqueous gelatin solution beneath the surface of said solution, said reaction zone being confined within and in liquid contact with said aqueous gelatin solution.

15. The method of claim 14 in which the aqueous metal halide solution is a solution of potassium bromide.

16. A method of preparing a silver halide emulsion which comprises

- (1) continuously introducing a soluble silver salt and a soluble halide salt as reactants into a reaction zone defined by confining means having inlet and outlet openings communicating directly with a body of aqueous peptizer solution surrounding said confining means, while continuously circulating peptizer solution from said surrounding body into said zone, and
- (2) continuously agitating the reactants and peptizer solution within said zone to effect precipitation of silver halide by reaction of said reactants within said zone, and
- (3) continuously expelling reaction product with peptizer solution by centrifugal force from said zone into said body of solution as more of said reactants are continuously introduced into said zone and as more peptizer solution is continuously circulated into said zone from said body.

17. A method defined by claim 16 wherein said silver salt comprises silver nitrate, said halide salt comprises potassium halide and said aqueous peptizer solution is a solution comprising photographic gelatin as a peptizer.

18. A method defined by claim 16 wherein said reaction zone is defined within a rotating shell having inlet openings at each of its ends communicating directly with said surrounding body of solution and having peripheral outlet openings in its side walls communicating directly with said surrounding body of solution and said reactants are introduced, each separately at one of said inlet openings, by separate conduit means each communicating between said inlet opening and a source remote from said body of solution.

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U.S. Cl. X.R.

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