

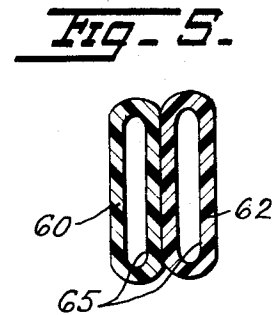
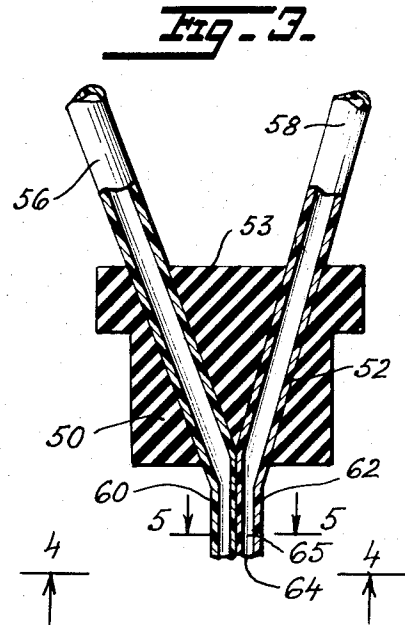
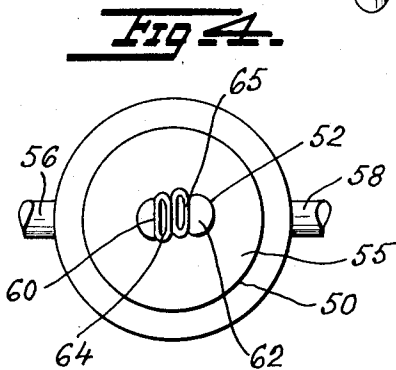
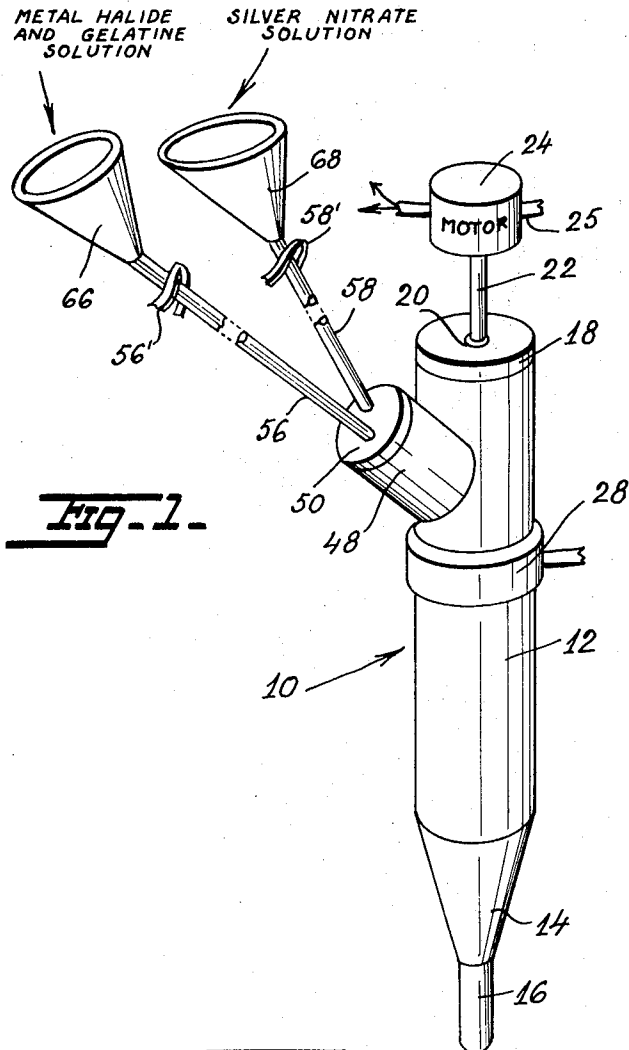
Dec. 5, 1972

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PROCESS AND APPARATUS FOR PRODUCING IMPROVED
PHOTOGRAPHIC EMULSION

3,705,034

Filed June 10, 1968

2 Sheets-Sheet 1



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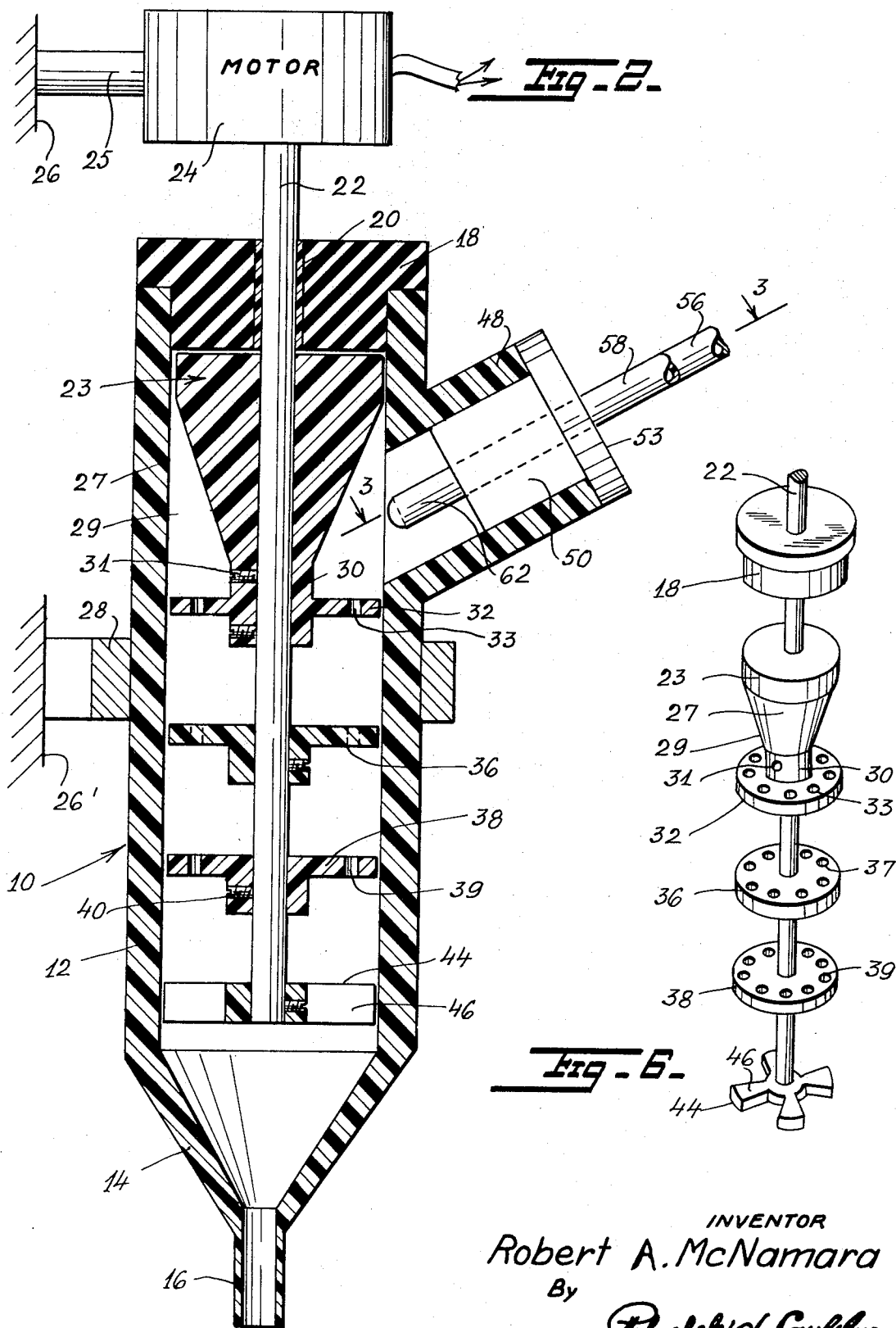


Fig. 6.

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**PROCESS AND APPARATUS FOR PRODUCING
IMPROVED PHOTOGRAPHIC EMULSION**

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5 Claims

ABSTRACT OF THE DISCLOSURE

The disclosure describes a continuous flow cylindrical precipitation reactor having a lateral opening through which reactants are introduced from two adjacent orifices. In the reactor are rotating apertured disk agitators which stir the reactants to form an emulsion. The emulsion flows axially through the reactor, and leaves the reactor at its open bottom. The process involves use of active gelatin, gold sensitization, and immediate combining of input flow streams of reactants just prior to agitation.

The invention concerns a process and apparatus for making photographic emulsions which have a high contrast, fine grain, uniform grain size (small standard deviation from the average grain size of the grain size frequency distribution curve).

It is known that grain size determines the sensitivity of a photographic emulsion to different intensities of a given light to which the emulsion is sensitive to. The light may be from a tungsten source or other source and may be a specific band separated by the use of filters or an optical monochrometer. Grain composition, sensitizing dyes and chemicals determine the sensitivity of an emulsion to specific wave lengths of light, color of light. More uniform grain size gives greater contrast in photographic products, that is, there will be fewer discrete steps in density between full black and full white on paper or maximum transmission through film base after development of a product that has been exposed to light through a characteristic photographic step wedge used in the evaluation of photographic products. Numerous attempts have been made heretofore to produce photograph emulsions which have uniform small grain size. In one such method, which is typical, a given quantity of silver nitrate solution is added through an orifice at a predetermined volumetric rate to a kettle containing a solution of gelatin and soluble metal halides. As the first silver halide molecules are formed, an excess of halide ions exists in the kettle. The first formed silver halide grains contain a silver ion to halide ion ratio where the halide ions are in excess of the silver ions and therefore the grains formed have a net negative charge. Some of the first formed silver halide grains are circulated in the kettle and come in contact with the entering stream of positively charged silver ions and unite with them. Thus some of the already formed silver halide grains grow larger by the addition of more silver ions and in turn add more halide ions also. As the addition of silver nitrate to the kettle is being ended the ratio of free equivalents of halide ions to free equivalents of silver ions is almost one to one. In the titration of a halide solution with silver nitrate the most insoluble silver halides are formed quantitatively first in the order of iodide, bromide to chloride. Therefore it is reasonable to assume that during the precipitation of a mixed silver halide emulsion the first formed grains will contain a greater concentration of the most insoluble silver halide ions then the last formed grains that will be richer in the most soluble silver halide. As a result the silver halide grains vary in both size and composition over a wide range. If the contents of the kettle are not stirred during

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the precipitation process the grain size will have greater nonuniformity and the resulting photographs will have less contrast. If the contents of the kettle are stirred during the addition of silver nitrate the grain size will be less diverse than without stirring, but there will still be a wide range of grain size and composition.

In the present invention, improvements are proposed in the reaction and emulsification process and in the apparatus employed for the process, which together produce an emulsion in which the silver halide grains are smaller and more uniform in size and composition than is otherwise obtainable. According to the invention there is provided a generally cylindrical reactor closed at the top and open at the bottom. In the reactor is an axially disposed rotatable agitator having a series of apertured stirring discs. The reactor has a lateral branch opening. A pair of conduits with flattened, juxtaposed ends are supported in the lateral opening of the reactor and feed a combined stream of gelatin-metal halide solution and silver nitrate solution into the reactor. The silver and halide ions combine while in movement and flow immediately from one rotating disc to the next. A gelatin emulsion containing fine grains of silver halide uniform in size and composition leaves the reactor through its bottom outlet.

The invention will be further explained in connection with the drawings, wherein:

FIG. 1 is a perspective view, somewhat diagrammatic in form of a reactor assembly embodying the invention.

FIG. 2 is an enlarged longitudinal sectional view of the assembly of FIG. 1 parts being omitted.

FIG. 3 is a fragmentary enlarged sectional view taken on line 3—3 of FIG. 2.

FIG. 4 is an end view taken on line 4—4 of FIG. 3.

FIG. 5 is a further enlarged cross sectional view taken on line 5—5 of FIG. 3.

FIG. 6 is a perspective view of an agitator unit employed in the assembly of FIG. 1.

Referring to the drawings, there is shown in FIGS. 1 and 2 a reactor assembly 10 having a long, axially vertical tubular container 12 open at top and bottom ends. The lower end terminates in a funnel section 14 and outlet nozzle 16. The upper end is closed by a stopper 18. In the stopper is a cylindrical bearing sleeve 20 through which extends axially vertical stainless steel shaft 22 attached to motor 24. The motor can be supported by a bracket 25 on a lateral fixture 26. The body 12 can be supported by a bracket 28 on a suitable lateral support 26'.

Secured to the shaft 22 is a body 23 which has a frusto-conical section 27; see FIGS. 2 and 6. The tapered wall 29 of this section is disposed adjacent to a lateral opening 48 in the side of container 12. Body 23 has a cylindrical hub 30 secured by stainless steel set screws 31 to shaft 22. A disk 32 extends radially from hub 30. This disk is provided with holes 33 circumferentially spaced around the disk. Two other disks 36, 38 are mounted by screws 40 on shaft 22. The bottom end of the shaft is mounted in a bearing which is attached to the walls in such a manner as to allow the emulsion to flow by and exit at the bottom.

A short cylindrical nipple 48 extends laterally and upward from the side of container 12. The open end of this nipple is closed by a stopper or plug 50; see FIGS. 1—5. In this plug are two angular disposed passages 52 best shown in FIGS. 1 and 3. The passages are spaced widely apart the outer flanged end 53 of the plug and merge to a common opening at the other, lower end 55 of the plug. Two pipes 56 and 58 are inserted in the respective passages. The pipes have flattened ends 60, 62 extending out of end 65 of the plug and defining narrow orifices 65 adjacent each other. The tips of the pipe ends 60, 62 can

be cut obliquely oppositely to each other as clearly shown in FIG. 3.

Funnels 66 and 68 or other suitable containers are connected to the pipes 56, 58 respectively. One pipe supplies silver nitrate in aqueous solution to the reactor and the other pipe supplies combined a solution of gelatin and metal halides. Valves or clamps 56' and 58' hold the pipes 56, 58 closed until the valves or clamps are removed.

In operation of the assembly 10, while the motor 24 is running, a metal halide and gelatine solution is supplied through pipe 56 and silver nitrate solution is supplied through pipe 58. The two streams issuing from ends 60, 62 of the pipes merge at tips 64 and the common stream then impinges on the rotating body 23. The reaction and precipitation of silver halide grains occurs instantly and the emulsion flows through holes 33 in rotating disk 32 on which the emulsion spreads in a flat stream, the finely divided streams issuing from holes 33 fall to disk 36 where they spread out in a thin film on the disk and then new streams pour through holes 37 in disk 36. The same spreading occurs on disk 38 and again fine streams are formed in holes 39. Finally the streams pass out of the reactor through funnel 14 and nozzle 16 to a suitable container (not shown). It will be noted that there is no chance for the newly added solutions to mix with emulsion where reaction of reagents and precipitation of silver halide has already taken place. The entire operation is continuous and thus adapted to high speed mass production of photographic emulsions. It results in an emulsion containing very fine grains of substantially uniform size and composition.

In use of the apparatus the following process and reagents has been found to yield optimum results:

The silver ion solution may be made by dissolving silver nitrate (AgNO_3) in distilled or deionized water. Silver complexing ions may be present in the solution, such as ammonium ion from NH_3 or NH_4OH and or nitrate ions from a metal nitrate or nitric acid. Silver chelating compounds may be present in the silver ion solution such as EDTA type or citric acid. The silver ion concentration may vary from 1×10^{-2} gram equivalents of silver ion per liter of solution to saturation. The pH of the silver ion solution may vary by the addition of compounds such as HNO_3 or NH_4OH . The temperature of the silver ion solution may vary between 35°F . and 170°F .

The gelatin and metal halide solution could have fine particles of an insoluble metal halide that may serve as nuclei for silver halide, grain formation. The metal halide formulation may be $\text{M}_i\text{-X}_n$, where M may be any metal ion, X may be a halide ion such as chloride or bromide, i may be any positive integer 1 through 4 inclusive, and n may be any positive integer 1 through 6 inclusive. The solution of ionic bonded metal halides may be made by dissolving soluble metal halide salts in water or by neutralization reactions between halide acids and alkaline and metal compounds such as hydroxides. The metal halide solutions may also be made by reduction-oxidation reaction in water. The total halide ion concentration may vary from 0.1 gram equivalents per liter to saturation minus 0.1 gram equivalents of total halide ions per liter of solution. The pH of the gelatin and halide solution may vary from pH 3.0 to pH 9.0. The temperature of the gelatin-metal halide solution may vary from 35°F . to 170°F .

There are several possible gelatin-metal halide solutions:

- (1) The solution may contain only one type of metal ions and one type of halide ions plus gelatin.
- (2) The solution may contain different types of metal ions and one type of halide ion plus gelatin.
- (3) The solution may contain only one type of metal ions and different types of halide ions plus gelatin.
- (4) The solution may contain different types of metal ions and different types of halide ions plus gelatin.

The above listed possible solutions may contain all possible ratios of different type metal and halide ions to one another. The gelatin in the above solutions may be only one type or any combination of two or more different types. The total gelatin content may vary from 0.2 gram of gelatin per total gram equivalent of all halide ions to 2.0 grams of gelatin per total gram equivalents of all halide ions.

The formation of silver grains or grain agglomerates is accomplished by mixing the silver ion solution and metal halide-gelatin solution in the flow through reactor assembly 10 described above. The reactants enter the reactor container 12 through the two orifices 65 which direct each reactant into the stream of the other reactant. The angle defined between the planes of the laminar streams emitted from the orifices 65 may vary from 0° to 180° . The plane parallel to and through the centers of the streams of flow emitted from each orifice may form any angle with the net of resultant direction of flow of the common stream which enters the reactor. This common stream impinges on rotating agitator body 23.

The orifice 65 from which the two streams ejected into the reactor container 12 may be generally rectangular with parallel sides as shown in FIG. 5. The streams issue as laminas which merge into a common lamina. The merging streams allow each reactant to come into contact with the other reactant and this minimizes the opportunity of excessive local concentration of either reactant away from the other one. Thus the tendency to form irregular grain sizes and diverse grain compositions is minimized. The merged lamina is deflected off of the cone on the agitator shaft and then off the sides of the reactor and is forced through the agitator system to assure complete mixing.

If desired, the rectangular orifices can be perpendicular rather than parallel to each other. Alternatively the orifice can be elliptical or circular. In any case, the orifices are arranged to direct two streams at each other or at a common point in the reactor. The essential point to be observed is that reaction takes place at such a point where the precipitated silver halide is quickly drawn or flows away so that it cannot be contacted by fresh metal halide or silver nitrate.

Following is a description of preferred procedure for forming one type of photographic emulsion.

(1) Metal halide-gelatin solution.—About 60 grams of active gelatin containing sulphur sensitizer are added

Following is a description of preferred procedure for is agitated. The gelatin is allowed to soak about one hour. The gelatin solution is then heated to 150°F . and filtered through a porous paper filter. Then 25 grams of potassium bromide (KBr), 55 grams of sodium chloride (NaCl), and 108 grams of cadmium chloride ($\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$) are dissolved in about one liter of water. The gelatin and metal salt solutions are then combined and brought to a volume of 2.5 liters. The combined solution is heated to 111°F . To this solution is then added 21 milliliters of rhodium chloride.

(2) Silver nitrate solution.—A 2.5 liter solution containing about 340 grams of silver nitrate in water is made up and heated to 85°F .

(3) Reaction and agitations.—The two solutions are placed in the containers 66 and 68 of assembly 10. The motor 24 is started. Ambient white lights are turned off, and clamps 56' and 58' are opened. The solutions are mixed in the assembly 10 and discharged from nozzle 16 into a stainless steel beaker provided with a motor driven agitator.

(4) Coagulation.—The discharged emulsion containing the precipitate is then heated and held at 125°F . for 15 minutes. Then the emulsion is cooled to 94°F . and its pH is adjusted to 4.0 with 6 N sulfuric acid. Then 900 grams of a 40% solution of ammonium sulfate are added followed in $\frac{1}{2}$ minute by a 20% solution of sulfanic acid and partially oxidized cellulose. After allow-

ing time for a complete mix, the agitator is stopped and the coagulated precipitate is cooled and allowed to settle. The liquid above the precipitate is then poured off. Approximately 3,000 milliliters of water with pH adjusted to 4.0 are then added to the precipitate and agitated. The precipitate is allowed to settle and the water is poured off. This washing procedure is repeated for a total of six washes.

(5) Gold sensitizing.—One quarter of the total curd is heated to approximately 100° F. after water is added to bring the weight to 650 grams. The pH is adjusted to 6.3 and the millivolts to 405 ± 5 with a solution of 1 part of 10% NaCl and 1 part of 5% KI (approximately 10 milliliters of this solution was required). The curd is then heated to 115° F. and 12 milliliters of 69 mg./l. of sodium thiosulfate solution is added. The temperature is increased to 125° F. and 1.2 milliliters of 200 mg./l. of gold chloride solution is added. The curd is ripened for 15 minutes at 125° F. after addition of gold chloride solution.

(6) Reconstitution.—The curd is reconstituted to emulsion state by mixing it with a 10% gelatine solution of 1:1 H-14 and B-13 gels. The amount of gelatin added is one gram per gram of silver present by analysis. The silver concentration is adjusted with water to 41 grams of silver to one 1000 grams of emulsion.

(7) Bulk ripening.—The emulsions heated to 130° F. and held there for 90 minutes. The pH of the emulsion is then adjusted to 6.5. A sensitizing dye, wetting agent, hardener, toner and stabilizer all as known in the art are then added. The emulsion is then coated on a sheet of clear film base or paper and dried. The coated sheet is cut into strips and they are then exposed through a negative to white light or specific colors of light. The negatives have different opacity ranging from white to black. After exposure and processing in Kodak type D-72 continuous tone developer, it will be noted that the range of density of the developed sheets cover only two and a half steps between white and black. This contrasts with four to five steps as the minimum obtainable by use of the conventional method of making a photographic emulsion described above, where the silver nitrate is perked into a gelatin-metal halide solution which is under agitation.

The distinguishing features of the invention described above involve use of the following:

- (1) Use of active gelatin.
- (2) Sensitizing of the emulsion by gold chloride and sodium thiosulfate.
- (3) Use of higher pH values for the emulsion coating than may be customary.
- (4) Use of orifices in mixing solutions whereby the streams of flow merge prior to agitation.
- (5) Continuous flow through the reactor assembly of the emulsion while being agitated, the flow pattern being arranged so that newly entering solutions do not mix with emulsion containing precipitated silver halide grains.

While I have illustrated and described the preferred embodiments of my invention it is to be understood that I do not limit myself to the precise construction herein disclosed and that various changes and modifications may be made within the scope of the invention as defined in the appended claims.

What is claimed is:

1. A process for producing a light-sensitive photographic emulsion suitable for coating a photographic support, consisting essentially of: employing an agitator means including an elevated surface substantially surrounded by a free space and including below said free space at least one laterally extending substantially horizontal surface perforated by a plurality of apertures; em-

ploying movement means laterally moving said horizontal surface; employing a collection-vessel means for isolating collected mixed stream separate from contact with said elevated surface, said horizontal surface, and said free space above said horizontal surface; directing a first aqueous stream and a second aqueous stream along respective separate axes sufficiently to intersect to thereby form a mixing-stream directed along a resultant axis of flow impinging upon said elevated surface and thereafter upon said moving horizontal surface; thereafter passing substantially all of diverse portions of said mixing-stream through said plurality of apertures downwardly into said collection-vessel means; said first stream consisting essentially of substantially a gelatin and a solution of non-silver-metal halide; said second stream consisting essentially of a solution of substantially silver nitrate, and said passed stream being sufficiently homogeneously admixed by said intersecting, said impinging, and said passing to consummate reaction between said metal halide and said silver nitrate sufficiently to form said collected stream consisting essentially of silver halide grains characterized by substantially uniform and predetermined desired minimal size; said metal halide's total halide concentration of said first solution ranging from about 0.1 gram equivalents per liter to about saturation minus about 0.1 gram equivalents of total halide ion per liter of solution; said silver nitrate's silver ion concentration ranging from about 0.01 gram equivalents per liter to saturation; said first stream ranging from about pH 3 to about pH 9; and each of said first and second streams ranging in temperature from about 35 degrees to about 170 degrees Fahrenheit.

2. A process according to claim 1, in which said laterally extending horizontal surface is a rotatable disc rotatable around an axis extending upwardly through about said elevated surface, and in which said moving is rotary movement, said rotary movement being a revolving motion of said disc around said upwardly extending axis extending through about said disc's center.

3. A process according to claim 1, including employing at least additional successive one of said laterally extending horizontal surface also perforated by a second plurality of apertures, and further impinging said passed stream upon said additional one and thereafter further passing said further-impinged stream's respective portions through said second plurality of apertures prior to collection in said collection-vessel means.

4. A process according to claim 3, further operatively including: batch coagulating; batch gold-sensitizing; batch re-constituting; and batch bulk-ripening.

5. A process according to claim 2, in which said first and second streams form said mixing stream upon entering said free space; including employing a reactor vessel defining said free space; and in which said first and second streams are each directed with predetermined low velocities.

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