

[54] APPARATUS FOR THE PREPARATION OF
A PHOTOGRAPHIC EMULSION3,376,023 4/1968 Lage 259/4
3,776,702 12/1973 Chant 259/4[75] Inventors: Donald M. Forster; Gerald J.
Culhane, both of Rochester, N.Y.Primary Examiner—Harvey C. Hornsby
Assistant Examiner—Alan Cantor
Attorney, Agent, or Firm—L. F. Seebach[73] Assignee: Eastman Kodak Company,
Rochester, N.Y.

[22] Filed: Aug. 29, 1974

[21] Appl. No.: 501,564

Related U.S. Application Data

[62] Division of Ser. No. 305,764, Nov. 13, 1972.

[52] U.S. Cl. 259/4

[51] Int. Cl.² B01F 5/04[58] Field of Search 259/4, 18, 36, 60, 150,
259/180

References Cited

UNITED STATES PATENTS

2,747,974 5/1956 Felger 259/4

[57] ABSTRACT

Apparatus is disclosed in which each of a silver salt and halide salt or other salt solution is separately diluted with a part of a peptizer solution but remote from the bulk of the latter. These separate mixtures are then comixed and returned to the bulk peptizer solution. By the diluting and comixing of the reactants with a part of the bulk peptizer solution outside of the bulk vessel, greater control can be exercised with respect to a variety of parameters, irrespective of the bulk size of the peptizer solution.

7 Claims, 6 Drawing Figures

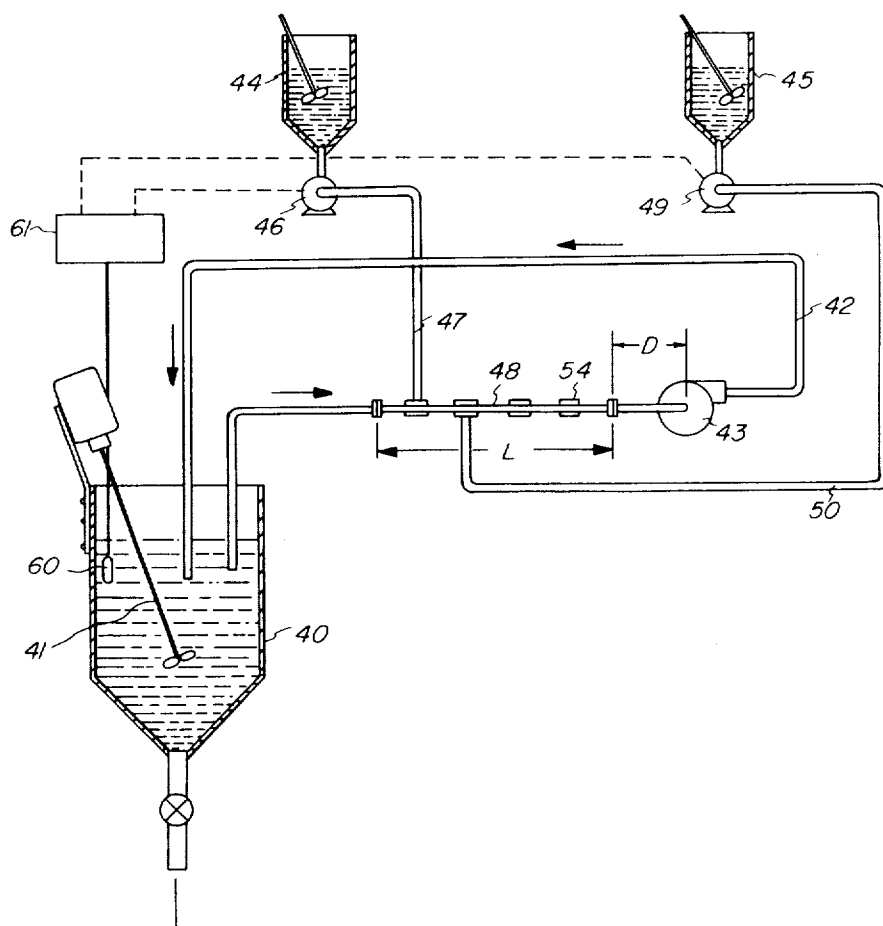


FIG. 1

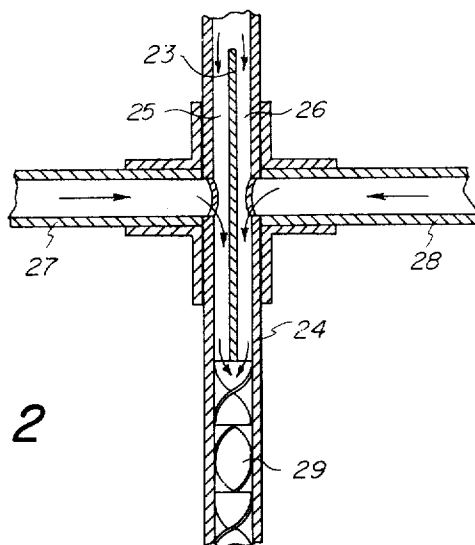
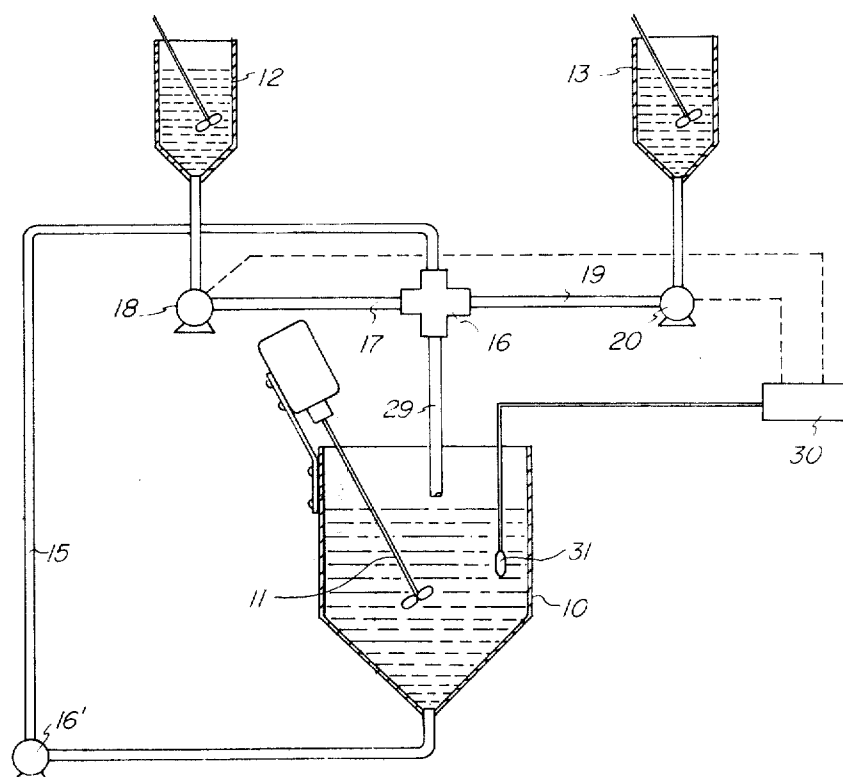


FIG. 2

FIG. 3

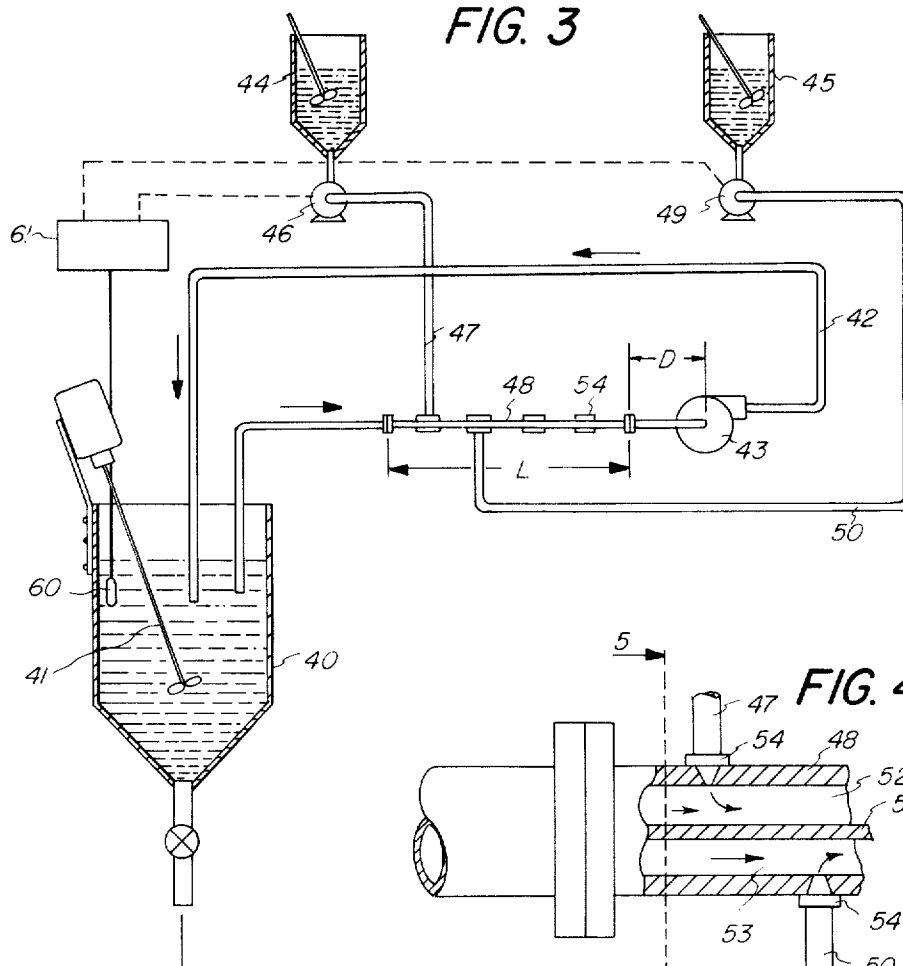


FIG. 4

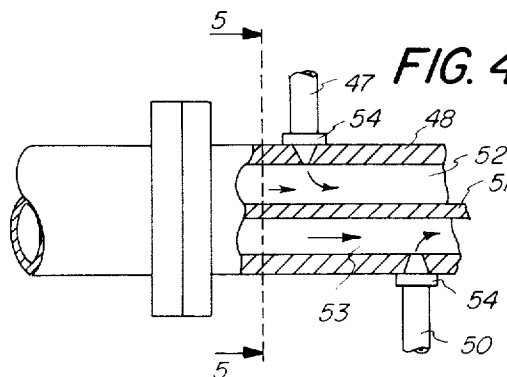


FIG. 6

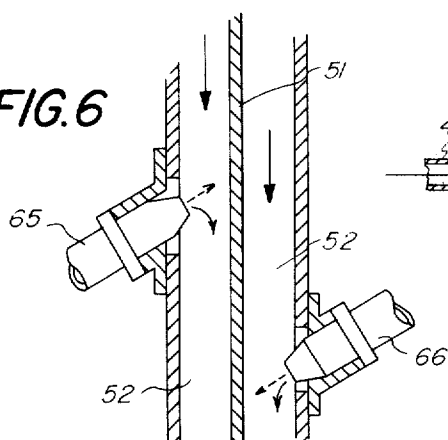
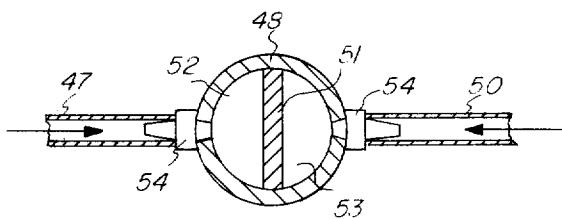


FIG. 5



APPARATUS FOR THE PREPARATION OF A PHOTOGRAPHIC EMULSION

This is a division of application Ser. No. 305,764, filed Nov. 13, 1972.

FIELD OF THE INVENTION

The invention relates to an improved apparatus for combining and mixing a number of liquid reactants; and, more particularly, to an apparatus for preparing a photographic emulsion.

DESCRIPTION OF THE PRIOR ART

In the preparation of photographic emulsions, it is often desirable that the silver halide crystals or grains be precipitated in a finely divided form. The making of such an emulsion with finely divided silver halide grains has normally been accomplished by the precipitation of the silver halide grains by means of a so-called double decomposition reaction in which the reactants are introduced into an aqueous solution, such as an aqueous solution of gelatin. Such a solution is normally referred to as a peptizer solution, although this latter term can be used generically to define nonaqueous solutions as well as aqueous solutions.

The method by which the decomposition reaction is obtained is characterized by the manner in which the reactants are introduced into the peptizer solution. In *THE THEORY OF THE PHOTOGRAPHIC PROCESS*, Third Edition, C. E. K. Mees and T. H. James, MacMillan, 1966, Chapter 2, page 34, there is a disclosure of emulsions that are made by methods which are usually referred to as a "single-jet" or a "double-jet" method.

In the preparation of an emulsion made by the double-jet method, an aqueous solution of a water soluble, silver salt and an aqueous solution of water soluble, halide or other salt are added simultaneously to an aqueous peptizer (gelatin) solution. As the silver halide grains are precipitated, the discrete grain sizes tend to vary considerably, which is not a desired property, particularly in the preparation of an emulsion wherein narrow grain size distribution is a requisite. With nonuniformity in the size of the precipitated silver halide grains, adverse photographic characteristics will be imparted to the material coated with such an emulsion; for example, reduced contrast or an undesired phenomenon known as a "pepper fog" caused by clumped or aggregate crystals tending to develop spontaneously. These same adverse characteristics are experienced by photographic emulsions that are prepared by the single-jet method.

There have been several attempts to produce an emulsion in which the silver halide grains have a narrow grain size distribution; that is, an emulsion having grains of substantially uniform size throughout. Specifically, photographic emulsions have been prepared which contain substantially fewer nonuniform large grains than were possible with the prior and well-known precipitation techniques.

U.S. Pat. Nos. 2,996,287 and 3,415,650 are examples of improved silver halide precipitation techniques. These patents disclose, respectively, an apparatus and method for improving the dispersion of a salt solution into a peptizer solution, and a method of removing the reaction product from a reaction zone so as to diminish the possibilities of crystal aggregate formation. While

some of the disadvantages related to single- and double-jet precipitations have been overcome, the limitations imposed by such improved methods have also posed problems. For example, the presently existing methods and apparatus do not permit achievement of an increase in emulsion production by increasing the concentration of the liquid reactants, because the resultant grain size distribution also increases, thereby producing pepper fog as referred to hereinabove.

In an attempt to increase photographic emulsion bulk or production, U.S. Pat. No. 3,785,777 discloses a method by which one of the silver and salt solutions is mixed with a portion of a peptizer solution while remote from the bulk and prior to ejection into and contact with the bulk peptizer solution. This is accomplished by a mixing device enclosed in a housing that is submerged in the bulk peptizer solution. In such a system, the mixing device is provided with two mixing chambers in each of which the reactants are mixed with peptizer solution and then brought into contact with one another upon being expelled from the mixing device and into the bulk peptizer solution.

In U.S. Pat. No. 3,342,605, a method is disclosed by which addenda that is prone to cause the formation of coagulated particles in a gelatin solution is added to the gelatin solution only after being diluted with the gelatin solution outside of the bulk vessel in which the gelatin solution is contained. Following this teaching, the disclosure in Porter et al could be moved outside of the vessel to obtain somewhat greater control as in U.S. Pat. No. 3,342,605.

However, the amount of emulsion that can be mixed is limited because of the type of apparatus. In view of the improvements made in coating an emulsion on a support and, particularly, as related to the rate at which such coating is effected, preparation of an emulsion must proceed at a much greater rate than is presently possible with the processes disclosed by the prior art. In other words, the prior art processes do not permit greater concentration and quantities of peptizer solutions and reactant compositions to be handled in preparation of the emulsion, while at the same time producing an emulsion in which there is a substantial increase in the precipitation of silver halide grains with an accompanying production of silver halide grains that are generally uniform in size.

The preparation of a photographic emulsion, whether a monodispersed or a polydispersed emulsion, requires a carefully controlled environment; that is control of all variables, such as temperature, pAg, pH, rate of addition, time and uniformity in mixing of two or more reactants that can be added jointly or severally. These variables are difficult to control independently as the size of the emulsion preparation, bulk, or batch becomes larger. For example, the addition of reactant compositions from at least two separate sources tends to cause localized, high concentration of the reactants because it is difficult to disperse small amounts of reactants uniformly and rapidly into a large volume of emulsion, or any other fluid or liquid. If these reactant compositions are not dispersed uniformly, some silver halide crystals will grow more rapidly than others, thereby resulting in a nonuniform size distribution of the crystals.

SUMMARY OF THE INVENTION

It is an object of the invention to provide an im-

proved apparatus by which each of a number of liquid reactants is individually and separately diluted by the same one reactant and then intermixed to form a single continuous flow of the reactants.

It is another object of the invention to provide apparatus by which a large batch of a photographic emulsion can be prepared which will have uniform size distribution of the silver halide crystals.

It is still another object of the invention to provide apparatus by which a photographic emulsion can be prepared and in which each of the silver and halide salts is first diluted with a part of the peptizer solution but separate from the bulk thereof and which dilutions are then combined so as to precipitate silver halide crystals of generally uniform size.

It is yet a further object of the invention to provide apparatus for the preparation of a photographic emulsion having silver halide grains of generally uniform size and comparable sensitometric properties and characteristics.

Further objects and advantages of the invention will be apparent to those skilled in the art by the description which follows.

The objects of the invention are attained by apparatus in which each of a silver and salt solution is separately diluted with a part of a peptizer solution but remote from the bulk thereof. These separate mixtures are then comixed and returned to the bulk peptizer solution. The circulatory path through which the bulk peptizer moves outside of the bulk vessel includes a tube reactor, having two chambers formed by an axial divider that also splits the flow of peptizer solution, and a pump. The reactor is arranged between the bulk vessel and the suction side of the pump. Each of the silver and salt solutions is metered through a feed line connected to a respective chamber at a predetermined flow rate by a pump arranged in each respective feed line. The silver and salt solutions can be introduced into their respective chamber at diametrically opposite points or at different points with respect to each other longitudinally along the divided tube for dilution with the flow of peptizer solution. The points at which the solutions are introduced will be determined by the required mixing time for the solution with that of the peptizer solution. Preferably, the end of the divided tube is arranged adjacent to the pump in the circulatory path so that the separate flows of silver salt and peptizer solution and halide salt and peptizer solution are combined and mixed immediately within the pump. With such intermixing of the peptizer, diluted silver and salt solutions, the silver halide grains are precipitated and the solution is then returned by the pump to the bulk vessel.

By diluting and comixing the reactants with a part of the bulk peptizer solution outside of the bulk vessel, greater control can be exercised with respect to the flow rates, dilution and mixing of each reactant with respect to the peptizer solution, irrespective of the bulk size of the peptizer solution. Such control was not heretofore possible in processes in which the reactants were combined either directly within the bulk peptizer solution or first diluted within the peptizer solution. It has been found that the aforementioned process and apparatus provides more uniform fine grain growth and such growth is not affected by the size of the batch of emulsion because of the controls that can now be exercised. Likewise, the sensitometric characteristics of the emul-

sion remain constant irrespective of the emulsion batch size. Another advantage is that the silver halide grains are not subjected to a high concentrated silver ion or halide ion environment when individually diluted and mixed, thereby eliminating a possible source of nonuniformity in grain morphology, grain size and photographic sensitivity.

DESCRIPTION OF THE DRAWINGS

Reference is now made to the accompanying drawings wherein like reference numerals designate like parts and wherein:

FIG. 1 is a schematic view of one embodiment of the invention showing the manner in which at least two liquid reactants are combined with a liquid composition on the discharge side of a pump;

FIG. 2 is a vertical sectional view through the junction at which each of the two liquid reactants is introduced into a separate flow of the liquid composition;

FIG. 3 is a schematic view of another embodiment of the invention in which the introduction of the two liquid reactants into the liquid composition takes place on the suction side of the pump;

FIG. 4 is a partial, sectional view through one end of a divided conduit or tube in the circulatory path shown in FIGS. 1 and 3 in which each liquid reactant is introduced into a respective chamber for dilution by the liquid composition;

FIG. 5 is a sectional view taken substantially along the lines 5—5 in FIG. 4; and

FIG. 6 is a partial, sectional view through the divided tube shown in FIG. 4 and showing alternate ways in which the reactant compositions can be introduced relative to the flow of the other composition.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Before describing the invention in detail, it is thought that a better understanding of the invention might be had if a photographic emulsion making process were first described.

A colloidal system is a multiphase system in which there is one finely divided discharge phase more or less uniformly distributed or discharged through a continuous phase usually referred to as the discharge medium. A quantity obtained in investigating the behavior of the colloidal particles under the action or forces, chiefly centrifugal forces, is defined as the sedimentation constant. As a result, a monodispersed system is one of colloidal particles in which the value of the sedimentation constant is constant for successive time intervals, thereby indicating that the system comprises particles of generally uniform size. On the other hand, a polydispersed emulsion is one in which the sedimentation constant is not of uniform value, thereby indicating particles of nonuniform size.

The process to be described hereinafter is one which can be used for either aqueous or nonaqueous silver halide emulsions. Such emulsions can be used in photosensitive and photothermographic materials and can be applied or coated on transparent or opaque supports. Hence, the peptizer solution as well as the salts that are used in an aqueous or nonaqueous emulsion are set forth in more detail in U.S. Pat. No. 3,672,904, the emulsion per se forming no part of the present invention.

In general, the term "peptizer solution," as used throughout the following description and the claims is, therefore, meant to include either an aqueous or a non-aqueous solution. Also, the terms "silver" and "halide" salts can be construed to include any of such salts used in the making of photosensitive emulsions. Even more generally, in a process in which the reactants must be thoroughly mixed, first in a dilution stage and then combined, the process and apparatus about to be described will be found to be applicable and to provide satisfactory results.

With particular reference to FIG. 1 of the drawings, a gelatin solution and any required addenda are dissolved in a kettle or tank 10 to form a peptizer solution. A suitable stirring or mixing device 11 is provided for continuously agitating and mixing the gelatin solution in tank 10 as the process is carried out. A halide salt is dissolved in a suitable liquid and contained in a tank 12 and a silver salt is dissolved in a suitable liquid and combined in tank 13. The solvent media will be dependent upon whether the process is one involving the preparation of an aqueous or nonaqueous emulsion and related reactants. A circulatory path comprises a conduit designated by the numeral 15 and a pump 16' for withdrawing the peptizer solution and moving it through the conduit 15 which returns it to the tank 10, as shown in FIG. 1. The conduit or path 15 also includes a junction connector 16, as shown in detail in FIG. 2. The portion of the conduit which passes through connector 16 includes a plate 23 which divides the conduit at that point into two chambers designated 25 and 26 which can be of equal or unequal cross section. It will be noted from FIG. 2 that the plate 23 extends beyond the point at which the silver and halide salts are introduced via lines 27 and 28 into the conduit and into their respective chambers 25 and 26. The plate 23 divides the flow of the peptizer solution and with the introduction of the silver and halide salts, mixing and dilution of the salts with the peptizer solution in their respective chamber takes place before the mixtures are combined at the downstream end of plate 23. At the downstream end of plate 23, a plurality of twisted elements 29 are arranged in serial relation to provide an in-line mixing device for insuring complete mixing of the silver salt-peptizer and halide salt-peptizer solutions prior to return and entry into the tank 10. The flow rate of the peptizer solution from tank 15 to connector 16 is determined by pump 16'. In a similar manner, the pumps 18 and 20 can be controlled by a device 30 to vary the flow rate of the silver and halide salts into connector 16. It is with such control rates that the particle size, as well as uniformity of size, can be closely controlled irrespective of the peptizer batch size within tank 10. The control device 30 can, by means of a sensor 31 in the peptizer solution, be responsive to the silver concentration (pAg) in the peptizer solution and/or the pH of the peptizer solution, thereby insuring complete control of the emulsion parameters.

With reference to FIG. 3, the peptizer solution is contained within a tank 40 and is continuously agitated and mixed by the mixer 41. In this embodiment, the circulatory path comprises a conduit 42 and a pump 43 interconnected in the conduit or path. The diluted halide salt is contained in a tank 44 and the diluted silver salt is contained in a tank 45. Pump 46 moves the halide salt from the tank 44 via line 47 to an inlet in a portion

48 of the conduit or path 42. Likewise, the silver salt solution is moved by a pump 49 via line 50 into the portion 48 of the conduit 42.

As shown more clearly in FIGS. 3-5, the portion 48 is of a length L and arranged in the path and relative to pump 43 by a distance designated as D. The tubular portion 48 is provided throughout its length L with a plate 51 that divides the portion 48 into two chambers designated by the numerals 52 and 53, as shown in FIG. 5. Depending on the requirements of the process, the plate 51 can be arranged centrally within portion 48 to provide chambers of generally equal cross section or displaced to provide chambers of unequal cross section. The lines 47 and 50 introduce the salt solutions into one of the respective chambers 52, 53 in which the solutions are diluted by and mixed with the peptizer solution. The plate 51 divides the flow of peptizer solution for movement through each of chambers 52, 53. The lines 47 and 50 can be connected by any one of several junctions or inlets in the portion 48, as designated by the numeral 54. The location at which the lines 47 and 50 are connected to the portion 48 will determine the time allotted for mixing of that particular salt with the peptizer solution. As in the previously described embodiment, the flow rate of the halide and silver salts can be varied through the media of pumps 46 and 49 to control the pAg and/or pH of the peptizer solution. Also, as in the previous embodiment, a sensor 60 can be positioned in the peptizer solution and utilized to generate a signal corresponding to the existing pAg and/or pH of the solution which is then used by device 61 to adjust the flow rates of the pumps 46 and/or 49. The flow rate of one or both of the halide and silver salts is thereby adjusted until the desired pAg and/or pH level is reached.

As shown in FIG. 3, the distance D can be varied and may or may not include an in-line mixer 29, as shown in FIG. 2. In some instances, it may be desirable to connect the end of portion 48 directly to the pump 43 without any intermediate mixing action. When the silver and halide salts are introduced into the respective chambers 52 and 53, as shown in FIGS. 4 and 5, the solutions are usually introduced at an angle that is generally perpendicular to the flow of the peptizer solution. However, as shown in FIG. 6, the desired mixing action that is required can be varied by arranging the discharge angle relative to the flow of the peptizer solution. As shown by the position of the conduit 65, this can be at an angle in opposition to or as shown by the conduit 66 at an angle with the flow of peptizer solution. In both cases, the actual angle can be varied in accordance with the result desired. Also, the direction of flow of the peptizer solution can be in a vertical direction as in FIGS. 1 and 6 or in a horizontal direction as in FIG. 3. The flow of peptizer solution can also be divided so as to form two flows, each of which is directed into a separate conduit. In this case, each salt solution will be introduced into a respective conduit and the separate flows then recombined. As shown in FIGS. 1 and 3, the chambers 25, 26 and 52, 53 can be located on either side of the pump, that is, on the discharge side (25, 26) or on the suction side (52, 53).

The type and degree of agitation desired through precipitation can also be controlled by varying the rate or speed of pump 16' or pump 43. The actual precipitation of the silver halide grains takes place in the mixing action provided by either pump 43 or the in-line mixer

29. In addition to the silver and halide salts, chemical sensitizers, spectral sensitizers and coating aids can also be introduced through the media of portion 48. Each of such addenda can be mixed with the proper salt and diluted with the peptizer solution prior to full mixture in pump 43. The length L as well as the diameter of the portion 48 can be varied to provide an optimum velocity and mixing time in accordance with the reactants, concentrations, temperatures, etc., or any combination of these and other parameters that might be used.

Although the invention has been described primarily as apparatus for the preparation of monodispersed emulsions, it will be obvious to those skilled in the art that the invention can be used for combining and mixing other reactant compositions wherein dilution prior to complete mixing will produce a more reliable and homogeneous mixture. The apparatus is also capable of considerable flexibility and of vernier adjustment so that the degree and time of mixing can be controlled within very narrow limits.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. Apparatus for preparing a photographic emulsion, the combination comprising:
 - first means for containing a bulk quantity of a peptizer solution;
 - second means for containing a bulk quantity of a salt solution;
 - third means for containing a bulk quantity of a silver salt solution;
 - means operatively connected to the first means for moving the peptizer solution in a prescribed flow path;
 - means arranged in the flow path and interconnected between the first means and the moving means for dividing the flow of peptizer solution between each of two separate and discrete chambers for a predetermined length of the flow path after which the di-

vided flows combine;

means interconnecting the second means to one of the chambers for introducing a flow of the salt solution into the one chamber for mixing with the flow of peptizer solution being moved therethrough; and means interconnecting the third means to the other of the chambers for introducing a flow of the silver salt solution into the other chamber for mixing with the flow of peptizer solution being moved there-through;

the combined divided flows mixing and precipitating the emulsion.

2. Apparatus in accordance with claim 1 wherein the moving means comprises a pump for moving the peptizer solution through the flow path defined by a conduit, and the dividing means comprises a plate of predetermined length arranged within a portion of the conduit for dividing the flow of peptizer solution being moved therethrough and for dividing the portion of the conduit into two separate and distinct chambers.

3. Apparatus in accordance with claim 2 wherein the introducing means are interconnected to their respective chamber at substantially the same position axially of the conduit and relative to the length of the plate.

4. Apparatus in accordance with claim 2 wherein the introducing means are interconnected to their respective chamber at different positions axially of the conduit and relative to the length of the plate.

5. Apparatus in accordance with claim 2 wherein the plate is arranged in the portion of the conduit connecting the first means to the pump.

6. Apparatus in accordance with claim 1 wherein the introducing means for the flow of salt solution and for the flow of silver salt solution are interconnected to their respective chamber so as to introduce the solutions at an angle to the direction of flow of the peptizer solution being moved through the chambers.

7. Apparatus in accordance with claim 6 wherein the angle is generally normal to the direction of flow of the peptizer solution.

* * * * *

45

50

55

60

65